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# THE USE OF GRAPHS IN THE KINETIC ANALYSIS OF MULTIROUTE REACTIONS

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The author presents the graph theory calculations necessary to evaluate the rates of elementary steps corresponding to the multiroute interaction of n-hexane with supported platinum catalysts

The use of graph theory in chemical kinetics allows to apply an alternative procedure, besides the quasi-steady state approximation in order to get rate equations[1-8]. In some of our previous works methods based on graph theory were used for obtaining rate equations of catalytic and gas-phase chain reactions[9-12]. Following our research, in this paper some of our results concerning the multiroute transformations of n-hexane on supported platinum catalysts are presented. The literature data suggest that the transformation occurs according to the following mechanism[12]:

(1) N + K $\rightleftharpoons$ NK
(2) NK $\rightleftharpoons$ IK
(3) NK $\rightleftharpoons$ MCK
(4) MCK $\rightleftharpoons$ MC + K
(5) NK $\longrightarrow$ P + K
(6) NK $\longrightarrow$ B + K
(7) IK $\rightleftharpoons$ MCK
(8) IK $\rightleftharpoons$ I + K
(9) IK $\longrightarrow$ I + K
(10) MCK $\longrightarrow$ B + K

where: N, I, B, MC and P are the concentrations of n-hexane, isomers of hexane, benzene, methylcyclopentane and products of cracking resepectively; K, NK, MCK and IK – concentrations of corresponding surface intermediates.

The rate of an elementary step,s, in a complex multiroute reaction, $r_s$, can be calculated with the formula:

$$r_s = \frac{\sum_{i=1}^{M} \Omega_i P_i}{D} \qquad (1)$$

where: M is the number of cycles at which step s attends, $\Omega_i$; is the cyclic characteristics of cycle i given by relation (2); $\upsilon$ stands for the number of arcs in the cycle i and $P_i$ is the conjugation parameter of cycle i indicating how the compounds non included in the cycle influence its reaction rate and $\omega^{+}(\upsilon)$ and $\omega^{-}(\upsilon)$ are, respectively, the frequencies of the direct and inverse elementary steps, H is the number of cycles which remains after cycle i shrinks to a point in its base, and D is the sum of the base determinant of the graph vertices. The conjugation parameter of a cycle is defined as the weight of the forest which ends in the cycle without including the arcs of the cycle[6].

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For the reaction mechanisms described by only one cycle P=1:

$$\Omega_i = \prod_{\upsilon} \omega^{+}(\upsilon) - \prod_{\upsilon} \omega^{-}(\upsilon) \qquad (2)$$

$$P_i = \sum_{H} \omega(H) \qquad (3)$$

The graph associated to the suggested mechanism is:

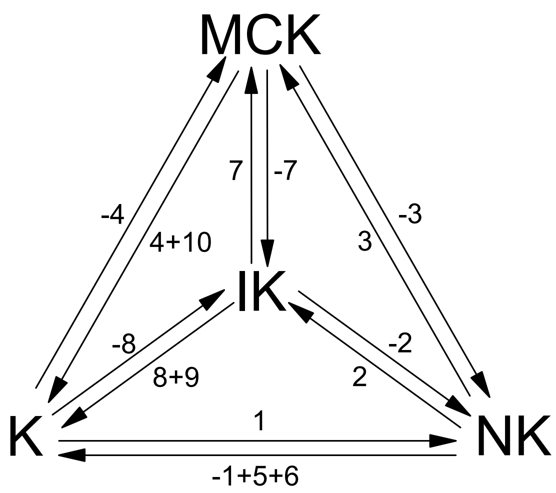


Fig.1

As one can easily see, the weights (frequencies) of some edges are obtained by summing the weights of some elementary steps.

$$\omega_{NK-K} = \omega_{-1} + \omega_5 + \omega_6$$
$$\omega_{IK-K} = \omega_{+8} + \omega_9$$
$$\omega_{MCK-K} = \omega_4 + \omega_{10}$$

For the considered mechanism one can mention the calculations of cyclic characteristics and conjugation parameters necessary to calculate the rate of stage 3, $r_3$ according to formula (1)[12]. The denominator, D, has not been calculated.

The aim of this work is to perform all the calculations necessary to apply the formula (1) for all the 10 steps and stages of the considered mechanism.

Thus, for stage 1 and cycle 1, K-NK-IK-K, we get:

$$\Omega_1^1 = \omega_1(\omega_8 + \omega_9)\omega_2 - (\omega_{-1} + \omega_5 + \omega_6)\omega_{-2}\omega_{-8}$$
$$P_1^1 = \omega_4 + \omega_{10} + \omega_{-7} + \omega_{-3}$$

where the lower index corresponds to the stage and the upper one to the cycle.

For stage 1 and cycle 2, K-NK-MCK-K,we get:

$$\Omega_1^2 = \omega_3(\omega_4 + \omega_{10})\omega_1 - \omega_{-3}\omega_{-4}(\omega_{-1} + \omega_5 + \omega_6)$$
$$P_1^2 = \omega_{-2} + \omega_7 + \omega_8 + \omega_9$$

Using the same rules of calculation we obtain successively:

For stage 1 and cycle 3, K-NK-IK-MCK-K, we get:

$$\Omega_1^3 = (\omega_4 + \omega_{10})\omega_1\omega_2\omega_7 - (\omega_{-1} + \omega_5 + \omega_6)\omega_{-2}\omega_{-4}\varpi_{-7}$$
$$P_1^3 = 1$$

For stage 1 and cycle 4 , K-NK-MCK-IK-K we get:

$$\Omega_1^4 = \omega_1\omega_3\omega_{-7}(\omega_8 + \omega_9) - \omega_{-3}(\omega_{-1} + \omega_5 + \varpi_6)\omega_7\omega_{-8}$$
$$P_1^4 = 1$$

Stage 2:

Cycle 1, NK-IK-MCK-NK:

$$\Omega_2^1 = \omega_2\omega_7\omega_{-3} - \omega_{-2}\omega_{-7}\omega_3$$
$$P_2^1 = \omega_1 + \omega_{-8} + \omega_{-4}$$

Cycle 2, NK-IK-K-NK:

$$\Omega_2^2 = \omega_2(\omega_8 + \omega_9)\omega_1 - \omega_{-2}\omega_{-8}(\omega_{-1} + \omega_5 + \omega_6)$$
$$P_2^2 = \omega_{-7} + \omega_4 + \omega_{10} + \omega_{-3}$$

Cycle 3, NK-IK-MCK-K-NK:

$$\Omega_2^3 = \omega_2\omega_7(\omega_4 + \omega_{10})\omega_1 - \omega_{-2}\omega_{-4}\omega_{-7}(\omega_{-1} + \omega_5 + \omega_6)$$
$$P_2^3 = 1$$

Cycle 4, NK-IK-K-MCK-NK:

$$\Omega_2^4 = \omega_{-4}\omega_{-3}\omega_2(\omega_8 + \omega_9) - \omega_4\omega_3\,\omega_{-2}\omega_{-8}$$
$$P_2^4 = 1$$

Stage 3:

Cycle 1, NK-MCK-IK-NK:

$$\Omega_3^1 = \omega_3\omega_{-7}\omega_{-2} - \omega_{-3}\omega_7\omega_2$$
$$P_3^1 = \omega_{-4} + \omega_{-8} + \omega_1$$

Cycle 2, NK-MCK-IK-K-NK:

$$\Omega_3^2 = \omega_3\omega_{-7}(\omega_8 + \omega_9)\omega_1 - \omega_{-3}\omega_7(\omega_{-1} + \omega_5 + \omega_6)\omega_{-8}$$
$$P_3^2 = 1$$

Cycle 3, NK-MCK-K-IK-NK:

$$\Omega_3^3 = \omega_{-2}(\omega_4 + \omega_{10})\omega_3\omega_{-8} - \omega_2\omega_{-4}(\omega_8 + \omega_9)\omega_{-3}$$
$$P_3^3 = 1$$

Cycle 4, NK-MCK-K-NK:

$$\Omega_3^4 = \omega_3(\omega_4 + \omega_{10})\omega_1 - \omega_{-3}\omega_{-4}(\omega_{-1} + \omega_5 + \omega_6)$$
$$P_3^4 = (\omega_8 + \omega_9) + \omega_7 + \omega_{-2}$$

Stage 4:

Cycle 1, K-IK-MCK-K:

$$\Omega_4^1 = \omega_{-8}\omega_7(\omega_4 + \omega_{10}) - (\omega_8 + \omega_9)\omega_{-7}\omega_{-4}$$
$$P_4^1 = \omega_3 + \omega_2 + (\omega_{-1} + \omega_5 + \omega_6)$$

Cycle 2, K-IK-NK-K:

$$\Omega_4^2 = \omega_{-8}\omega_{-2}(\omega_{-1} + \omega_5 + \omega_6) - (\omega_8 + \omega_9)\omega_2\omega_1$$
$$P_4^2 = \omega_4 + \omega_{10} + \omega_{-7} + \omega_{-3}$$

Cycle 3, K-IK-MCK-NK-K:

$$\Omega_4^3 = \omega_{-8}\omega_7\omega_{-3}(\omega_{-1} + \omega_5 + \omega_6) - (\omega_8 + \omega_9)\omega_{-7}\omega_3\omega_1$$
$$P_4^3 = 1$$

Cycle 4, K-IK-NK-MCK-K:

$$\Omega_4^4 = \omega_{-8}\omega_{-2}\omega_3(\omega_4 + \omega_{10}) - \omega_{-4}\omega_{-3}\omega_2(\omega_8 + \varpi_9)$$
$$P_4^4 = 1$$

Step 5:

Cycle 1, NK-K-IK-NK:

$$\Omega_5^! = (\omega_{-1} + \omega_5 + \omega_6)\omega_{-8}\omega_{-2}$$
$$P_5^1 = \omega_4 + \omega_{10} + \omega_{-7} + \omega_{-3}$$

Cycle 2, NK-K-MCK-NK:

$$\Omega_5^2 = (\omega_{-1} + \omega_5 + \omega_6)\omega_{=4}\omega_{-3}$$
$$P_5^2 = (\omega_8 + \omega_9) + \omega_7 + \omega_{-2}$$

Cycle 3, NK-K-IK-MCK-NK:

$$\Omega_5^3 = (\omega_{-1} + \omega_5 + \omega_6)\omega_{-8}\omega_7\omega_{-3}$$
$$P_5^3 = 1$$

Cycle 4, NK-K-MCK-IK-NK:

$$\Omega_5^4 = (\omega_{-1} + \omega_5 + \omega_6)\omega_{-4}\omega_{-7}\omega_{-2}$$
$$P_5^4 = 1$$

Step 6:

Cycle 1, NK-K-IK-NK:

$$\Omega_6^1 = (\omega_{-1} + \omega_5 + \omega_6)\omega_{-2}\omega_{-8}$$
$$P_6^1 = (\omega_4 + \omega_{10}) + \omega_{-3} + \omega_{-7}$$

Cycle 2, NK-K-MCK-NK:

$$\Omega_6^2 = (\omega_{-1} + \omega_5 + \omega_6)\omega_{-4}\omega_{-3}$$
$$P_6^2 = \omega_7 + \omega_8 + \varpi_9 + \omega_{-2}$$

Cycle 3, NK-K-IK-MCK-NK:

$$\Omega_6^3 = (\omega_{-1} + \omega_5 + \omega_6)\omega_{-8}\omega_7\omega_{-3}$$
$$P_6^3 = 1$$

Cycle 4, NK-K-MCK-IK-NK:

$$\Omega_6^4 = (\omega_{-1} + \omega_5 + \omega_6)\omega_{-4}\omega_{-7}\omega_{-2}$$
$$P_6^4 = 1$$

Stage 7:

Cycle 1, NK-MCK-IK-NK:

$$\Omega_7^1 = \omega_3\omega_{-7}\omega_{-2} - \omega_{-3}\omega_7\omega_2$$
$$P_7^1 = \omega_{-4} + \omega_{-8} + \omega_1$$

Cycle 2, NK-IK-MCK-NK:

$$\Omega_7^2 = \omega_2\omega_7\omega_{-3} - \omega_{-2}\omega_{-7}\omega_3$$
$$P_7^2 = \omega_1 + \omega_{-8} + \omega_{-4}$$

Cycle 3, NK-MCK-IK-K-NK:

$$\Omega_7^3 = \omega_3\omega_{-7}(\omega_8 + \omega_9)\omega_1 - \omega_{-3}\omega_7\omega_{-8}(\omega_{-1} + \omega_5 + \omega_6)$$
$$P_7^3 = 1$$

Cycle 4, NK-IK-MCK-K-NK:

$$\Omega_7^4 = \omega_2\omega_7(\omega_4 + \omega_{10})\omega_1 - \omega_{-2}\omega_{-7}\omega_{-4}(\omega_{-1} + \omega_5 + \omega_6)$$
$$P_7^4 = 1$$

Stage 8:

Cycle 1, IK-K-MCK-IK:

$$\Omega_8^1 = \omega_{-4}\omega_{-7}(\omega_8 + \omega_9) - \omega_4\omega_7\omega_{-8}$$

$$P_8^1 = (\omega_{-1} + \omega_5 + \omega_6) + \omega_2 + \omega_3$$

Cycle 2, IK-K-NK-IK:

$$\Omega_8^2 = (\omega_8 + \omega_9)\omega_2\omega_1 - \omega_{-8}\omega_{-2}(\omega_{-1} + \omega_5 + \omega_6)$$

$$P_8^2 = (\omega_4 + \omega_{10}) + \omega_{-7} + \omega_{-3}$$

Cycle 3, IK-K-MCK-NK-IK:

$$\Omega_8^3 = (\omega_8 + \omega_9)\omega_{-4}\omega_{-3}\omega_2 - \omega_{-8}(\omega_4 + \omega_{10})\omega_{-2}\varpi_3$$

$$P_8^3 = 1$$

Cycle 4, IK-K-NK-MCK-IK:

$$\Omega_8^4 = \omega_1\omega_3\omega_{-7}(\omega_8 + \omega_9) - (\omega_{-1} + \omega_5 + \omega_6)\omega_{-3}\varpi_7$$

$$P_8^4 = 1$$

Step 9:

Cycle 1, MCK-IK-K-MCK:

$$\Omega_9^1 = \omega_{-7}(\omega_8 + \omega_9)\omega_{-4}$$

$$P_9^1 = (\omega_{-1} + \omega_5 + \omega_6) + \omega_2 + \omega_3$$

Cycle 2, NK-IK-K-NK:

$$\Omega_9^2 = \omega_2(\omega_8 + \omega_9)\omega_1$$

$$P_9^2 = (\omega_4 + \omega_{10}) + \omega_{-7} + \omega_{-3}$$

Cycle 3, NK-MCK-IK-K-NK:

$$\Omega_9^3 = \omega_3\omega_{-7}(\omega_8 + \omega_9)\omega_1$$

$$P_9^3 = 1$$

Cycle 4, NK-IK-MCK-K-NK:

$$\Omega_9^4 = \omega_1\omega_2\omega_7(\omega_4 + \omega_{10})$$

$$P_9^4 = 1$$

Step 10:

Cycle 1, MCK-K-IK-MCK:

$$\Omega_{10}^1 = \omega_{-8}\omega_7(\omega_4 + \omega_{10})$$

$$P_{10}^1 = \omega_3 + \omega_2 + (\omega_{-1} + \omega_5 + \omega_6)$$

Cycle 2, MCK-K-NK-MCK:

$$\Omega_{10}^2 = \omega_3(\omega_4 + \omega_{10})\omega_1$$

$$P_{10}^2 = \omega_7 + (\omega_8 + \omega_9) + \omega_{-2}$$

Cycle 3, MCK-K-NK-IK-MCK:

$$\Omega_{10}^3 = (\omega_4 + \omega_{10})\omega_1\omega_2\omega_7$$

$$P_{10}^3 = 1$$

Cycle 4, MCK-K-IK-NK-MCK:

$$\Omega_{10}^4 = \omega_{-2}\omega_3\omega_{-8}(\omega_4 + \omega_{10})$$

$$P_{10}^4 = 1$$

The basis determinants of the representative graph are:

$$D_{MCK} = (\omega_8 + \omega_9)\omega_{-4} + \omega_{-4}\omega_7 + (\omega_{-1} + \omega_5 + \omega_6)\omega_{-4} + \omega_{-2}\omega_3 + \omega_1\omega_3 + \omega_3\omega_7 + \omega_3\omega_{-4} + \omega_2\omega_7 + \omega_{-8}\omega_7$$

$$D_{NK} = \omega_{-3}\omega_{-2} + \omega_1\omega_{-3} + \omega_{-4}\omega_{-3} + \omega_7\omega_{-3} + (\omega_4 + \omega_{10})\omega_1 + (\omega_8 + \omega_9)\omega_1 + \omega_{-7}\omega_{-2} + \omega_1\omega_{-2} + \omega_{-8}\omega_{-2}$$

$$D_{IK} = (\omega_4 + \omega_{10})\omega_{-8} + \omega_{-4}\omega_{-7} + \omega_3\omega_{-7} + \omega_1\omega_2 + (\omega_{-1} + \omega_5 + \omega_6)\omega_{-8} + \omega_2\omega_{-3} + \omega_2\omega_{-8} + \omega_{-7}\omega_{-8} + \omega_2\omega_{-7}$$

$$D_K = \omega_7(\omega_4 + \omega_{10}) + \omega_{-7}(\omega_8 + \omega_9) + \omega_{-2}(\omega_{-1} + \omega_5 + \omega_6) + \omega_{-3}(\omega_{-1} + \omega_5 + \omega_6) + (\omega_4 + \omega_{10}))(\omega_8 + \omega_9) +$$
$$+ (\omega_4 + \omega_{10})(\omega_{-1} + \omega_5 + \omega_6) + \omega_2(\omega_8 + \omega_9) + \omega_{-1}(\omega_8 + \omega_9) + \omega_3(\omega_4 + \omega_{10})$$

## CONCLUSIONS

1. For the interaction of n-hexane with supported platinum catalysts, using graph theory, the author presents the results of the following calculations:

– the cyclic characteristic as well as the conjugation parameter for 9 of the 10 mechanistic steps/stages,

– the basic determinant of each vertex of the mechanistic representative graph.

2. The obtained rates could be eventually used as kinetic stability indexes.

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