

Isopropylbenzene oxidation reaction computer simulation

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Abstract

Isopropylbenzene (cumene) oxidation by air oxygen is intermediate stage of phenol and acetone production in cumene method. Cumene method of synthesis is currently the most wide-spread in the world to produce these two chemicals. Reaction is radical-chained and there also unwanted byproducts received along with desired ones.

This reaction has been subject of study since 30th of XX century. Different authors propose different ways of chain reactions, initiation mechanisms and influence degree of different factors and parameters during process.

In this paper different kinetic models of this reaction are compared and results of computations are shown.

Keywords: isopropylbenzene; oxidation; phenol; acetone; radical-chain mechanism; mathematic modeling.

1. Introduction

Phenol and acetone are very important substances in today petrochemistry industry. Acetone is used in paints, varnishes and solvents production. Also it is used as intermediate substance in petrochemistry industry. Phenol is used as intermediate substance in big number of petrochemistry units, such as bisphenol-A (which is lately used for polycarbonate and epoxies production), phenolic resins production, etc. Currently world industry produces more than 7 million tons of phenol per year [1] and this number growth annually. More than 97 % of phenol in the world is produced from cumene method and isopropylbenzene oxidation [1].

2. Isopropylbenzene oxidation reaction computer simulation

First cumene type production units were built at 40th years of XX century in USSR (Russia) and Canada [2], but more detailed studies of process kinetics and mathematical model appeared in 60-70th of XX century [3,4,5,6]. Because of low calculation machines capacities of that time researchers tried to simplify kinetics and mathematical models making different assumptions.

The general scheme of substances conversion is shown on Fig. 1 [7]:

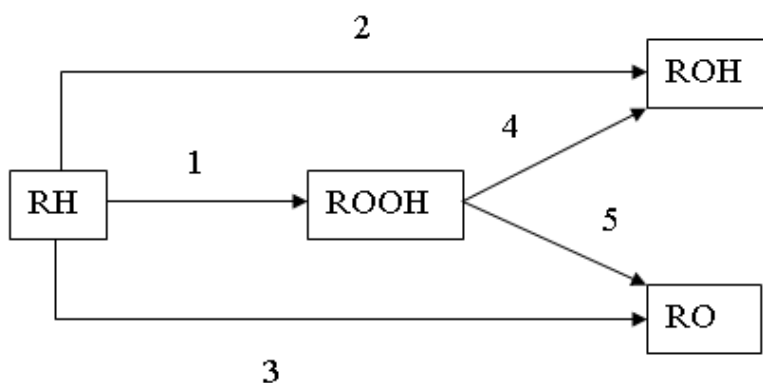


Fig. 1. General reactions scheme.

R• is cumyl radical ($C_6H_5(CH_3)_2C\bullet$), RH is cumene ($C_6H_5(CH_3)_2CH$), ROOH is cumene hydroperoxide ($C_6H_5(CH_3)_2COOH$), ROH – dymethylphenylcarbinol (DMPC is $C_6H_5(CH_3)_2COH$), RO is acetophenone ($C_6H_5CH_3CO$).

But in reality this reactions follow radical-chain mechanism. There are number of elementary steps on which decomposition of particles and radicals recombination happens. Let's look at Hattori radical-chain reaction mechanism and on reaction scheme from [6] as examples [3].

Where In is initiator, which decomposes on radicals with an easy, so overall reaction process is enhanced. In some experiments author used benzene hydroperoxide as initiator [3] but we studied experiment without any additional initiator. Cumene hydroperoxide itself is used as initiator in most production units and laboratory researches. So reactions of stage 1 (1a and 1b) are replaced by 3a, 3b, 3c reactions for this case.

B1 and B2 are some substances which can be detected exactly (different organic acids, aldehydes, alcohols).

Reaction number	Reaction	Constant
1a	$\text{In}_2 \rightarrow 2 \text{In}\cdot$	-
1b	$\text{In}\cdot + \text{RH} \rightarrow \text{R}\cdot + \text{InH}$	-
2a	$\text{RH} \rightarrow \text{R}\cdot + \text{H}\cdot$	k2a
2b	$\text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HO}_2\cdot$	k2b
3a	$\text{ROOH} \rightarrow \text{RO}\cdot + \cdot\text{OH}$	k3a
3b	$\text{RO}\cdot + \text{RH} \rightarrow \text{R}\cdot + \text{ROH}$	k3b
3c	$\cdot\text{OH} + \text{RH} \rightarrow \text{R}\cdot + \text{H}_2\text{O}$	k3c
4a	$\text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2\cdot$	k4a
4b	$\text{RO}_2\cdot + \text{RH} \rightarrow \text{R}\cdot + \text{ROOH}$	k4b
5a	$2 \text{R}\cdot \rightarrow \text{R-R}$	k5a
5b	$\text{R}\cdot + \text{RO}_2\cdot \rightarrow \text{ROOR}$	k5b
5c	$2 \text{RO}_2\cdot \rightarrow \text{ROOR} + \text{O}_2$	k5c
6a	$\text{RO}\cdot \rightarrow (\text{C}_6\text{H}_5)\text{CH}_2\text{CO} + \text{CH}_3\cdot$	k6a
6b	$\text{CH}_3\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2\cdot$	k6b
6c	$\text{CH}_3\text{O}_2\cdot + \text{RH} \rightarrow \text{HCHO} + \text{H}_2\text{O} + \text{R}\cdot$	k6c
6d	$\text{RO}\cdot + \text{RH} \rightarrow (\text{C}_6\text{H}_5)\text{CCH}_2\text{CH}_2 + \text{H}_2\text{O} + \text{R}\cdot$	k6d

Table 2. Cumene oxidation kinetics scheme [6].

Reaction number	Reaction	Constant
0	$\text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HO}_2\cdot$	k0
1	$\text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2\cdot$	k1
2	$\text{RO}_2\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot$	k2
3	$\text{ROOH} + \text{RH} \rightarrow \text{RO}\cdot + \text{R}\cdot + \text{H}_2\text{O}$	k3
4	$2 \text{ROOH} \leftrightarrow [\text{ROOH}]_2$	k4
5	$[\text{ROOH}]_2 \rightarrow \text{RO}_2\cdot + \text{RO}\cdot + \text{H}_2\text{O}$	k5
6	$\text{RO}\cdot + \text{RH} \rightarrow \text{ROH} + \text{R}\cdot$	k6
7	$\cdot\text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O}$	k7
8	$\text{RO}\cdot \rightarrow \text{R}'\text{O} + \text{CH}_3\cdot$	k8
9	$\text{CH}_3\cdot + \text{RH} \rightarrow \text{CH}_4 + \text{R}\cdot$	k9
10	$\text{CH}_3\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{OO}\cdot$	k10
12	$\text{CH}_3\text{OO}\cdot + \text{RH} \rightarrow \text{CH}_3\text{OOH} + \text{R}\cdot$	k11
13	$\text{H}_2\text{CO} + \text{R}\cdot \rightarrow \text{HC}\cdot\text{O} + \text{R}\cdot$	k12
14	$\text{HC}\cdot\text{O} + \text{O}_2 \rightarrow \text{HCOOO}\cdot$	k13
15	$\text{HCOOO}\cdot + \text{RH} \rightarrow \text{HCOOOH} + \text{R}\cdot$	k14
16	$\text{HCOOOH} \rightarrow \text{HCOO}\cdot + \cdot\text{OH}$	k15
17	$\text{HCOO}\cdot + \text{RH} \rightarrow \text{HCOOH} + \text{R}\cdot$	k16
18	$\text{HCOO}\cdot \rightarrow \text{CO}_2 + \cdot\text{OH}$	k17
19	$2 \text{RO}_2\cdot \rightarrow 2 \text{R}'\text{O} + 2 \cdot\text{CH}_3 + \text{O}_2$	k18
20	$2 \text{RO}_2\cdot \rightarrow \text{B1}$	k19
21	$\text{RO}_2\cdot + \text{R}\cdot \rightarrow \text{B2}$	k20

For Hattori reaction scheme simulation we made equations system based on Table 1 [8] where rate reactions are unknown:

$$W_{2a} = k2a \cdot [\text{RH}] \quad (1)$$

$$W_{2b} = k2b \cdot [\text{RH}] \cdot [\text{O}_2] \quad (2)$$

$$W_{3a} = k3a \cdot [\text{ROOH}] \quad (3)$$

$$W_{3b} = k3b \cdot [\text{RO}\cdot][\text{RH}] \quad (4)$$

$$W_{3c} = k3c \cdot [\cdot\text{OH}][\text{RH}] \quad (5)$$

$$W_{4a} = k4a \cdot [\text{R}\cdot] \cdot [\text{O}_2] \quad (6)$$

$$W_{4b} = k4b \cdot [RO_2 \cdot][RH] \quad (7)$$

$$W_{5a} = k5a \cdot [R \cdot]^2 \quad (8)$$

$$W_{5b} = k5b \cdot [R \cdot][RO_2 \cdot] \quad (9)$$

$$W_{5c} = k5c \cdot [RO_2 \cdot]^2 \quad (10)$$

$$W_{6a} = k6a \cdot [RO \cdot] \quad (11)$$

$$W_{6b} = k6b \cdot [CH_3 \cdot] \cdot [O_2] \quad (12)$$

$$W_{6c} = k6c \cdot [CH_3O_2 \cdot][RH] \quad (13)$$

$$W_{6d} = k6d \cdot [RO \cdot][RH] \quad (14)$$

Then we created system of differential equations, in which reagents concentration changing through time is shown [3,8]:

$$\frac{d[RH]}{dt} = -k2a \cdot [RH] - k2b \cdot [RH] - k3b \cdot [RO \cdot][RH] - k3c \cdot [\cdot OH][RH] - k4b \cdot [RO_2][RH] - k6c \cdot [CH_3O_2 \cdot][RH] - k6d \cdot [RO \cdot][RH] \quad (15)$$

$$\frac{d[ROOH]}{dt} = -k3a \cdot [ROOH] + k4b \cdot [RO_2][RH] \quad (16)$$

$$\frac{d[R \cdot]}{dt} = k2a \cdot [RH] + k2b \cdot [RH] + k3b \cdot [RO \cdot][RH] - k4a \cdot [R \cdot] + k4b \cdot [RO_2][RH] - k5a \cdot [R \cdot]^2 - k5b[R \cdot][RO_2] + k6c \cdot [CH_3O_2 \cdot][RH] + k6d \cdot [RO \cdot][RH] \quad (17)$$

$$\frac{d[RO_2 \cdot]}{dt} = -k4b \cdot [RO_2 \cdot][RH] + k4a \cdot [R \cdot] - k5b \cdot [R \cdot][RO_2 \cdot] - k5b \cdot [R \cdot][RO_2 \cdot] \quad (18)$$

$$\frac{d[RO \cdot]}{dt} = -k3b \cdot [RO \cdot][RH] + k3a \cdot [ROOH] - k6a \cdot [RO \cdot] - k6d \cdot [RO \cdot][RH] \quad (19)$$

$$\frac{d[\cdot OH]}{dt} = k3a \cdot [ROOH] - k3c \cdot [\cdot OH][RH] \quad (20)$$

$$\frac{d[R-R]}{dt} = k5b \cdot [R \cdot][RO_2 \cdot] + k5c \cdot [RO_2 \cdot]^2 \quad (21)$$

$$\frac{d[ROOR]}{dt} = -k2a \cdot [RH] - k2b \cdot [RH] - k3b \cdot [RO \cdot][RH] - k3c \cdot [\cdot OH][RH] - k4b \cdot [RO_2] \quad (22)$$

$$\frac{d[H_2O]}{dt} = k3c \cdot [\cdot OH][RH] + k6c \cdot [CH_3O_2 \cdot][RH] + k6d \cdot [RO \cdot][RH] \quad (23)$$

$$\frac{d[ROH]}{dt} = k3b \cdot [RO \cdot][RH] \quad (24)$$

$$\frac{d[H \cdot]}{dt} = k2a \cdot [RH] \quad (25)$$

$$\frac{d[HO_2 \cdot]}{dt} = k2b \cdot [RH] \quad (26)$$

$$\frac{d[CH_3 \cdot]}{dt} = k6a \cdot [RO \cdot] - k6b \cdot [CH_3 \cdot] \quad (27)$$

$$\frac{d[CH_3O_2 \cdot]}{dt} = k6b \cdot [CH_3 \cdot] - k6c \cdot [CH_3O_2 \cdot][RH] \quad (28)$$

$$\frac{d[HCHO]}{dt} = k6c \cdot [CH_3O_2 \cdot][RH] \quad (29)$$

$$\frac{d[(C_6H_5)CCH_3CH_2]}{dt} = k6d \cdot [RO \cdot][RH] \quad (30)$$

In order to solve this equation system we used MATLAB program. In fact we need to solve reverse kinetic problem [9] which means that we need to find chemical rates reactions constants for given experimental data. We used data from [3,6,7]. On Fig.2 graphs of concentration are shown, both for experimental and calculated data for experiment in [3].

3. Conclusion

In this paper different cumene oxidation mechanism were shown and calculation experiment was conducted.

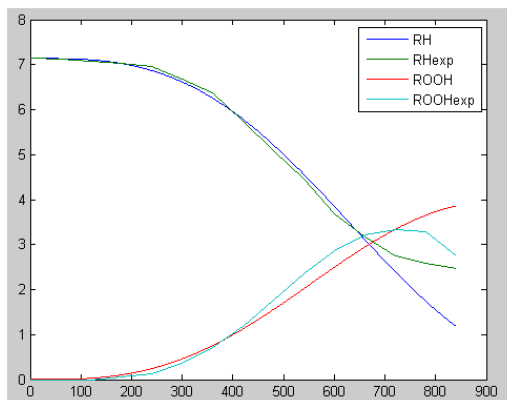


Fig. 2. MATLAB calculations result and experimental data [3].

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