

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

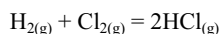
E. Segal*

Following the graph treatment of straight chain reactions presented in a previous note, the author illustrates it by some more examples.

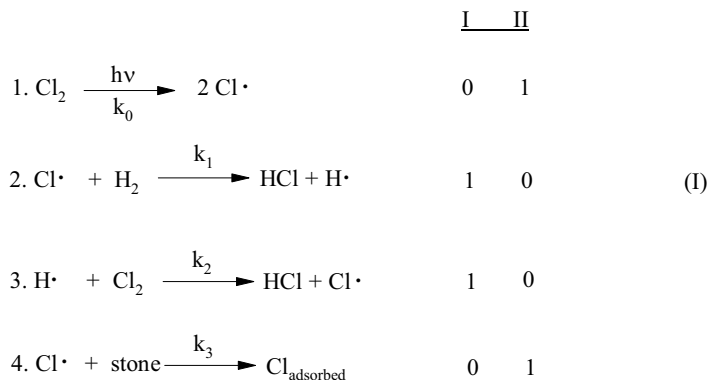
In a previous note a graph treatment of propagation steps of straight chain reactions was suggested. This paper contains some more examples illustrating the mentioned procedure and already treated by means of the quasi-steady-state-approximation.

1. Photochemical Synthesis of Hydrochloric Acid [2]

The reaction:



occurs according to the following mechanism:



with the following associated graph:

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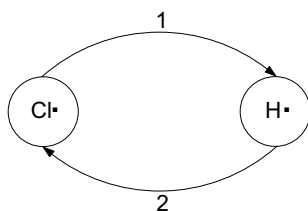


Fig. 1: Graph associated to sequence I.

Taking into account the similitude between this graph and the previous one, considering the chlorine atoms as rate determining active centers as well as the equality between the rates of initiation and termination and operating the detailed calculations one obtains:

$$r = \frac{k_0 k_1}{k_3} c_{\text{H}_2} c_{\text{Cl}_2} \quad (1)$$

and

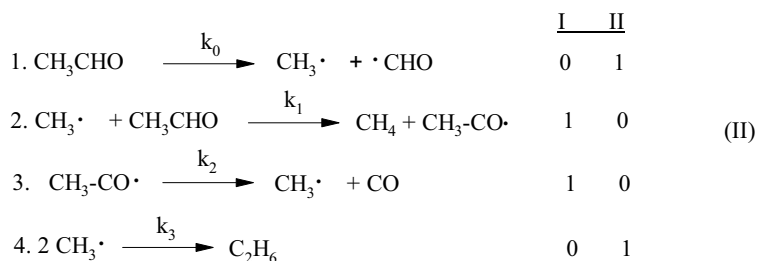
$$\frac{d c_{\text{HCl}}}{d t} = 2 \frac{k_0 k_1}{k_3} c_{\text{H}_2} c_{\text{Cl}_2} \quad (2)$$

equation which coincides with the one derived by help of only QSSA as well as with the experimentally verified one [2].

2. The Thermal Decomposition of Acetaldehyde

The simplest known mechanism of this reaction is a Rice-Herzfeld one [3,4].

In the two-route variant it has the following form:



Correspondingly the associated graph is:

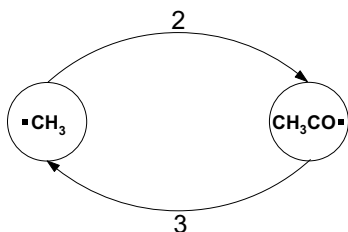


Fig. 2: Graph associated to sequence II.

Using the known procedure we get:

$$D_{\text{CH}_3\cdot} = \omega_2, \quad D_{\text{CH}_3\text{CO}\cdot} = \omega_1$$

$$r = \frac{k_1 k_2 c_{\text{CH}_3\text{CHO}}}{k_1 c_{\text{CH}_3\text{CHO}} + k_2} (c_{\text{CH}_3\cdot} + c_{\text{CH}_3\text{CO}\cdot}) \quad (3)$$

If the radicals $\text{CH}_3\cdot$ are rate determining active centers i.e.,

$$c_{\text{CH}_3\cdot} > c_{\text{CH}_3\text{CO}\cdot} \quad \text{and} \quad k_1 c_{\text{CH}_3\text{CHO}} < k_2$$

equation (3) turns into:

$$r = k_1 c_{\text{CH}_3\text{CHO}} c_{\text{CH}_3\cdot} \quad (4)$$

The equality of the rates of initiation and termination steps leads to:

$$c_{\text{CH}_3\cdot} = \left(\frac{k_0}{k_3} \right)^{\frac{1}{2}} (c_{\text{CH}_3\text{CHO}})^{\frac{1}{2}} \quad (5)$$

Taking into account this last result, equation (4) changes into:

$$r = k_1 \left(\frac{k_0}{k_3} \right)^{\frac{1}{2}} (c_{\text{CH}_3\text{CHO}})^{\frac{3}{2}} \quad (6)$$

equation which is identical with that obtained using QSSA.

If the radicals $\text{CH}_3\text{-CO}\cdot$ are rate determining active centers i.e.,

$$c_{\text{CH}_3\text{CO}\cdot} > c_{\text{CH}_3\cdot} \quad \text{and} \quad k_1 c_{\text{CH}_3\text{CHO}} > k_2$$

equation (3) turns into:

$$r = k_2 c_{\text{CH}_3\cdot} \quad (7)$$

Taking into account the condition:

$$k_0 c_{\text{CH}_3\text{CHO}} = k_3 (c_{\text{CH}_3})^2$$

it follows that

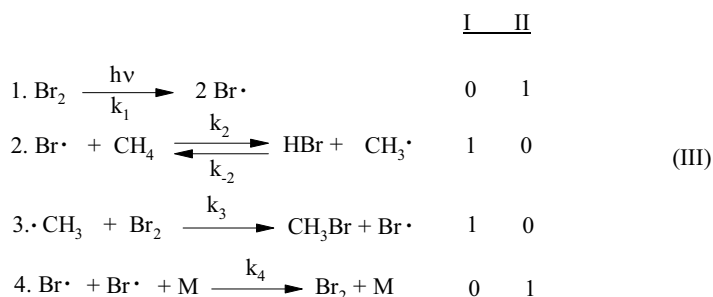
$$r = k_2 \left(\frac{k_1}{k_3} \right)^{\frac{1}{2}} (c_{\text{CH}_3\text{CHO}})^{\frac{1}{2}} \quad (8)$$

i.e. in this case the reaction order with respect to acetaldehyde should equal $\frac{1}{2}$.

Equation (8) is also identical with that obtained by applying only QSSA [4].

3. Photochemical Interaction between Bromine and Methane [3,5]

The reaction occurs according to the following two-route mechanism:



where M is an inert. The associated graph is shown in figure 3.

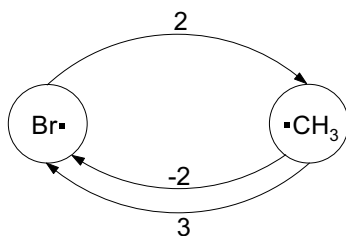


Fig. 3: Graph associated to sequence III.

By applying the already known procedure one obtains successively:

$$D_{\text{Br}} = \omega_{-2} + \omega_3, \quad D_{\text{CH}_3} = \omega_2$$

$$r = \frac{\omega_2 \omega_3}{\omega_2 + \omega_{-2} + \omega_3} (c_{\text{Br}} + c_{\text{CH}_3})$$

$$\omega_2 = k_2 c_{\text{CH}_4}; \quad \omega_{-2} = k_{-2} c_{\text{HBr}}; \quad \omega_3 = k_3 c_{\text{Br}_2}$$

$$r = \frac{k_2 k_3 c_{\text{CH}_4} c_{\text{Br}_2}}{k_2 c_{\text{CH}_4} + k_{-2} c_{\text{HBr}} + k_3 c_{\text{Br}_2}} (c_{\text{Br}} + c_{\text{CH}_3})$$

If $c_{\text{Br}} > c_{\text{CH}_3}$ and $k_2 c_{\text{CH}_4} < k_3 c_{\text{CH}_3}$

then

$$r = \frac{k_2 c_{\text{CH}_4} c_{\text{Br}}}{1 + \frac{k_{-2} c_{\text{HBr}}}{k_3 c_{\text{Br}_2}}} \quad (9)$$

Taking into account the equality between the rates of initiation and termination

$$k_1 c_{\text{Br}_2} I = k_4 c_{\text{Br}_2} c_{\text{M}} \quad (10)$$

equation (9) turns into:

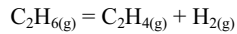
$$r = \frac{\text{const} \left(\frac{k_1}{k_2} \right)^{\frac{1}{2}} c_{\text{CH}_4} (c_{\text{Br}_2})^{\frac{1}{2}} \left(\frac{1}{P} \right)^{\frac{1}{2}}}{1 + \frac{k_{-2} c_{\text{HBr}}}{k_3 c_{\text{Br}_2}}} \quad (11)$$

where P is the total pressure in the considered system.

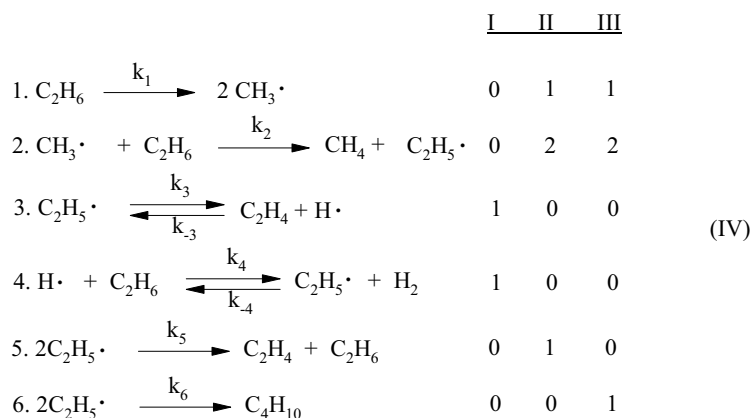
Equation (11) is identical with that obtained by applying only QSSA as well as with the experimental verified one.

4. Thermal Decomposition of Ethane

It was shown that the reaction:



occurs according to the following straight chain three-route mechanism [3,6,7]:



The associated graph is shown in figure 4.

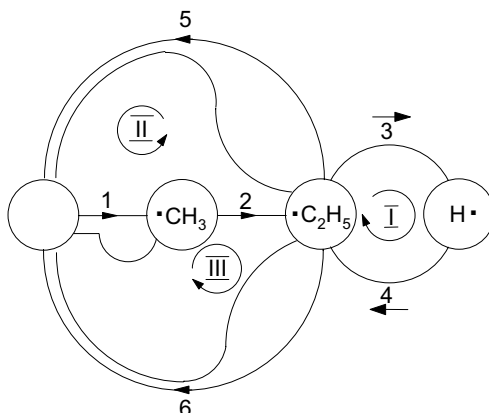


Fig. 4: Graph associated to sequence IV

The graph has three cycles, which correspond to the initiation and termination steps (cycles II and II), and one cycle, which corresponds to the propagation steps (cycle I). In this graph the irreversible stages are represented by lines with arrows i.e., directed primary edges. As shown by Temkin, the numbers of these steps are not supplied with arrows since irreversible stages are customarily considered to have the same direction as their elementary steps [6,8].

Considering the direct steps of stages 3 and 4, and applying for the propagation steps the same treatment as in previous cases we get:

$$r = \frac{\omega_3 \omega_4}{\omega_3 + \omega_4} (c_{C_2H_5\cdot} + c_{H\cdot}) \quad (12)$$

It was shown [7] that at low values of the conversion the ethyl radicals are rate determining active centers, i.e.,

$$c_{C_2H_5} \gg c_{H\cdot}, c_{CH_3\cdot} \text{ and } \omega_4 > \omega_3$$

Under such conditions equation (12) turns into:

$$r = k_3 c_{C_2H_5} \quad (13)$$

The concentration of ethyl radicals can be obtained from the obvious condition:

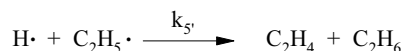
$$k_1 c_{C_2H_6} = (k_5 + k_6) (c_{C_2H_5})^2 \quad k_1 c_{C_2H_6} = (k_5 + k_6) c_{C_2H_5}^2$$

Under such conditions relation (13) turns into:

$$r = k_3 \left(\frac{k_1}{k_5 + k_6} \right)^{\frac{1}{2}} (c_{C_2H_6})^{\frac{1}{2}} \quad (14)$$

which is actually the rate equation experimentally verified for low conversion [7]. The same equation was obtained by applying only QSSA [7].

As far as the classical mechanism is concerned [3], this contains the thermal step:



Instead of steps 5 and 6 a QSSA treatment of such a mechanism leads to the rate equation:

$$r = \left(\frac{k_1 k_3 k_4}{k_5} \right)^{\frac{1}{2}} c_{C_2H_6}$$

i.e., the reaction order with respect to ethane equals unity.

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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