Mathematical modeling of radical-chain reaction of isopropylbenzene oxidation

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Abstracts. Isopropylbenzene (IPB) oxidation by air oxygen is an intermediate stage of phenol and acetone production process. Hydroperoxide of isopropylbenzene (HP IPB) is a target product of this process. In this article reaction scheme of isopropylbenzene oxidation was proposed and kinetic model based on reaction scheme developed. Also it was important to choose approach for mathematical simulation of chemical reaction. In this work system of differential equations was used for oxidation reaction simulation. Different types of numerical methods were used for model solution. The results we obtained were compared with data from other researches.

1. Introduction
Isopropylbenzene (or cumene) oxidation by air oxygen is an intermediate stage of industrial process of acetone and phenol production (cumene method). Cumene method is the most world spread industrial method for phenol and acetone production nowadays [1]. Isopropylbenzene reacts with oxygen and the hydroperoxide of isopropylbenzene (HP IPB) is formed along with some undesired by-products. Gross formula for main oxidation reaction represented below:

\[ C_6H_5(CH_3)_2CH + O_2 \rightarrow C_6H_5(CH_3)_2COOH \]  

(1)

Of course gross formula doesn’t represent complicated mechanism of oxidation reaction. IPB oxidation is radical-chained reaction, which means that there is great number of different types of particles (radicals, molecules) which take part in numerous elementary stages of reaction (decomposition of molecules and large radicals, recombination of radicals, etc) [2,3]. Different authors propose various reactions schemes and kinetic models of the IPB oxidation but some principles stay the same, such as main phases of radical-chained reaction (initiation, propagation and termination) and coincidence of some elementary stages throw various models [2-5].

2. Kinetic model of isopropylbenzene oxidation

2.1. Reaction scheme
IPB oxidation by the air oxygen is a radical-chain reaction, as we mentioned earlier. It has been studied since the middle of XX century. We reviewed various existing studies about the reaction by
different authors [2-5] during our research. As results we established some principles which are true for most of reaction schemes and kinetic models of isopropylbenzene oxidation:

- Initiation mechanism is very important for overall reaction scheme, and there are two types of it: with HP IPB (by its decomposition on radicals) and without it [3, 5].
- Elementary stages which lead to HP IPB formation (propagation stage reactions) are same through different reaction schemes.
- There are various types of side reactions which may lead to formation of different radicals and by-products.

After study of different researches [1-5] the reaction scheme represented below (Table 1) was established. It consists of 15 elementary stages and has 19 individual components in it.

**Table 1. Reaction scheme of isopropylbenzene oxidation [3].**

| № of elementary stage | Reaction |
|-----------------------|----------|
| 1 RH (X1)→R•(X12)+H•(X13) | |
| 2 RH(X1)+O₂(X2)→R•(X12)+HO₂•(X14) | |
| 3 ROOH(X3)→RO•(X15)+HO•(X16) | |
| 4 RH(X1)+RO•(X15)→R•(X12)+ROH(X4) | |
| 5 RH(X1)+ HO•(X16)→R•(X12)+H₂O(X5) | |
| 6 R•(X12)+O₂(X2)→RO•(X17) | |
| 7 ROO•(X17)+ RH(X1) →ROOH(X3)+ R•(X12) | |
| 8 RO•(X15)+ROOH(X3)→ROO•(X17)+ROH(X4) | |
| 9 R•(X12)+RO₂•(X17)→ROOR(X7) | |
| 10 2RO₂•(X17)→ROOR(X7)+O₂(X2) | |
| 11 RO•(X15)→ACP(X8)+CH₃•(X18) | |
| 12 CH₃•(X18)+ O₂(X2)→ CH₃O₂•(X19) | |
| 13 CH₃O₂•(X19)+RH(X1)→CH₃COOH(X9)+R•(X12) | |
| 14 RO•(X15)+RH(X1) → α-MS(X10)+H₂O(X5)+R•(X12) | |
| 15 CH₃O₂•(X19)+ RO₂•(X17)→ROH(X4)+ HCOH(X11)+ O₂(X2) | |

ACP is the acetophenone, α-MS is the alpha-methyl styrene, RH is the IPB (or cumene), ROOH is the HP IPB (or cumene hydroperoxide), R• is the cumyl radical.

Elementary stages (1)-(5) correspond to the initiation phase of radical-chained reaction. As mentioned earlier there are two ways of initiation of the chain. In first case HP IPB decomposes to radicals (3) and then these radicals interact with IPB, so cumyl radical is formed ((4), (5)). In second oxygen interacts with IPB which leads to cumyl radical formation ((1) and (2)). Summary rate of elementary stages (1) and (2) is significantly lesser than summary rate of elementary stages (3)-(5) [1,3], so some in some researches this elementary stages don’t included in reaction schemes and kinetic models [3,5].

Elementary stages (6)-(7) correspond to the main reaction chain in which the HP IPB is formed. These stages are similar in different reaction schemes [2-5]. Theoretically, once started, chain is continuous, but in reality chain can be interrupted by side reactions.

Elementary stages (8)-(16) correspond to side-chain reactions and chain termination reactions during which by-products are formed. We considered ACP, DMPC, α-MS as main by-products, so we
include reaction in which these substances are formed ((11), (14), (15)) in reaction scheme. Also reactions with participation of CH$_3^•$ radical and its derivatives were included.

2.2. Mathematical simulation

Different approaches for the mathematical simulation of chemical reactions exist. In this paper we were using system of differential equations to establish the dependence of substances concentration from time [6]. We developed mathematic model for isopropylbenzene oxidation reaction based on reaction scheme (Table 1) and experimental data [3]. Equations (2)-(11) represent individually rates of elementary stages:

\[
\begin{align*}
W_1 &= k_1 \cdot X_1 \\
W_2 &= k_2 \cdot X_1 \cdot X_2 \\
W_3 &= k_3 \cdot X_3 \\
W_4 &= k_4 \cdot X_1 \cdot X_{15} \\
W_5 &= k_5 \cdot X_1 \cdot X_{16} \\
W_6 &= k_6 \cdot X_{12} \cdot X_2 \\
W_7 &= k_7 \cdot X_{17} \cdot X \\
W_8 &= k_8 \cdot X_{15} \cdot X_3 \\
W_9 &= k_9 \cdot X_{12} \cdot X_{17} \\
W_{10} &= k_{10} \cdot X_{17} \cdot X_{17} \\
W_{11} &= k_{11} \cdot X_{15} \\
W_{12} &= k_{12} \cdot X_{18} \cdot X_2 \\
W_{13} &= k_{13} \cdot X_{19} \cdot X_1 \\
W_{14} &= k_{14} \cdot X_{15} \cdot X_1 \\
W_{15} &= k_{15} \cdot X_{19} \cdot X_{17},
\end{align*}
\]

where $W_j$ is the rate of $j$-th elementary reaction, [mole*min], $j$ is the number of elementary reaction in kinetic model ($j = 1..16$), $k_j$ is the constant of $j$-th elementary reaction rate, $X_i$ is the concentration of $i$-th substance, $i$ is the number of substance ($i = 1..19$).

System of differential equations which determines concentrations change over reaction time represented below:

\[
\frac{dc_i}{dt} = \sum_{j=1}^{J} v_j w_j (k_j, k_{0j}, E_j, T, c_i), \quad i = 1,...,I
\]

where $c_i$ is the concentration of $i$-th substance, [mole/lit], $i$ is the number of substance, $I$ is the overall number of elementary stages reactions ($I = 14$), $j$ is the number of elementary reaction in kinetic model ($j = 1..14$), $t$ is the time, [min], $k_{0j}$ is the preexponential coefficient for $j$-th constant of elementary reaction rate, $T$ is the temperature [K], $E_j$ is the activation energy of $j$-th reaction [kJ/mole] [6-8].

We solved direct and inverse kinetic tasks using mathematical model represented above (model №1). For the inverse kinetic task we used genetic algorithm which was implemented in MATLAB software environment [9] and the experimental data from [3]. For the direct kinetic task we applied Runge-Kutta method of 4th order in MATLAB software environment with different set of concentrations of initial components.

Also we took kinetic model №2 [9] as example, in order to compare its results with data received from model №1. Model №2 was obtained by simplification of reaction scheme represented in [2]. Model №2 consists from four differential equations [9]. Reaction scheme [2] got 22 elementary reactions. Initially there were two initiation mechanisms in scheme but researcher used matrix route method and method of quasi-stationary concentrations and developed kinetic model which consists from only four differential equations (for such stable compounds as IPB, HP IPB, DMPC, ACP). Concentrations of stable compounds are variables in equation of this system. Without oxygen and radicals concentrations represented in the model there is no way to represent two types of initiation mechanism.

On Figures 1-6 results received from both two models at same conditions are represented. On Figure1 and Figure2 are shown results obtained from such initial conditions [10-12]:
$\omega_{\text{IPB}0} = 98\%$, $\omega_{\text{HPIPB}0} = 2\%$, $T = 391$ K, \hspace{1cm} (18)

where the $\omega_{\text{IPB}0}$ is initial mass fraction of IPB (% mass.), $\omega_{\text{HPIPB}0}$ is the initial mass fraction of HP IPB (% mass.), $T$ is the temperature (K).

**Figure 1.** IPB concentration profile, model №1 (IPB(1)) and model №2 (IPB(2)), $\omega_{\text{HPIPB}0} = 2$ (% mass.).

**Figure 2.** HP IPB concentration profile, model №1 (HP IPB(1)) and model №2 (HP IPB(2)), $\omega_{\text{HPIPB}0} = 2$ (% mass.).

Figure 1 shows that the finite concentration of IPB per model №1 results is less than the finite concentration of IBP, received from model №2, although, the finite concentration of HP IPB from model №1 is also lesser than the finite concentration of HP IPB from model №2. It is assumed that the contribution of side reactions, which lead to the formation of by-products, as well as to the decomposition of the HP IPB, in the model №1 is more significant that in the model №2.

On Figure 3 and Figure 4 are shown results obtained from such initial conditions:

$\omega_{\text{IPB}0} = 97\%$, $\omega_{\text{HPIPB}0} = 3\%$, $T = 391$ K, \hspace{1cm} (19)

**Figure 3.** IPB concentration profile, model №1 (IPB(1)) and model №2 (IPB(2)), $\omega_{\text{HPIPB}0} = 3$ % mass.

**Figure 4.** HP IPB concentration profile, model №1 (HP IPB(1)) and model №2 (HP IPB(2)), $\omega_{\text{HPIPB}0} = 3$ % mass.

It is shown that increasing initial concentration of HP IPB (on 1 % mass. in our calculations) leads to significant increase of the finite HP IPB concentrations in both models, although same relation between model (1) and model (2) calculated concentrations remains.

On Figure 5 and Figure 6 are shown results obtained from such initial conditions:

$\omega_{\text{IPB}0} = 100\%$, $\omega_{\text{HPIPB}0} = 0\%$, $T = 391$ K, \hspace{1cm} (20)

On Figure 5 and Figure 6 extreme case is shown when initial concentration of HP IPB equals to zero. It is seen that while we received results from the model №1 (HP IPB concentration value is obviously lesser than in previous calculation experiments), the model №2 shows that there is no HP IPB formation during time of reaction. The reason of this is that the model №2 only uses HP IPB decomposition on radicals as initiation mechanism.
From analysis of the results it is seen that HP IPB finale concentration obtained with model №1 is lesser then concentration value calculated by model №2 at same initial conditions (17),(18). But at the same time model №2 is not possible to be used for direct kinetic task solution when HP IPB concentration equals to zero. We can make assumption that model №2 gives less reliable results when initial concentration of HP IPB value “approaches” to zero.

In second part of our research we used experimental data [13]. Reaction scheme was same as represented in Table 1.

This time we used Gyr method for the direct kinetic task solution and method of annealing simulation was used for the inverse kinetic task solution. These algorithms were implemented in C++ program software.

Results of these calculations represented below on Figure 7 and Figure 8.
On Figure 7 the IPB experimental and calculated concentrations profiles are shown. Initial HP IPB concentration nearly equals to zero. It is seen that curve of calculated IPB concentration profile almost matches with experimental values. But in the end two lines start to diverge, although insignificantly. Final calculated concentration value is lesser compared to experimental value at that time.

On Figure 8 the HP IPB experimental profile and calculated concentrations profiles are shown. It is seen that calculated curve at the beginning diverge significantly, but to the end of reaction time the difference between them diminishes.

In Table 2 values of some kinetic constants of chemical reaction at 118° C are represented (model №1 experimental data [13]).

![Figure 8. IPB concentration change, model (1) and model (2), $\omega_{IPB}=0$ (% mass.).](image)

| № of elementary stage | Value         |
|-----------------------|---------------|
| 1                     | 0.00157492    |
| 3                     | 0.000146375   |
| 5                     | 3.00E-09      |
| 8                     | 2.73E-08      |
| 12                    | 4.03E-10      |
| 14                    | 9.35E-02      |
| 16                    | 1.84E-08      |

3. Conclusion

Through analysis of different reaction schemes of the isopropylbenzene oxidation reaction certain reaction scheme were designed. Initiation mechanism without HP IPB decomposition was purposefully included in reaction scheme. It was established that model with such initiation mechanism along with HP IPB decomposition mechanism included is more reliable, although if there is some amount of HP IPB (>1 (%mass.) in initial mixture, it is possible to use models and reaction schemes with the HP IPB decomposition as only initiation mechanism. Also it is quit reliable to use system of differential equations for a reaction model simulation. Although it is needed to keep in mind that implementation of different numerical methods may result in different type of concentration curves.

4. References

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