

# ON THE POSSIBILITY OF USING GRAPHS IN ORDER TO DERIVE RATE EQUATIONS FOR STRAIGHT CHAIN REACTIONS (PART I)

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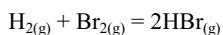
The author presents some results of an attempt to apply the graph theory for the kinetic description of straight chain reactions. Using some classical examples already solved by help of the quasi-steady-state approximation, a critical discussion on the capabilities of the graph-treatment is brought up.

The kinetic analysis of straight chain reactions by help of plane diagrams originates in the work of Christiansen [1]. On the other hand, beginning with the work of King and Altman [2] the graph theory was successfully applied in order to describe kinetically closed catalytic sequences\*\*[3÷6]. Taking into account that the straight chain reactions are also based on closed sequences, the idea of describing them by help of graph theory appears as natural. This is the reason why Temkin suggested a method to derive rate equations for catalytic and straight chain with linear mechanism reactions by help of graphs [7]. In such a theoretical frame the graphical schemes of Christiansen were transposed in graphs [8]. Detailed kinetic treatments of concrete straight chain reactions are rather difficult. This is probably due to the nonlinear character of the mechanisms associated to straight chain reactions. At least one elementary step of such reactions involves more than an active center. As known, rate equations for catalytic sequences can be obtained relatively easy mainly for linear mechanisms. The problem is whether the difficulties related to the nonlinearity of the straight chain mechanisms could be removed and consequently whether graphs can be used in order to allow derivation of the corresponding rate equations [9].

In the following, the capabilities of graph theory to describe kinetically straight chain reactions are going to be discussed. We are going to consider gas phase straight chain reactions which were already analyzed by help of the quasi-steady-state approximation [QSSA].

## 1. The Reaction between Hydrogen and Bromine

It is a well known reaction whose kinetics was investigated by Bodenstein and Lind [10] and whose mechanism was suggested in the works of Christiansen [11], Herzfeld [12] and Polanyi [13]. They showed that the experimental rate equation for the reaction:

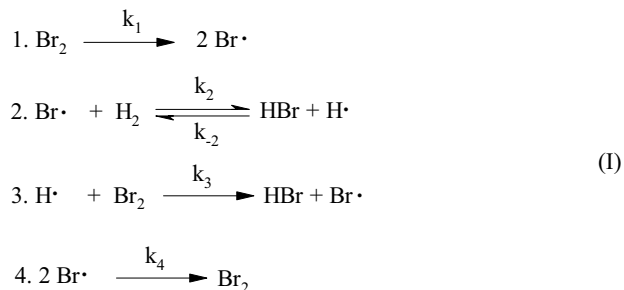


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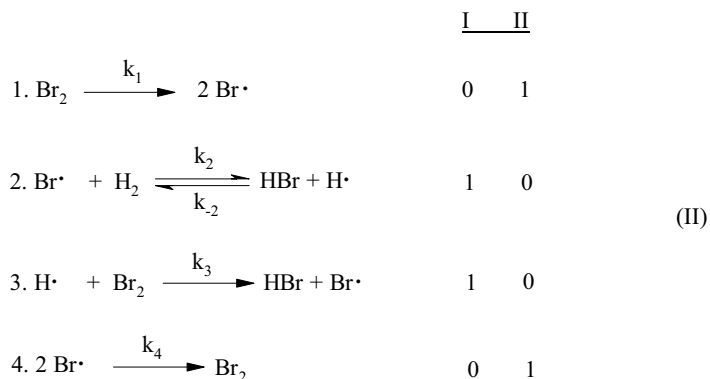
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\*\* The author supposes that the readers of this article possess the necessary knowledge concerning the use of graphs in kinetics of catalytic reactions.

can be accounted for if the following sequence of elementary steps is considered:



Actually sequence (I) corresponds to a mechanism with two basic routes, I and II [8].



with stoichiometric numbers of the elementary steps written in the corresponding columns.

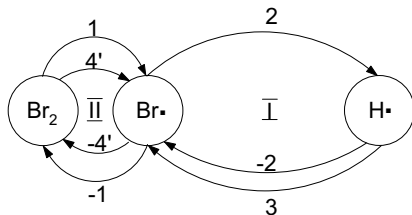


Fig. 1: Graph associated to sequence II (according to reference [8]).

The graph associated to mechanism (II) has the following form [8] (figure 1):

The dotted secondary edges account for the fact that two active centers are generated in step 1, and two active centers are consumed in step 4. For simplicity sake the frequencies of the elementary steps which usually label the edges,  $\omega_i$ , have been substituted only by figure i. Unlike graphs corresponding to catalytic sequences the active center attending the first step, according to Temkin [7], was substituted by a so called zero compound whose

concentration is supposed equal to unity and which is noted by  $\circ$ . The two mentioned routes correspond to the two cycles of the shown graph. Cycle I contains the propagation steps 2 and 3 while cycle II contains the initiation step 1, and termination step, 4.

As, according to Emanuel and Knorre, the rate along the propagation route can be considered as the rate of the chain reaction [14], in order to get this rate one can treat cycle I by help of King, Altman, Volkenshtein and Goldshtein procedures. According to the mentioned authors the reaction rate can be calculated by help of the formula:

$$r = \frac{\sum_i \omega_i D_i}{\sum_i D_i} \sum_k c_k \quad (1)$$

where  $D_i$  is the basic determinant of the vertex  $i$  of the representative graph,  $\omega_i$  is the frequency of the linear elementary step  $i$  which equals its rate divided by the concentration of the active center attending it and  $c_k$  is the concentration of the active center  $k$ . Formula (1) is valid for linear catalytic sequences as well as for the linear propagation steps of straight chain reactions. Thus for cycle I, taking into account the rules of calculation of determinants  $D_i$  [8], one obtains successively:

$$\begin{aligned} D_{Br} &= \omega_2 + \omega_3 \\ D_{H} &= \omega_2 \end{aligned} \quad (2)$$

$$r = \frac{\omega_2 D_{Br} - \omega_{-2} D_H}{\omega_2 + \omega_{-2} + \omega_3} (c_{Br} + c_H) \quad (3)$$

or taking into account relations (2),

$$r = \frac{\omega_2 \omega_3}{\omega_2 + \omega_{-2} + \omega_3} (c_{Br} + c_H) \quad (4)$$

Taking into account the meanings of  $\omega_i$  we get:

$$r = \frac{k_2 k_3 c_{H_2} c_{Br_2}}{k_2 c_{H_2} + k_{-2} c_{HBr} + k_3 c_{Br_2}} (c_{Br} + c_H) \quad (5)$$

It is known that in the occurrence conditions of the reaction [15], the rate determining active centers are the bromine atoms i.e.,  $c_{Br} > c_H$ . Under such conditions equation (5) takes the simple form:

$$r = \frac{k_2 k_3 c_{H_2} c_{Br_2}}{k_2 c_{H_2} + k_{-2} c_{HBr} + k_3 c_{Br_2}} c_{Br} \quad (6)$$

In order to obtain equation (6) we managed to bypass the use of QSSA [16].

Equation (6) contains the unknown concentration of bromine atoms. This can be eliminated taking into account that, according to the theory of straight chain reactions, the rate of chain

initiation (step 1) should be equal to the rate of chain termination (step 4) [17,18]. This equality gives:

$$c_{\text{Br}} = \left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} (c_{\text{Br}_2})^{\frac{1}{2}} \quad (7)$$

Introducing this last result in equation (6) one obtains:

$$r = \frac{\left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} k_2 k_3 c_{\text{H}_2} c_{\text{Br}_2} (c_{\text{Br}_2})^{\frac{1}{2}}}{k_2 c_{\text{H}_2} + k_{-2} c_{\text{HBr}} + k_3 c_{\text{Br}_2}} \quad (8)$$

or

$$r = \frac{\left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} k_2 c_{\text{H}_2} (c_{\text{Br}_2})^{\frac{1}{2}}}{1 + \frac{k_2 c_{\text{H}_2}}{k_3 c_{\text{Br}_2}} + \frac{k_{-2} c_{\text{HBr}}}{k_3 c_{\text{Br}_2}}} \quad (9)$$

As  $E_2 = 17.6 \text{ kcal mole}^{-1}$  and  $E_3 = 1.200 \text{ kcal mole}^{-1}$  [19] it follows that

$$\frac{k_2 c_{\text{H}_2}}{k_3 c_{\text{Br}_2}} \ll 1$$

and the rate equation (9) reduces to:

$$r = \frac{\left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} k_2 c_{\text{H}_2} (c_{\text{Br}_2})^{\frac{1}{2}}}{1 + \frac{k_{-2} c_{\text{HBr}}}{k_3 c_{\text{Br}_2}}} \quad (10)$$

or

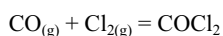
$$\frac{d c_{\text{HBr}}}{d t} = \frac{2 \left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} k_2 c_{\text{H}_2} (c_{\text{Br}_2})^{\frac{1}{2}}}{1 + \frac{k_{-2} c_{\text{HBr}}}{k_3 c_{\text{Br}_2}}} \quad (11)$$

Equation (11) is identical with that obtained using only QSSA as well as with the equation obtained experimentally by Bodenstein and Lind [11].

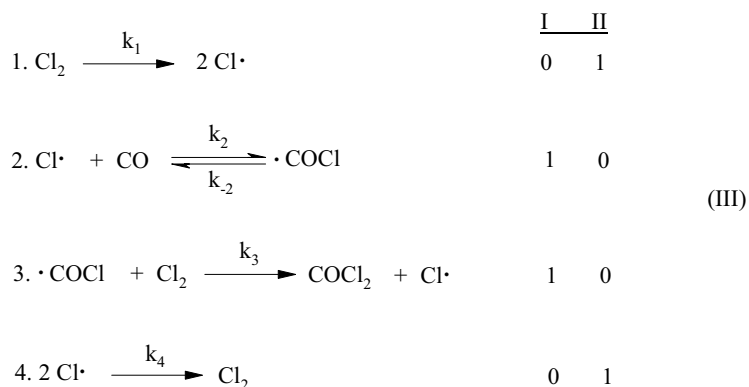
It is true that in order to get equation (9), besides the graph theory we had to use relation (7), but this equation is more general than the steady state one. In a way this equation could take another particular form for different conditions.

## 2. The Reaction between Chlorine and Carbon Monoxide [17,18]

For the reaction:



The following two route mechanism, similar to the previous one, can be considered:



The associated graph has the form shown in figure 2 where taking into account the previously mentioned reasons, only the propagation steps corresponding to route I are considered.

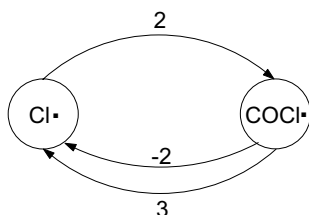


Fig. 2: Graph associated to sequence III.

By applying the same procedure as in the previous case one obtains the following rate equation:

$$r = \frac{\omega_2 \omega_3}{\omega_2 + \omega_{-2} + \omega_3} (c_{\text{Cl}} + c_{\text{COCl}}) \quad (12)$$

or taking into account that

$$\omega_2 = k_2 c_{\text{CO}}; \quad \omega_{-2} = k_{-2}; \quad \omega_3 = k_3 c_{\text{Cl}_2}$$

and considering the chlorine atoms as rate determining active centers i.e.,

$$c_{\text{Cl}} > c_{\text{COCl}} \quad \text{and} \quad k_2 c_{\text{CO}} \ll k_{-2}; k_3 c_{\text{Cl}_2}$$

we get:

$$r = \frac{k_2 k_3 c_{\text{CO}} c_{\text{Cl}}}{k_{-2} + k_3 c_{\text{Cl}_2}} c_{\text{Cl}} \quad (13)$$

Considering again the equality of the rates of initiation and termination, it is easy to obtain:

$$c_{\text{Cl}} = \left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} (c_{\text{Cl}_2})^{\frac{1}{2}} \quad (14)$$

By introducing this last result in equation (13), the following form of the rate equation is obtained:

$$r = \frac{\left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} k_2 k_3}{k_{-2} + k_3 c_{\text{Cl}_2}} c_{\text{CO}} (c_{\text{Cl}_2})^{\frac{3}{2}} \quad (15)$$

If one takes into account that  $k_{-2} \gg k_3 c_{\text{Cl}_2}$  (step 3 requires high activation energy) as well as that active center  $\cdot\text{COCl}$  is relatively unstable, equation (15) turns into:

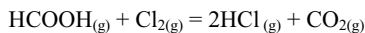
$$r = \left( \frac{k_1}{k_4} \right)^{\frac{1}{2}} \frac{k_2 k_3}{k_{-2}} c_{\text{CO}} (c_{\text{Cl}_2})^{\frac{3}{2}} \quad (16)$$

equation which coincides with the experimental verified one [18].

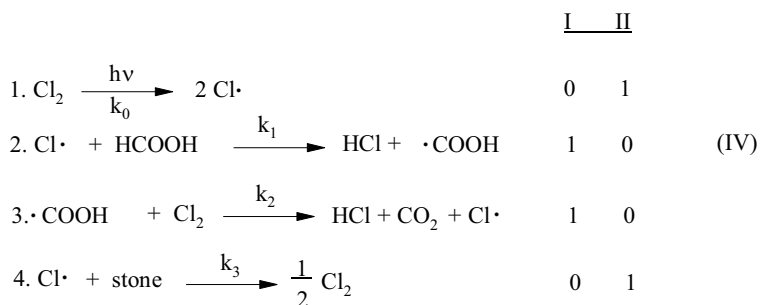
We managed to bypass the nonlinearity of step 4 using the equality of the initiation and termination rates, in this case too.

### 3. Photochemical Chlorination of Formic Acid [18]

According to literature data, the reaction:



is actually a straight chain reaction which occurs through the following two route sequence:



with the associated graph:

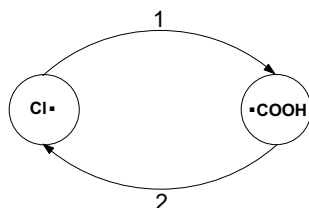


Fig. 3: Graph associated to sequence IV.

Using the same procedure as in previous cases one obtains successively:

$$D_{\text{Cl}} = \omega_2, D_{\text{COOH}} = \omega_1$$

$$r = \frac{\omega_1 \omega_2}{\omega_1 + \omega_2} (c_{\text{Cl}\cdot} + c_{\text{COOH}\cdot})$$

or

$$r = \frac{k_1 k_2 c_{\text{HCOOH}} c_{\text{Cl}_2}}{k_1 c_{\text{HCOOH}} + k_2 c_{\text{Cl}_2}} (c_{\text{Cl}\cdot} + c_{\text{COOH}\cdot}) \quad (17)$$

Considering the chlorine atoms as rate determining active centers or  $k_2 c_{\text{Cl}_2} > k_1 c_{\text{HCOOH}}$  and taking into account the equality between the rates of initiation and termination one obtains finally:

$$r = \frac{k_1 k_0}{k_3} c_{\text{Cl}_2} c_{\text{HCOOH}} \quad (18)$$

rate equation which coincides with the one obtained using only QSSA [18].

Some other examples of treatment of straight chain reactions by means of graphs will be presented in a next paper.

## Conclusions

1. A mixed procedure, using graph theory for the propagation steps as well as the condition of the equality between the initiation and termination steps, was applied in order to obtain rate equations of straight chain reactions.
2. The obtained rate equations are more general than those based on the use of QSSA only and offer the possibility to predict changes in the kinetic behaviour at the change of experimental conditions.

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