Numerical Revelation of the Molecular Structure for Reaction Effective Stimulator or Inhibitor by the Method of Hamiltonean Systematization of Chemical Reaction System Kinetic Models

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1 Introduction

The fundamental question of theoretical chemistry is to find the relationship between the electronic structure of reacting particles and their reactivity. In the case of reactions proceeding through complex multi-step mechanisms the problem to determine specie reactivity's is of difficult solution. This report presents a new numerical method, which enables to reveal the structure of reaction optimal (effective) stimulator (catalyst, promoter, *etc.*) and inhibitor based upon the kinetic model available for the multi-step chemical reaction.

1.1 Theoretical Fundamentals

Calculus of variations using the Pontjagin principle of maximum forms the basis for the non-empirical solution of the problem concerning the revelation of molecular structure an optimal stimulator is to be of, in the case of a complex (multistep) reaction [1,2].

In order to solve the mentioned above problem we have suggested for the characteristics of reaction component molecular structure to be presented as control parameters. The solution infers to step by stage execution of the following steps:

a) Based upon chemical reaction kinetic model, selection of the aimed control character – F : the functional, characterizing the chosen indicator of reaction stimulator or inhibitor reactivity (for example, the rate of purposeful product formation, the rate of initial species consumption, *etc.*);

$$I(t)=\int_0^t F(t)dt = extremum \tag{1}$$

b) Presentation of rate constants for individual steps in the reaction system kinetic model with participation of reaction stimulator and intermediate products from its conversion as a function of parameters, which characterize the molecular structure of reaction stimulator or inhibitor

$$k_j = \varphi_j(D), \tag{2}$$

where D is a numerical parameter characterizing the molecular structure of reaction stimulator and inhibitor (e.g. bond energy, ionization potential, steric parameters, *etc*);

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c) setting up kinetic equations and the respective Hamiltonian H with selecting the control parameters;

$$dc_i/dt = f_i(k,c,D) \qquad i=1,2,...m, \tag{3}$$

$$H = -F + \sum_{i=1}^{m} \psi_i f_i(k,c,D) \tag{4}$$

where $c(t)$ is the m-vector for the concentration of c_i components, $c(t_0) = c^0$; k- the n-vector of rate constants; ψ_i – the function conjugate to the concentrations c_i, D – p-vector of parameters for a reaction stimulator or inhibitor molecular structure.

The control parameters of D are assumed to be varied in a range of

$$D_l^{min} \le D_l \le D_l^{max}, \quad l=1,2,\ldots,p \tag{5}$$

d) setting up a system of differential equations for conjugate functions $\psi_i(t)$ (value of components)

$$\frac{d\psi_i}{dt} = -\frac{\partial H}{\partial c_i}, \qquad i=1,2,...,m \tag{6}$$

e)Determination of conjugate function values $\psi_i(t_0)$ for the initial moment of time [3].

f) Finding of the optimum via parameters of reaction stimulator molecular structure. In respect to the principle of maximum the conditions for the optimum are:

$$\sup H(\psi^*, c^*, D^*) = 0 \tag{7}$$

The solution of the system of kinetic equations (3) and that of differential ones (6) with simultaneous observance of extremum conditions (7) correspond to optimal value for D^*. At this D^* is chosen from values of D^{min}, D^{max} and D^{cl}, where D^{cl} is the value of D, corresponding to condition $\partial H/\partial D = 0$.

The time-constancy condition for molecular structure parameters of reaction stimulator and inhibitor: $D = const$, significantly simplifies the problem. The value of D found for the initial moment of time corresponds to parameter values characterizing the molecular structure of reaction optimal stimulator for the given conditions of that reaction proceeding.

g) Determination of chemical reaction effective stimulator molecular structure using the calculated values of D^*.

h) Numerical ranging of stages and components in accordance with their value contributions and significance to have the dominating chemical stages and components be revealed, which in the result, determine the molecular structure of the most effective (optimal) stimulator or inhibitor for chemical reaction under the given conditions [3]. (It makes the obtained results evident from the chemical point of view).

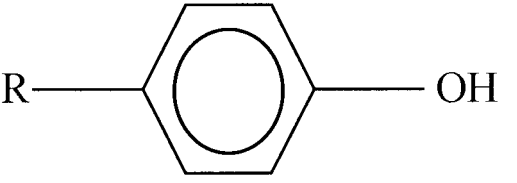
2 An Illustrative Example. Computational Determination of the Molecular Structure for Reaction Effective Antioxidant in the Inhibited Reaction of the Ethylbenzene Liquid Phase Oxidation

For the example presented, the solution of the stated problem infers to the determination of molecular structure of the effective inhibitor from the class of p-substituted phenols (InH) for ethylbenzene (RH) liquid phase oxidation.

Table 1. Kinetic model of ethylbenzene (RH) oxidation reaction inhibited by p-substituted phenols (InH).

№	Reactions	Rate constant, k, lgk= $\varphi(D_{OH})$ /60°C
1.	$2RH + O_2 \rightarrow 2R^{\cdot} + H_2O$	9,26 x 10^{-13}
2.	$\dot{R} + O_2 \rightarrow R\dot{O}_2$	8,75 x 10^{8}
3.	$R\dot{O}_2 + RH \rightarrow RO_{2H} + \dot{R}$	2,74
4.	$RO^{\cdot} + RH \rightarrow ROH + \dot{R}$	2,32 x 10^{6}
5.	$OH + RH \rightarrow H_2O + \dot{R}$	10^{9}
6.	$RO_2H \rightarrow RO^{\cdot} + \dot{O}H$	10^{-9}
7.	$RO_2H \rightarrow R(-H)O + H_2O$	3 x 10^{-9}
8.	$R\dot{O} + RO_2H \rightarrow ROH + R\dot{O}_2$	4,9 x 10^{8}
9.	$R\dot{O}_2 + R\dot{O}_2 \rightarrow 2R\dot{O} + O_2$	5,5 x 10^{6}
10.	$R\dot{O}_2 + R\dot{O}_2 \rightarrow ROH + R(-H)O + O_2$	10^{7}
11.	$R\dot{O}_2 + InH \rightarrow ROH + \dot{I}n$	lgk_{11}=34,24-0,082 D_{OH}
12.	$R\dot{O} + InH \rightarrow \dot{I}n + ROH$	lgk_{12}=17,5-0,025 D_{OH}
13.	$RO_2H + InH \rightarrow \dot{I}n + R\dot{O} + H_2O$	lgk_{13}=50,1-0,157 D_{OH}
14.	$\dot{I}n + R\dot{O}_2 \rightarrow In(-H)O + ROH$	7 x 10^{8}
15.	$\dot{I}n + \dot{I}n \rightarrow InH + In(-H)$	3,5 x 10^{8}
16.	$\dot{I}n + RH \rightarrow InH + \dot{R}$	lgk_{16}=-25,2+0,066 D_{OH}
17.	$\dot{I}n + RO_2H \rightarrow InH + RO_2$	lgk_{17}=-22,24+0,072 D_{OH}

Note: rate constants are given in units of M, sec.; the value for phenolic OH bond energy in the molecule of *p*-substituted phenol (D_{OH}) - kJ/mole. The bond energy is changed in a range of 355-382,5 kJ/mole. The temperature of the reaction equals to 60°C. The structural formula of the substituted phenol is: (R - substituting group)



The solution of the problem is performed using the reaction scheme presented in Table 1[4]. Authors of the present report experimentally approve the choice of this kinetic model.

For the reaction model given in Table 1, the value of D_{OH} relating to OH bond energy of *p*-substituted phenol is presented as the control parameter. Following this purpose there are given the correlation equations in Table 1, for the reaction steps (11)-(13), (16), and (17). These equations describe the dependence of constants for stages proceeding with participation of p -substituted phenol and phenoxyl radical on OH bond energy in p -substituted phenol.

The purpose functional was chosen taking into account that the effective inhibitor is to be considered the one that the most retards the chemical reaction, decreasing its overall rate (r). In respect with this statement the following purpose functional is to be chosen for this problem:

$$I(t) = \int_0^t r dt = \min \tag{8}$$

where $r = dc_{RH}/dt$; c_{RH} is the concentration of ethylbenzene.

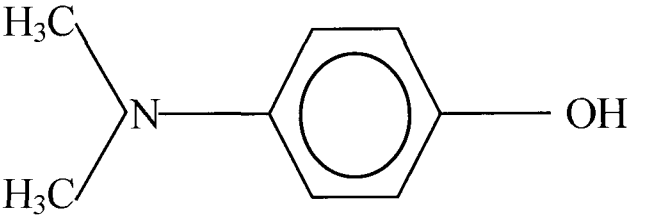
Then, performing the following operations, in accordance with procedures (method) described in items (b)-(g), the Hamiltonian values are accounted depending on D_{OH} for various initial concentrations of the inhibitor.

For a certain $[InH]_{\!o}$ the value of optimal D^*_{OH} and respectively, the molecular structure of the effective antioxidant-inhibitor for oxidation reaction of ethylbenzene correspond to the minimal value of Hamiltonian.

Numerical accounts have been performed using computer program VALKIN that we have developed. The algorithm of the program VALKIN is developed on the basis of Hamiltonian systematization for chemical reaction system mathematical models [1,3]. In this program the differential equations are solved by the program ROW-4A [5]. Simulations were carried out using personal computer. Results from simulations may be reduced to graphics, diagrams and other visual convenient forms.

The following result is obtained in the result of simulations:

In a wide range of inhibitor initial concentration (10^{-4} - 10^{-2} M) D^{*}_{OH} equaled to its minimal possible value (355 kJ/mole) and the following molecular structure of p-substituted phenol corresponds to it



As it was mentioned above, the useful information contains the significance of value contribution individual steps (11-13, 16, 17) with participation of effective inhibitor and phenoxile radical, the speed constants of which are sensitive to the index of reaction ability of D_{OH} . Be reminded that the value contribution (h_j) stage characterizing its kinetic significance is calculated with joint solution of equation (3) and (6) of Hamilton systematization [1,3]

$$h_j(t) = v_j(t) G_j(t), \qquad G_j(t) = \frac{\partial F\left[v_1(t), \ldots v_n(t)\right]}{\partial v_j}\Big|_{v_j = v_j(t_0)}, \quad (9)$$

where $v_j(t)$ is the speed of j -th stage, n -the number in kinetic model of the chemical reaction. In the case being examined $F \equiv r$.

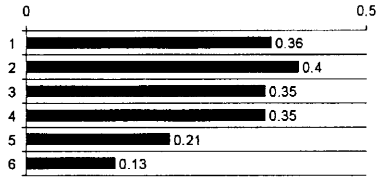
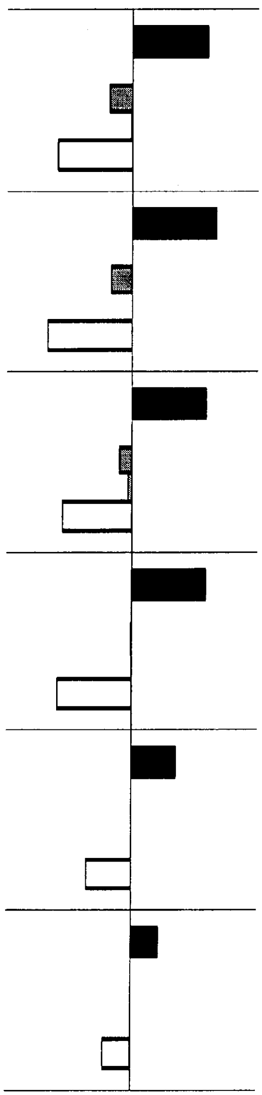
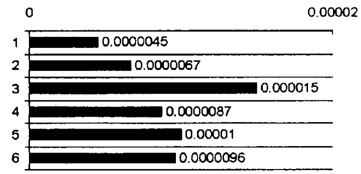
According to the findings acquired from the Table 2, much more ponderable contributions have the step (11) and the step (17) which is opposite to (11).

It's obvious that in the process of inhibited oxidation the balance is carried out namely by means of these reaction steps;

$$RO_2^{\bullet} + InH \underset{k_{17}}{\overset{k_{11}}{\rightleftharpoons}} RO_2H + In^{\bullet} \qquad (v_{11} \approx v_{17})$$

Now it's quite evident that the effective inhibitor with minimal significance of Don ensures the highest displacement of the given balance in the law: from the carrier of chain peroxide radical to the side of the phenoxide radical formation.

Table 2. The acquired value step contributions dependinf on D_{OH} for the liquid-phase auto-oxidation of ethil-benzene are inhibited by effective anti-oxidant of p – dimethilaminophenol. The temperature is equal to 60^0 C. The level of antioxidant conversion is 70%. The initial antioxidant and hydroperoxide ethyl-benzene concentrations are 10^{-3}, 10^{-5} M, respectively.

<table>
<tr><th>№</th><th>Reactions</th><th>$\bar{h}_j$</th></tr>
<tr><td>11.</td><td>$R\dot{O}_2 + InH \rightarrow ROH + \dot{I}n$
 
</td><td rowspan="5">  </td></tr>
<tr><td>12.</td><td>$R\dot{O} + InH \rightarrow \dot{I}n + ROH$
 
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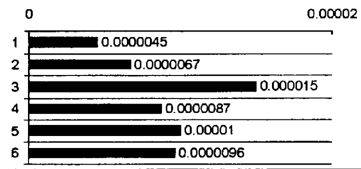
<tr><td>13.</td><td>$RO_2H + InH \rightarrow \dot{I}n + R\dot{O} + H_2O$
 
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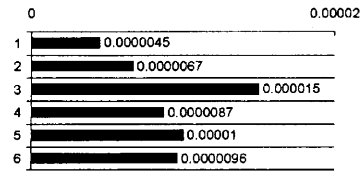
<tr><td>16.</td><td>$\dot{I}n + RH \rightarrow InH + \dot{R}$
 
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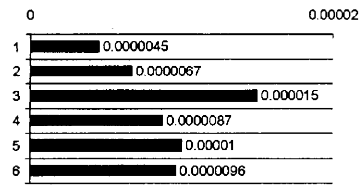
<tr><td>17.</td><td>$\dot{I}n + RO_2H \rightarrow InH + R\dot{O}_2$
 
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where $\overline{h}_j$ is the radical value contribution of j -th stage

$$\overline{h}_j = h_j \left(\sum_{j=1}^{17} h_j^2 \right)^{-1/2}$$

3 Conclusions

Based upon the presented research the following conclusions are made:
Hamiltonian systematization using the Pontjagin principle of maximum is an operative method to be applied for multi-stage chemical reaction system mathematical model to have the molecular structure of chemical reaction optimal stimulator be numerically revealed.
The definition of kinetic significance of the stage by means of value contributions made it possible to define stages including inhibitor and its intermediate-phenoxile radical which determine the efficacy of the action of the initial inhibitor.
Computer program VALKIN worked out on the basis of value analysis for kinetic models of complex chemical reaction systems is an effective program to be used for the computational solution of analogous problems in chemistry and relating disciplines.

References

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