

A Possible Construction of a Complex Chemical Reaction Network

II. Applications

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The new procedure suggested in Part I for the construction of a complex chemical reaction network is applied to two different and complex reaction systems.

In the case of the oxidation of ethylbenzene in the liquid phase the most important network is the carbon skeleton sequence network derived from a possible mechanism of the overall process. In experiments designed for this purpose this carbon skeleton sequence network has been verified and slightly modified.

For the high temperature methane oxidation in the gas phase three sequence networks are constructed: the carbon, hydrogen and oxygen sequence networks. The carbon and oxygen sequence networks show characteristics corresponding to evidence obtained experimentally on this reaction although direct proof has not been given so far, in order to establish the formation sequence of the products.

Key words: Ethylbenzene oxidation – Methane oxidation – Carbon skeleton sequence network

1. Introduction

In Part I [1] we described a possible construction of some especially complex chemical reaction networks, introduced the concept of kinetic communications and defined the relation: complete network \supset subnetwork \supset partial subnetwork \supset sequence network.

In this part we apply the construction procedure to two complex oxidation processes and indicate the use of the networks in planning the experimental work and in making conclusions from the results.

2. The Sequence Network of the Liquid Phase Oxidation of Ethylbenzene at Temperatures between 40–130°C

The procedure suggested for the construction of the networks is based on the Possible Mechanism (PM) [2, 3]. In the case of ethylbenzene oxidation the PM comprises 52 elementary processes given in Table 1.

Table 1. The possible mechanism of the oxidation of ethylbenzene

$\text{RH}_2 + \text{O}_2 \rightarrow \text{HR}' + \text{HO}_2'$	(1)	$\text{HROOH} + \text{HROH} \rightarrow 2\text{HRO}' + \text{H}_2\text{O}$	(19)
$2\text{RH}_2 + \text{O}_2 \rightarrow 2\text{HR}' + \text{H}_2\text{O}_2$	(2)	$2\text{HROOH} \rightarrow \text{HRO}' + \text{HRO}_2' + \text{H}_2\text{O}$	(20)
$\text{HO}_2' + \text{RH}_2 \rightarrow \text{HR}' + \text{H}_2\text{O}_2$	(3)	$2\text{HO}' \rightarrow \text{H}_2\text{O}_2$	(21)
$\text{HR}' + \text{O}_2 \rightarrow \text{HRO}_2'$	(4)	$2\text{HR}' \rightarrow \text{HRRH}$	(22)
$\text{HR}' + \text{HROH} \begin{cases} \rightarrow \text{HRO}' + \text{RH}_2 \\ \rightarrow \text{ROH} + \text{RH}_2 \end{cases}$	(5A) (5B)	$2\text{HRO}' \rightarrow \text{HROH} + \text{RO}$	(23)
$\text{HR}' + \text{HROOH} \begin{cases} \rightarrow \text{HRO}' + \text{HROH} \\ \rightarrow \text{HO}' + \text{RO} + \text{RH}_2 \end{cases}$	(6A) (6B)	$2\text{HRO}_2' \begin{cases} \rightarrow \text{HRO}' + \text{O}_2 + \text{HRO}' \\ \rightarrow \text{HROH} + \text{RO} + \text{O}_2 \end{cases}$	(24A) (24B)
$\text{HRO}' + \text{RH}_2 \rightarrow \text{HR}' + \text{HROH}$	(7)	$\text{HR}' + \text{HO}' \rightarrow \text{HROH}$	(25)
$\text{HRO}' + \text{HROOH} \begin{cases} \rightarrow \text{HRO}_2' + \text{HROH} \\ \rightarrow \text{HO}' + \text{RO} + \text{HROH} \end{cases}$	(8A) (8B)	$\text{HRO}' + \text{HO}' \rightarrow \text{H}_2\text{O} + \text{RO}$	(26)
$\text{HRO}_2' + \text{RH}_2 \rightarrow \text{HR}' + \text{HROOH}$	(9)	$\text{HRO}_2' + \text{HO}' \rightarrow \text{HROH} + \text{O}_2$	(27)
$\text{HRO}_2' + \text{HROH} \begin{cases} \rightarrow 2\text{HRO}' + \text{HO}' \\ \rightarrow \text{HROOH} + \text{ROH} \end{cases}$	(10A) (10B)	$\text{HR}' + \text{HRO}' \rightarrow \text{RH}_2 + \text{RO}$	(28)
$\text{HRO}_2' + \text{HROOH} \begin{cases} \rightarrow \text{HO}' + \text{HROOH} + \text{RO} \\ \rightarrow \text{HRO}' + \text{HROH} + \text{O}_2 \end{cases}$	(11A) (11B)	$\text{HR}' + \text{HRO}_2' \rightarrow \text{HROH} + \text{RO}$	(29)
$\text{HO}' + \text{RH}_2 \rightarrow \text{H}_2\text{O} + \text{HR}'$	(12)	$\text{HRO}' + \text{HRO}_2' \rightarrow \text{HROOH} + \text{RO}$	(30)
$\text{HO}' + \text{HROH} \begin{cases} \rightarrow \text{HRO}' + \text{H}_2\text{O} \\ \rightarrow \text{ROH} + \text{H}_2\text{O} \end{cases}$	(13A) (13B)	$\text{ROH} + \text{RH}_2 \rightarrow \text{HROH} + \text{HR}'$	(31)
$\text{HO}' + \text{HROOH} \begin{cases} \rightarrow \text{HRO}' + \text{H}_2\text{O}_2 \\ \rightarrow \text{HO}' + \text{RO} + \text{H}_2\text{O} \\ \rightarrow \text{HRO}_2' + \text{H}_2\text{O} \end{cases}$	(14A) (14B) (14C)	$\text{HRO}' + \text{HROH} \rightarrow \text{HROH} + \text{ROH}$	(32)
$\text{HO}' + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2' + \text{H}_2\text{O}$	(15)	$\text{ROH} + \text{O}_2 \rightarrow \text{RO} + \text{HO}_2'$	(33)
$\text{HRO}_2' \rightarrow \text{RO} + \text{HO}'$	(16)	$2\text{HO}_2' \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	(34)
$\text{HROOH} \rightarrow \text{HRO}' + \text{HO}'$	(17)	$\text{HO}_2' + \text{HR}' \rightarrow \text{HROOH}$	(35)
$\text{HROOH} + \text{RH}_2 \rightarrow \text{HR}' + \text{HRO}' + \text{H}_2\text{O}$	(18)	$\text{HO}_2' + \text{HRO}' \rightarrow \text{H}_2\text{O}_2 + \text{RO}$	(36)
		$\text{HO}' + \text{HRO}_2' \begin{cases} \rightarrow \text{HO}' + \text{HRO}' + \text{O}_2 \\ \rightarrow \text{H}_2\text{O} + \text{RO} + \text{O}_2 \end{cases}$	(37A) (37B)
		$\text{HO}_2' + \text{HROOH} \begin{cases} \rightarrow \text{H}_2\text{O}_2 + \text{RO} + \text{HO}' \\ \rightarrow \text{H}_2\text{O} + \text{HRO}' + \text{O}_2 \\ \rightarrow \text{H}_2\text{O}_2 + \text{HRO}_2' \end{cases}$	(38A) (38B) (38C)
		$\text{HO}_2' + \text{HROH} \begin{cases} \rightarrow \text{H}_2\text{O}_2 + \text{HRO}' \\ \rightarrow \text{H}_2\text{O}_2 + \text{ROH} \end{cases}$	(39A) (39B)

It may be noted that all elementary processes were included into the PM which have been suggested according to literature data and have not been excluded – so far – unambiguously by experimental evidence. No quantitative aspects were taken into consideration, that is, the PM does not make any distinction with respect to the role or importance of the respective processes and it is natural to assume that with changing experimental conditions the “prevailing” elementary processes also vary. On the other hand, special care was taken to include processes enabling the representation of the overall reaction by the PM up to high conversions and thus avoid limitation to the initial stages.

Since the PM given in Table 1 serves only as an example for the construction of the network we omit detailed discussion of the processes and motivation of their incorporation.

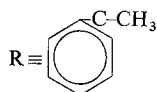
Table 2 shows the species-space, that is the species (with their symbols used in the PM) participating in the elementary processes and distinguished – due to reasons explained later – as stable products and free radicals. The corresponding + and – signs refer to the fact whether the respective species was determined experimentally (+), or only assumed to exist (–) during the overall reaction.

Table 2. Species participating in the possible mechanism of the oxidation of ethylbenzene

Stable species	Symbol	Exp.	Unstable species	Symbol	Exp.
ethylbenzene	RH ₂	+	phenylethylperoxy radical	HRO ₂ '	+
α -phenylethyl- hydroperoxide	HROOH	+	hydroxyl radical	ÖH	–
phenylmethylcarbinol	HROH	+	hydrogen peroxy radical	HO ₂ '	–
acetophenone	RO	+	phenylethoxy radical	HRO'	–
hydrogen peroxide	H ₂ O ₂	+	ethylbenzyl radical	HR'	–
water	H ₂ O	+	phenylmethylcarbinol radical	ÖOH	–
2,3-diphenylbutane	P	+			
oxygen	O ₂	+			

It seems reasonable to consider a complete reaction network corresponding to a PM of 52 elementary processes too complicated for practical purposes.

The experimental methods available for the authors studying this oxidation enable us to follow the fate of the so called “carbon-skeleton” defined here as:



It should be noted, however, that this choice excludes the possibility of tracing the fate of all species that do not contain carbon skeleton, such as O₂; HO₂'; H₂O₂; ÖH; H₂O.

The matrices representing the one-step carbon skeleton, hydrogen and oxygen subnetworks as well as the *one-step* carbon skeleton subnetwork are given in Tables 3 and 4, while the corresponding matrix-sum is shown in Table 5.

We intended to prove the correctness of the carbon skeleton subnetwork by the radioactive tracer method. It is obvious that this method is not suitable for obtaining direct information on unstable species (free radicals) since their molar and total radioactivities cannot be determined. Therefore we constructed the corresponding *carbon skeleton partial network* and finally, using the analysis described in Part I, the *carbon skeleton sequence network* which is represented in Fig. 1.

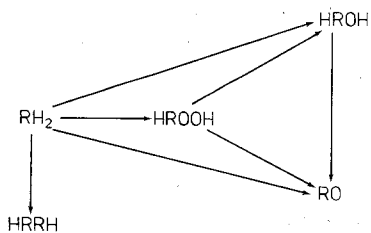
In recent publications [4–6] we have already reported our results supporting the existence of the kinetic communications represented in Fig. 1. In fact, these investigations suggested the thorough study of the alcohol-ketone transition [7] to be important for the understanding of the overall process at high conversions. Another conclusion obtained from our sequence studies was the necessary extension

Table 4. Matrix representing the one-step carbon skeleton subnetwork in the oxidation of ethylbenzene

	RH ₂	HR'	HRO ₂ '	HROH	HRO'	R'OH	HROOH	RO	HRRH
RH ₂	0	1	0	0	0	0	0	0	0
HR'	1	0	1	1	0	0	1	0	1
HRO ₂ '	0	0	0	1	1	0	1	1	0
HROH	0	0	0	0	1	1	0	0	0
HRO'	0	0	0	1	0	0	0	1	0
R'OH	0	0	0	1	0	0	0	1	0
HROOH	0	0	1	1	1	0	0	1	0
RO	0	0	0	0	0	0	0	0	0
HRRH	0	0	0	0	0	0	0	0	0

Table 5. Matrix representing the *L*-step carbon skeleton subnetwork in the oxidation of ethylbenzene

	RH ₂	HR'	HRO ₂ '	HROH	HRO'	R'OH	HROOH	RO	HRRH
RH ₂	1	1	1	1	1	1	1	1	1
HR'	1	1	1	1	1	1	1	1	1
HRO ₂ '	0	0	1	1	1	1	1	1	0
HROH	0	0	0	1	1	1	0	1	0
HRO'	0	0	0	1	1	1	0	1	0
R'OH	0	0	0	1	1	1	0	1	0
HROOH	0	0	1	1	1	1	1	1	0
RO	0	0	0	0	0	0	0	0	0
HRRH	0	0	0	0	0	0	0	0	0

**Fig. 1.**

of the PM which originally contained fewer elementary processes. On the other hand, our method did not enable us, however, to verify the existence of the $\text{RH}_2 \rightarrow \text{HROOH}$ as well as the $\text{RH}_2 \rightarrow \text{RO}$ transitions (with respect to the carbon skeleton).

The arrows in the network corresponding to the kinetic communications represent definite rates which are certain “compositions” of all parallel and consecutive elementary processes *via* which the given kinetic communication is realized. In addition, besides the qualitative proof of the sequence network we succeeded in calculating the individual rates represented by the arrows against conversion. Naturally, these rates refer solely to carbon skeleton transitions, which *eventually* might be identical with the transitions of other atoms or atomic groups.

It is interesting to note here (details will be given elsewhere [8]) that quantitative calculations led us to the modification of the carbon-skeleton sequence network, namely to the necessary incorporation of the radical HRO_2 into the network. Consequently, the modified network is slightly different from that obtained straight from the PM by matrix operations and given in Fig. 2.

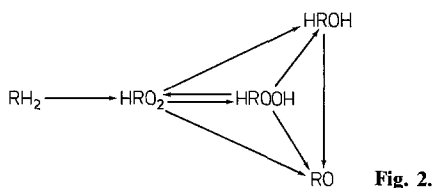


Fig. 2.

The rate values obtained from the sequence studies yield excess information compared to the “theoretical” network, mainly by indicating the role of the given kinetic communication played in the overall process. We note here that it would be interesting to also apply the recent network theory of Sinanoğlu [9] to the cases below, perhaps piece-by-piece on submechanisms to examine more general features.

3. The Sequence Networks of the Partial Oxidation of Methane

The construction procedure outlined in Part I [1] has been applied for the partial oxidation of methane at about 1500°K occurring in flames under 1–3 atmospheres. The corresponding PM was taken from the works of Benedek *et al.* [10] and is given in Table 6.

As can be seen from the PM, parallel to the oxidation pyrolytic processes also proceed. This means that besides oxygenated compounds (HCHO , CO , CO_2 and O_2) different hydrocarbons (C_2H_2 , C_2H_4 , C_2H_6) and hydrogen can also be detected among the products. Among the unstable products the radicals O^\cdot , H^\cdot , $\dot{\text{O}}\text{H}$, $\dot{\text{C}}\text{HO}$, $\dot{\text{C}}\text{H}_3$, $\dot{\text{C}}\text{H}_2$ are supposed to exist. The PM assumes the formation of water, too.

According to the PM the number of elementary processes is 32. Thus due to its complexity the complete network would be of hardly any importance. Owing to the

Table 6. The possible mechanism of the high temperature methane oxidation

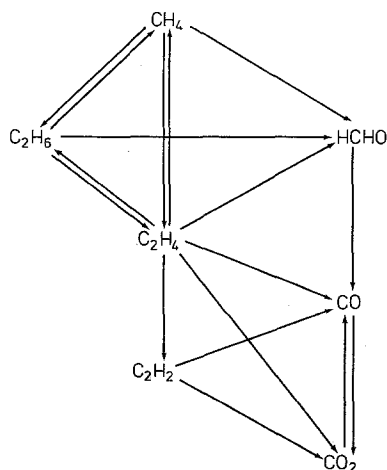
1. $\text{CH}_4 \rightarrow \dot{\text{C}}\text{H}_3 + \text{H}^\cdot$	17. $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 \rightarrow \text{C}_2\text{H}_6$
2. $\text{CH}_4 + \dot{\text{O}}\text{H} \rightarrow \dot{\text{C}}\text{H}_3 + \text{H}_2\text{O}$	18. $\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$
3. $\text{CH}_4 + \text{O}^{\cdot\cdot} \rightarrow \dot{\text{C}}\text{H}_3 + \dot{\text{O}}\text{H}$	19. $\text{C}_2\text{H}_4 + \text{O}^{\cdot\cdot} \rightarrow \dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}\text{O}$
4. $\text{CH}_4 + \text{H}^\cdot \rightarrow \dot{\text{C}}\text{H}_3 + \text{H}_2$	20. $\text{C}_2\text{H}_4 + \text{O}^{\cdot\cdot} \rightarrow \text{H}_2\text{C}^{\cdot\cdot} + \text{CH}_2\text{O}$
5. $\dot{\text{C}}\text{H}_3 + \text{H}^\cdot \rightarrow \text{CH}_4$	21. $\text{C}_2\text{H}_2 + \text{O}^{\cdot\cdot} \rightarrow \text{H}_2\text{C}^{\cdot\cdot} + \text{CO}$
6. $\dot{\text{C}}\text{H}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}^\cdot$	22. $\text{H}_2\text{O} + \text{H}^\cdot \rightarrow \dot{\text{O}}\text{H} + \text{H}_2$
7. $\dot{\text{C}}\text{H}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \dot{\text{O}}\text{H}$	23. $\text{H}^\cdot + \text{O}_2 \rightarrow \dot{\text{O}}\text{H} + \text{O}^{\cdot\cdot}$
8. $\dot{\text{C}}\text{H}_3 + \text{O}^{\cdot\cdot} \rightarrow \text{CH}_2\text{O} + \text{H}^\cdot$	24. $\dot{\text{O}}\text{H} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^\cdot$
9. $\text{CH}_2\text{O} + \dot{\text{O}}\text{H} \rightarrow \dot{\text{C}}\text{H}\text{O} + \text{H}_2\text{O}$	25. $\text{CO} + \dot{\text{O}}\text{H} \rightarrow \text{CO}_2 + \text{H}^\cdot$
10. $\text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	26. $\text{H}^\cdot + \text{CO}_2 \rightarrow \dot{\text{O}}\text{H} + \text{CO}$
11. $\dot{\text{C}}\text{H}\text{O} \rightarrow \text{CO} + \text{H}^\cdot$	27. $\text{O}_2 + \text{CO} \rightarrow \text{O}^{\cdot\cdot} + \text{CO}_2$
12. $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	28. $\text{O}^{\cdot\cdot} + \text{H}_2 \rightarrow \dot{\text{O}}\text{H} + \text{H}^\cdot$
13. $\text{C}_2\text{H}_6 \rightarrow \dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3$	29. $\dot{\text{O}}\text{H} + \dot{\text{O}}\text{H} \rightarrow \text{H}_2\text{O} + \text{O}^{\cdot\cdot}$
14. $\text{C}_2\text{H}_6 + \text{H}^\cdot \rightarrow \text{C}_2\text{H}_4 + \text{H}^\cdot + \text{H}_2$	30. $\text{H}^\cdot + \dot{\text{O}}\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O}$
15. $\text{C}_2\text{H}_6 + \dot{\text{C}}\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}^\cdot + \text{CH}_4$	31. $\text{H}^\cdot + \text{H}^\cdot + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_2$
16. $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}^\cdot + \text{H}^\cdot$	32. $\text{H}_2\text{C}^{\cdot\cdot} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}^\cdot + \text{H}^\cdot$

simultaneous occurrence of oxidative and pyrolytic processes, however, the carbon-, hydrogen- as well as oxygen-sequence network might be very useful for the detailed study of the overall process.

Omitting the initial matrices we give only the corresponding sequence networks in Figs. 3–5.

Concerning Figs. 3–5 it should be mentioned that in the partial subnetworks only stable species were taken into account and, consequently, the sequence networks contain also only these species.

It can be established from Fig. 3 that oxygenated species do not yield hydrocarbons, while ethane and ethylene are reformed into ethane. It would be very interesting to study these latter communications.

**Fig. 3.** Carbon sequence network in the high temperature oxidation of methane

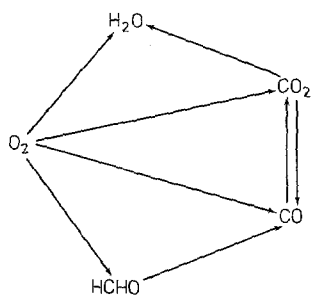


Fig. 4. Oxygen-sequence network in the high temperature methane oxidation

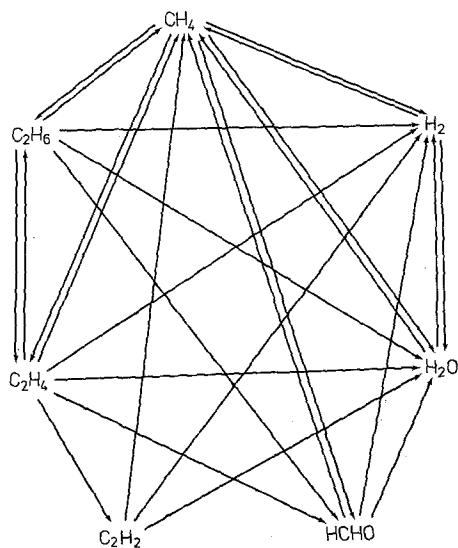


Fig. 5. Hydrogen-sequence network in the high temperature methane oxidation

The hydrogen-sequence network (Fig. 5) seems overcomplicated and its experimental verification would not give essentially more information even by application of deuterium labelling.

The oxygen-sequence network (Fig. 4) is rather simple and indicates that oxygen is incorporated into carbon dioxide both directly and via carbon monoxide and similarly the water molecules obtain their oxygen atom both from the oxygen molecules directly and via carbon dioxide.

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