

Article The Effect of Ca, Sr, and Ba Chloride Complexes with Dibenzo-18-Crown-6 Ether as Catalysts on the Process Criteria for the Efficiency of Cumene Oxidation (the First Stage in the Chain of Polymer Composite Production)

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Abstract: A study was made on the effect of Ca, Sr, and Ba chloride complexes with dibenzo-18crown-6 ether as catalysts on the process criteria of the efficiency of industrial cumene oxidation using kinetic modeling. It is the first stage in the process chain of polymer composite production. The kinetic scheme of the process is made of classical reactions of the radical chain mechanism (reactions of initiation, chain propagation, and chain termination), molecular reactions, reactions of formation of intermediate adducts "component of the reaction mixture-catalyst" and their decomposition, as well as reactions that take into account the specifics of the catalyst used: (1) formation of planar catalyst complexes with various substances; (2) formation of acetophenone along the catalytic path; (3) hydration of the intermediate adduct " α -methylstyrene—catalyst" to the required alcohol. It is shown that the kinetic model fully reproduces the experimental time dependencies of the cumene hydroperoxide concentration in the cumene oxidation and cumene hydroperoxide decomposition. Using the kinetic model, computational experiments were carried out, as a result of which the following conclusions were made: (1) among the considered catalysts, the complex of Sr chloride with dibenzo-18-crown-6 ether should be recognized as the best, provided that it is used at temperatures of 393–413 K and an initial concentration < 2 mmol/L; (2) to ensure selectivity comparable to the selectivity of a non-catalytic process, it is necessary to conduct the catalytic process at a lowest possible initial concentration of any of the considered catalysts.

Keywords: process chain of polymer composite production; cumene oxidation; Ca; Sr; Ba chloride complexes with dibenzo-18-crown-6 ether as catalysts

1. Introduction

Cumene begins the process chain of the polymer composite production, which is as follows: (1) cumene oxidation (obtained by alkylation of benzene with propylene) with air oxygen is the production of cumene hydroperoxide [1,2]; (2) cumene hydroperoxide decomposition into phenol and acetone (the catalyst is sulfuric acid) [1,2]; (3) production of precursors from phenol; (4) production of oligomers and polymers (epoxy resins [3], phenol-formaldehyde resins [4], polycarbonates [5], polysulfones [6], polyamides [7]) from precursors; (5) composite production [8,9] based on oligomers and polymers. It is obvious that the productivity of the first stage in this process chain (the stage of cumene oxidation) will have an effect on the productivity of all its other stages. As a rule, cumene oxidation is



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carried out in bubble column reactors at 353–403 K and 0.1–0.7 MPa until the cumene conversion reaches 10–25%, while the selectivity is 85–90% [10]. Industrial cumene oxidation is carried out without a catalyst, but the interest of researchers in catalysts that allow for accelerating the process while maintaining selectivity at the level of non-catalytic oxidation continues unabated. It is caused by the economic feasibility of intensifying this large-scale process. Significant progress has currently been made in the field of homogeneous and heterogeneous catalysis of cumene oxidation [11–19]. It is important to note that the effect of catalysts on the technological significance of the process (reagent conversion, selectivity, productivity) is studied in conditions far from industrial conditions, which does not allow catalysts to be used beyond the laboratories. This problem can be solved by modeling according to the following algorithm:

- (1) carrying out the experimental kinetic studies;
- (2) based on the experimental and theoretical prerequisites, a kinetic scheme of the process was proposed where the kinetic model is created using the mass action law;
- (3) the kinetic model is verified using experimental data (at this stage, the kinetic scheme and values of the model parameters can be revised); the kinetic model is basic, but often it is enough for preliminary calculations (the kinetic model can be made into a more complicated macrokinetic model to take into account the hydrodynamics of the reactor or can be built-in into the chemical process model which is implemented in a universal modeling program such as Aspen Hysys);
- (4) the computational experiments are carried out using the model, reproducing the industrial conditions of the process; according to the results of computational experiments, the catalyst can be either recommended or not recommended for use in industrial conditions.

The objects of study were complexes of Ca, Sr, and Ba chloride with dibenzo-18-crown-6 ether, which are used as catalysts for cumene oxidation and cumene hydroperoxide decomposition. Complexes of this kind have proven to be homogeneous catalysts readily soluble in alkylaromatic hydrocarbons [18]. The purpose of this work was to study the catalytic abilities of stable complexes of Ca, Sr, and Ba chlorides with dibenzo-18-crown-6 ether and to determine the prospects for their industrial use in cumene oxidation to cumene hydroperoxide using kinetic modeling.

2. Materials and Methods

2.1. Materials

In the experiments, the following substances were used:

- (1) cumene produced by PJSC Kazanorgsintez;
- (2) cumene hydroperoxide with the content of the main substance being 99.4% wt.;
- (3) air oxygen as an oxidizing agent;
- (4) Ca, Sr, and Ba chloride complexes with dibenzo-18-crown-6 ether are the catalysts for cumene oxidation and cumene hydroperoxide decomposition: they were synthesized by reacting a solution of Ca (or Ba) chloride in n-butanol or a solution of Sr chloride in ethanol with a solution dibenzo-18-crown-6 ether in acetone (stirring in a flask under reflux at a temperature of 343–348 K for 1–1.5 h); the resulting complexes in the form of white crystalline substances were filtered off, washed with n-butanol (Ca, Ba) or ethanol (Sr), and dried in air (the formation of complexes with a composition of 1:1 was proved by the molar mass of the complex, determined by cryoscopy: M(Ca) = 482.98 g/mol, M(Sr) = 527.55 g/mol, M(Ba) = 571.61 g/mol);
- (5) chlorobenzene is a solvent in the decomposition of cumene hydroperoxide.

2.2. Cumene Oxidation

Cumene ($[RH]_0 = 6.44 \text{ mol/L}$) mixed with a catalyst ($[Cat]_0 = 5 \text{ mmol/L}$) was used to fill a bubble column (diameter 36 mm, length 500 mm); thereafter the cumene was oxidized with air at a temperature of 393 K and pressure P = 1 atm. The air, preliminarily treated

from mechanical impurities and dried, was continuously supplied by a compressor (flow rate G = 0.6 L/min) down the reactor. The distribution of air in the liquid was carried out using a distribution grid with holes about 1 mm in diameter located at the bottom of the reactor. Samples of the reaction mixture were taken every hour through a valve on the side of the reactor. The quantitative content of cumene hydroperoxide in the sample was determined by iodometry method, and by-products were determined by gas–liquid chromatography (Chromatec Crystal 5000 chromatograph, the manufacturer is JSC SDO "CHROMATEC", Yoshkar-Ola, Russia; capillary column: sol–gel wax (polyethylene glycol) with a polar phase). The process was carried out for 6 h.

2.3. Cumene Hydroperoxide Decomposition

Glass ampoules were filled with a mixture of cumene hydroperoxide $([ROOH]_0 = 1 \text{ mol/L})$ and catalyst $([Cat]_0 = 5 \text{ mmol/L})$, sealed, then immersed in a thermostat heated to a temperature T = 403 K, and the shaking device was turned on. At certain intervals, the ampoules were removed one at a time, and the reaction was stopped by cooling the ampoules in ice water; the composition of the reaction mixture was analyzed in the same way as in the case of cumene oxidation (see Section 2.2). The process was carried out for 6 h.

3. Results

In Table 1 the cumene oxidation data are shown in the presence of various catalysts studied in this work and in [9,20,21]. Among the catalysts considered in this work, the Sr complex with dibenzo-18-crown-6 ether should be recognized as the best (Figure 1a): the reaction mass accumulates the largest amount of the target oxidation product, cumene hydroperoxide (1.43 mol/L).

Catalyst	Т, К	Oxidation Time, h	Cumene Conversion, %	Selectivity of the Process According to CHP, %
Acetylacetonate Fe Fe(acac)3/NHPI/Phen [9]	333	2.5	8.5–58	50–95
Carbon nanotubes [20]	353	8	24.1	88.4
Ni metal–organic frameworks [21]	363	7	6	91
Co metal–organic frameworks [21]	363	7	49	69
Zn metal–organic frameworks [21]	363	7	3	95
Ca, Sr, and Ba complexes with dibenzo-18-crown-6 ether (results of this work)	393	6	60–70	40–60

Table 1. Cumene oxidation in the presence of various catalysts ($[RH]_0 = 0 \text{ mol/L}$).

It is known that the initiation of the oxidation chain reaction runs due to free radicals formed during the cumene hydroperoxide decomposition [22]. As a rule, the cumene hydroperoxide decomposition is preceded by its activation in the "cumene hydroperoxide— catalyst" adduct [19]. Therefore, the acceleration of cumene oxidation in the presence of complexes of the chlorides Ca, Sr, and Ba with dibenzo-18-crown-6 ether runs due to the acceleration of the cumene hydroperoxide decomposition (Figure 2a). These data confirm the participation of the ROOH·Cat intermediate adduct in the formation of free radicals according to reaction (8). The high rate of cumene hydroperoxide accumulation in the presence of the Sr complex with dibenzo-18-crown-6 ether compared to other catalysts (Figure 1a) is due to the fact that cumene hydroperoxide decomposes faster in the presence of this complex compared to Ca and Ba complexes with dibenzo-18-crown-6 ether (Figure 2a).



Figure 1. The dependencies of the component concentrations of the reaction mixture in cumene oxidation versus time: dots are the experimental data, and lines are the calculation by the model; (a) ROOH; (b) ROH; (c) $C_6H_5C(CH_3) = CH_2$; (d) $C_6H_5C(O)CH_3$; (e) C_6H_5OH .



Figure 2. The dependencies of the component concentrations of the reaction mixture in cumene hydroperoxide decomposition versus time: dots are the experimental data, and lines are the calculation by the model; (**a**) ROOH; (**b**) ROH; (**c**) $C_6H_5C(CH_3) = CH_2$; (**d**) $C_6H_5C(O)CH_3$; (**e**) C_6H_5OH .

As a general kinetic scheme of cumene oxidation (when the oxygen concentration change rate in the reaction mixture due to its dissolution in it does not equal zero) and the cumene hydroperoxide decomposition (when the oxygen concentration change rate in the reaction mixture due to its dissolution in it is equal to zero) in the presence of Ca, Sr, and Ba chloride complex with dibenzo-18-crown-6 ether as catalysts, a set of reactions (1–50) was considered. Reactions (1–4), (6–45) are similar to the reactions proposed by us in [19] for the general kinetic scheme of cumene oxidation and cumene hydroperoxide decomposition in the presence of Zn, Cd, and Hg 2-ethylhexanoate as catalysts. Since Zn, Cd, and Hg and Ca, Sr, and Ba are metals incapable of valence transformations, and they can catalyze the

cumene oxidation through the formation of intermediate adducts with the components of the reaction mixture [23], it is obvious that reactions (1–4) and (6–45) should be in the general mechanism of cumene oxidation and cumene hydroperoxide decomposition in the presence of Zn, Cd, and Hg 2-ethylhexanoate and Ca, Sr, and Ba chloride complexes with dibenzo-18-crown-6 ether. In addition, the scheme of reactions (1–4) and (6–45) was supplemented with the following reactions:

- (1) reaction (5) is written by analogy with reaction (1);
- (2) reaction (46), which describes the decomposition of the intermediate ROH-Cat adduct to acetophenone (the formation of acetophenone also runs without the participation of a catalyst, which was experimentally shown in [24]; in the mechanism, the non-catalytic pathway for the formation of acetophenone is represented by reactions (21) and (44); however, much more acetophenone is formed in catalytic processes than in non-catalytic processes, which also indicates the catalytic pathway of its formation);
- (3) reaction (47) is shown by analogy with [25];
- (4) reaction (48) describes the formation of a planar complex of phenol with a catalyst since such compounds are characterized by the formation of planar complexes [26]; reaction (48) is irreversible since crown ethers are strong adsorbing agents, in particular, for phenol [26];
- (5) reaction (49) is shown by analogy with [27];
- (6) reaction (50) probably runs due to the ability of unsaturated hydrocarbons to be hydrated under the action of catalysts into the corresponding alcohols [28].

Formation of intermediate adducts:

$$RH + Cat \underset{k_{1'}}{\overset{k_1}{\longleftrightarrow}} RH \cdot Cat, \tag{1}$$

$$ROOH + Cat \underset{k_{2'}}{\overset{k_2}{\longleftrightarrow}} ROOH \cdot Cat,$$
(2)

$$\operatorname{ROH} + \operatorname{Cat} \underset{k_{2'}}{\overset{k_3}{\longleftrightarrow}} \operatorname{ROH} \cdot \operatorname{Cat}, \tag{3}$$

$$HC(O)H + Cat \xrightarrow{k_4} HC(O)H \cdot Cat.$$
(4)

$$C_6H_5C(CH_3) = CH_2 + Cat \underset{k_{\pi'}}{\longleftrightarrow} C_6H_5C(CH_3) = CH_2 \cdot Cat.$$
(5)

Chain initiation:

$$RH + O_2 \xrightarrow{k_6} R^{\bullet} + {}^{\bullet}OOH, \tag{6}$$

$$\mathrm{RH} \cdot \mathrm{Cat} + \mathrm{O}_2 \xrightarrow{k_7} \mathrm{R}^{\bullet} + {}^{\bullet}\mathrm{OOH} + \mathrm{Cat}, \tag{7}$$

$$\operatorname{ROOH} \xrightarrow{k_8} \operatorname{RO}^{\bullet} + {}^{\bullet}\operatorname{OH},\tag{8}$$

$$ROOH \cdot Cat \xrightarrow{k_9} RO^{\bullet} + {}^{\bullet}OH + Cat,$$
(9)

$$2\text{ROOH} \xrightarrow{k_{10}} \text{ROO}^{\bullet} + \text{RO}^{\bullet} + \text{H}_2\text{O}, \tag{10}$$

$$2\text{ROOH} \cdot \text{Cat} \xrightarrow{\kappa_{11}} \text{RO}^{\bullet} + \text{ROO}^{\bullet} + \text{H}_2\text{O} + 2\text{Cat.}$$
(11)

1.

Chain propagation:

$$R^{\bullet} + O_2 \xrightarrow{k_{12}} ROO^{\bullet}, \tag{12}$$

$$RH + ROO^{\bullet} \xrightarrow{\kappa_{13}} R^{\bullet} + ROOH,$$
(13)

$$RH \cdot Cat + ROO^{\bullet} \xrightarrow{k_{14}} R^{\bullet} + ROOH + Cat,$$
(14)

$$RH + RO^{\bullet} \xrightarrow{k_{15}} ROH + R^{\bullet}, \qquad (15)$$

$$RH \cdot Cat + RO^{\bullet} \xrightarrow{k_{16}} ROH + R^{\bullet} + Cat,$$
(16)

$$RH + {}^{\bullet}OH \xrightarrow{\kappa_{17}} R^{\bullet} + H_2O, \tag{17}$$

$$RH \cdot Cat + {}^{\bullet}OH \xrightarrow{\kappa_{18}} R^{\bullet} + H_2O + Cat,$$
(18)

$$ROOH + RO^{\bullet} \xrightarrow{k_{19}} ROO^{\bullet} + ROH,$$
(19)

$$ROOH \cdot Cat + RO^{\bullet} \xrightarrow{k_{20}} ROO^{\bullet} + ROH + Cat,$$
(20)

$$\mathrm{RO}^{\bullet} \xrightarrow{k_{21}} \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{C}(\mathrm{O})\mathrm{CH}_{3} + \mathrm{CH}_{3}^{\bullet}, \tag{21}$$

$$2\text{ROO}^{\bullet} \xrightarrow{k_{22}} 2\text{RO}^{\bullet} + \text{O}_2, \tag{22}$$

$$CH_3^{\bullet} + O_2 \xrightarrow{K_{23}} CH_3OO^{\bullet},$$
 (23)

$$CH_3OO^{\bullet} + RH \xrightarrow{\kappa_{24}} CH_3OOH + R^{\bullet}, \qquad (24)$$

$$CH_{3}OO^{\bullet} + RH \cdot Cat \xrightarrow{k_{25}} CH_{3}OOH + R^{\bullet} + Cat,$$
(25)

$$C_6H_5OH + ROO^{\bullet} \xrightarrow{k_{26}} C_6H_5O^{\bullet} + ROOH.$$
 (26)

Chain termination:

$$2R^{\bullet} \xrightarrow{\kappa_{27}} RR, \qquad (27)$$

$$R^{\bullet} + ROO^{\bullet} \xrightarrow{k_{28}} ROOR,$$
 (28)

$$CH_3^{\cdot} + {}^{\bullet}OH \xrightarrow{k_{29}} CH_3OH,$$
 (29)

$$2\text{ROO}^{\bullet} \xrightarrow{\kappa_{30}} \text{ROOR} + \text{O}_2, \tag{30}$$

$$CH_3OO^{\bullet} + ROO^{\bullet} \xrightarrow{k_{31}} ROH + HC(O)H + O_2,$$
 (31)

$$C_6H_5O^{\bullet} + ROO^{\bullet} \xrightarrow{k_{32}} C_6H_5OH + O_2 + C_6H_5C(CH_3) = CH_2, \qquad (32)$$

1.

$$C_6H_5O^{\bullet} + ROO^{\bullet} \xrightarrow{k_{33}} C_6H_5OOR + 0.5O_2,$$
(33)

$$R^{\bullet} + {}^{\bullet}OOH \xrightarrow{\kappa_{34}} ROOH.$$
(34)

Molecular reactions:

$$ROH \xrightarrow{k_{35}} C_6H_5C(CH_3) = CH_2 + H_2O, \tag{35}$$

$$ROH \cdot Cat \xrightarrow{\kappa_{36}} C_6H_5C(CH_3) = CH_2 + H_2O + Cat,$$
(36)

$$HC(O)H \cdot Cat + 0.5O_2 \xrightarrow{k_{37}} HCOOH + Cat, \qquad (37)$$

$$ROOH \xrightarrow{k_{38}} C_6H_5OH + CH_3C(O)CH_3, \tag{38}$$

$$\text{ROOH} \cdot \text{Cat} \xrightarrow{\kappa_{39}} \text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{Cat}, \tag{39}$$

$$ROOH + ROH \xrightarrow{\kappa_{40}} 2ROH + 0.5O_2, \tag{40}$$

$$ROOH \cdot Cat + ROH \xrightarrow{K_{41}} 2ROH + 0.5O_2 + Cat, \tag{41}$$

$$ROOH + HCOOH \underset{k_{42'}}{\underset{k_{42'}}{\longleftrightarrow}} ROOH \cdot HCOOH, \tag{42}$$

 $ROOH \cdot HCOOH \xrightarrow{k_{43}} C_6H_5OH + CH_3C(O)CH_3 + HCOOH,$ (43)

$$C_6H_5C(CH_3) = CH_2 + O_2 \xrightarrow{\kappa_{44}} C_6H_5C(O)CH_3 + HC(O)H,$$
(44)

$$\operatorname{Cat} \xrightarrow{k_{45}} \operatorname{Cat}',$$
 (45)

$$\operatorname{ROH} \cdot \operatorname{Cat} \xrightarrow{\kappa_{46}} \operatorname{C_6H_5C(O)CH_3} + \operatorname{CH_4} + \operatorname{Cat}, \tag{46}$$

$$ROOH \cdot Cat + C_6H_5C(CH_3) = CH_2 \xrightarrow{\kappa_{47}} ROH + C_6H_5C(CH_3)(O)(CH_2) + Cat, \quad (47)$$

$$C_6H_5OH + Cat \xrightarrow{K_{48}} C_6H_5OH \cdot Cat,$$
(48)

$$2\text{ROOH} \cdot \text{Cat} + \text{RH} \xrightarrow{\kappa_{49}} \text{ROH} + \text{ROOR} + \text{H}_2\text{O} + \text{Cat}, \tag{49}$$

$$C_6H_5C(CH_3) = CH_2 \cdot Cat + H_2O \xrightarrow{\kappa_{50}} ROH + Cat.$$
(50)

where RH is cumene (C₆H₅CH(CH₃)₂), Cat is the catalyst, RH·Cat is a "cumene—catalyst" intermediate adduct, ROOH is cumene hydroperoxide, ROOH·Cat is a "cumene hydroperoxide—catalyst" intermediate adduct, ROH is dimethylphenylcarbinol, ROH·Cat is a "dimethylphenylcarbinol—catalyst" intermediate adduct, HC(O)H is formaldehyde, HC(O)H·Cat is a "formaldehyde—catalyst" intermediate adduct, C₆H₅C(CH₃) = CH₂ is α-methylstyrene, C₆H₅C(CH₃) = CH₂·Cat is a "α-methylstyrene—catalyst" intermediate adduct, O₂ is oxygen, R[•] is a cumyl radical, •OOH is a hydroperoxide (hydroperoxyl) radical, RO[•] is a cumyloxyl radical, •OH is a hydroxyl radical, ROO[•] is a cumyl peroxyl radical, H₂O is water, C₆H₅C(O)CH₃ is acetophenone, CH₃[•] is a methyl radical, CH₃OO[•] is a methyl peroxyl radical, CH₃OOH is methyl hydroperoxide, C₆H₅OH is phenol, C₆H₅OOR is benzylcumonoate, HCOOH is formic acid, CH₃C(O)CH₃ is acetone, ROOH·HCOOH is a "cumene hydroperoxide—formic acid" intermediate adduct, Cat' is the deactivated catalyst, CH₄ is methane, C₆H₅C(CH₃)(O)(CH₂) is 2-methyl-2-phenyloxirane, C₆H₅OH·Cat is a planar complex of phenol with a catalyst.

Then, based on the scheme consisting of reactions (1–50), the kinetic model was written as a system of nonlinear differential equations, which describes, according to the mass action law, the rate of change of the concentrations of all reaction mixture species. The reaction rate coefficients in the kinetic model were set as functions of temperature according to the Arrhenius equation. To determine the values of the pre-exponential factor and the activation energy for each Arrhenius temperature dependence on the reaction rate coefficient, an inverse kinetic problem was solved. The inverse kinetic problem is the problem of determining such model parameters for which the discrepancy between the data calculated using the model and the experimental data is minimal [29]. The inverse kinetic problem was solved by the method of direct search of the zero order [30]. A comparison of experimental data and data calculated by the kinetic model with the found parameters (Table 2) is shown in Figures 1 and 2. The kinetic model, within the average relative error of 25%, satisfactorily described laboratory experimental data of cumene oxidation and cumene hydroperoxide decomposition.

k	A, 1/s is for Monomolecular Reactions, L/(mol \times s) is for Bimolecular Reactions, L ² /(mol ² \times s) is for Trimolecular Reactions			E, J/mol		
	Ca	Sr	Ba	Ca	Sr	Ba
k ₁	$4.63 imes10^4$	$3.57 imes 10^6$	$7.64 imes10^{14}$	55,000	58,900	130,000
$k_{1'}$	$3.97 imes10^4$	$2.20 imes10^5$	$1.65 imes 10^5$	70,100	74,700	69,000
k ₂	$1.37 imes 10^3$	$1.18 imes 10^3$	$1.73 imes10^{18}$	29,000	23,000	139,500
k _{2'}	$1.35 imes 10^{20}$	$4.01 imes 10^{12}$	$1.68 imes10^{15}$	123,800	63,300	89,400
k_3	$6.07 imes10^{14}$	1.72×10^3	$1.25 imes 10^{18}$	136,400	39,000	132,300
k _{3'}	$8.36 imes 10^{19}$	2.21×10^{16}	$1.05 imes 10^3$	107,600	79,000	35,000
k_4	$8.49 imes10^3$	$2.36 imes 10^3$	$4.25 imes10^7$	19,000	24,400	78,200
k_5	$1.30 imes 10^5$	$1.10 imes 10^3$	$1.91 imes 10^3$	38,500	22,200	10,400
$k_{5'}$	$1.25 imes 10^3$	$2.57 imes 10^3$	$1.55 imes10^4$	24,300	24,900	49,400
k ₆		$6.14 imes10^6$			106,500	
k ₇	$5.23 imes 10^7$	$1.16 imes 10^{10}$	$1.02 imes 10^{17}$	2900	15,000	103,100
k ₈		$9.27 imes10^6$			95,700	
k9	$9.97 imes10^5$	$6.27 imes10^{14}$	$8.87 imes10^6$	27,000	93,200	37,800
k_{10}		$1.28 imes 10^6$			94,700	
k ₁₁	$1.54 imes10^9$	$8.36 imes10^7$	$1.94 imes10^9$	46,100	36,600	46,700
k ₁₂		$9.60 imes10^{11}$			21,700	
k ₁₃		$1.43 imes10^{14}$			95,900	
k_{14}	$3.35 imes10^{10}$	$1.91 imes10^{13}$	2.66×10^{13}	23,100	40,400	68,800
k_{15}		$6.34 imes10^{10}$			42,000	
k ₁₆	$2.58 imes10^{14}$	$2.78 imes10^{13}$	$1.44 imes 10^{12}$	2500	600	32,500
k ₁₇		$5.96 imes10^{12}$			24,400	
k ₁₈	$7.64 imes 10^8$	$4.38 imes10^{10}$	$2.82 imes 10^{18}$	16,600	27,300	89,300
k ₁₉		$1.20 imes10^7$			3700	
k ₂	$2.31 imes 10^{10}$	$6.77 imes 10^9$	$1.33 imes10^{10}$	2700	1600	12,200
k ₂₁		5.83×10^{13}			60,200	
k ₂₂		$5.04 imes 10^7$			6700	
k ₂₃		8.82×10^{9}			8700	
k ₂₄		4.50×10^{6}	_		62,100	
k ₂₅	$5.47 imes 10^{19}$	8.32×10^{16}	9.02×10^{8}	107,600	86,700	35,500
k ₂₆		3.58×10^{12}			81,900	
k ₂₇		2.33×10^{11}			7700	
k ₂₈		4.99×10^{10}			420	
k ₂₉		7.60×10^{12}			21,100	
k ₃₀		2.26×10^{13}			59 <i>,</i> 300	
k ₃₁		7.41×10^{11}			36,200	
k ₃₂		1.65×10^{11}			63,400	
k ₃₃		4.89×10^{12}			99,100	
k ₃₄		4.39×10^{8}			2020	
k ₃₅	0	1.12×10^{7}	0		89,100	
k ₃₆	1.81×10^{9}	1.93×10^{14}	1.17×10^{9}	85,600	119,000	86,300
k ₃₇	3.88×10^{19}	1.11×10^{5}	2.66×10^{18}	145,300	42,600	85,000
k ₃₈		1.21×10^{5}			83,600	
k ₃₉	1.73×10^{5}	1.98×10^{10}	1.05×10^{4}	70,400	109,000	16,300
k ₄₀	0	6.38×10^{8}			102,200	
k ₄₁	5.38×10^{9}	1.20×10^{3}	1.83×10^{19}	24,700	9200	72,800
k ₄₂		$5.99 \times 10^{\circ}$			75,100	
k _{42'}		2.34×10^{12}			113,600	
k ₄₃		7.10×10^{7}			88,900	
k ₄₄	100 102	$2.94 \times 10^{\circ}$		(2.000	58,500	11 < 100
K45	1.32×10^{3}	1.20×10^{13}	8.85×10^{11}	62,000	130,000	116,400
k ₄₆	3.53×10^{2}	1.87×10^{10}	3.83×10^{4}	63,100	21,200	68,800

Table 2. Pre-exponential factor A and activation energy E in the Arrhenius equation $k = Ae^{\frac{-E}{RT}}$. (R = 8.31 J/(mol K); T is temperature, K).

k	A, 1/s is for Monomolecular Reactions, L/(mol \times s) is for Bimolecular Reactions, L ² /(mol ² \times s) is for Trimolecular Reactions			E, J/mol		
	Ca	Sr	Ba	Ca	Sr	Ba
k ₄₇	9.36×10^{8}	$9.63 imes 10^{12}$	$2.56 imes 10^4$	63,200	91,700	68,800
k ₄₈	$1.26 imes 10^{12}$	$8.39 imes 10^{16}$	$2.87 imes 10^6$	117,200	147,500	58,000
k49	$1.25 imes10^{10}$	$1.91 imes 10^{10}$	$2.26 imes 10^{11}$	85,100	86,200	88,800
k ₅₀	$2.17 imes10^{10}$	$8.19 imes10^3$	$1.24 imes 10^3$	76,700	28,500	12,900

Further, using the kinetic model, we carried out computational experiments simulating the cumene oxidation under industrial conditions (the initial concentrations of species were set in accordance with the composition of the flow charge from [29]). (It should be noted that in this article, the cumene oxidation was experimentally studied running in a bubble column reactor. The following approximations were included in the kinetic model: the reactor is a batch reactor in terms of the liquid phase and a plug flow reactor in terms of air. Various designs of cumene oxidation reactors are used in industry; therefore, in this case, computational experiments are close to industrial conditions only in terms of the composition of the reaction mixture.) The results of computational experiments and their discussion are shown below.

4. Discussion

Table 2. Cont.

The concentration of cumene hydroperoxide accumulates over time up to a certain maximum value, after which it reduces (Figure 3). The reduction of the cumene hydroperoxide concentration after the maximum value (Figures 1a and 3) is associated with the cumene hydroperoxide decomposition, which results in the formation of dimethylphenylcarbinol ROH (Figure 1b), α -methylstyrene C₆H₅C(CH₃) = CH₂ (Figure 1c), acetophenone $C_6H_5C(O)CH_3$ (Figure 1d), and phenol C_6H_5OH (Figure 1e). The concentration of cumene hydroperoxide grows linearly with an increase in the oxidation time until the maximum value is reached (Figure 1a). The time dependencies of the concentrations of dimethylphenylcarbinol ROH (Figure 1b), α -methylstyrene C₆H₅C(CH₃) = CH₂ (Figure 1c), and acetophenone $C_6H_5C(O)CH_3$ (Figure 1d) also have a form close to a linear one, which indicates the first-order versus cumene hydroperoxide of the reactions of cumene hydroperoxide decomposition with the formation of these compounds. The concentration of phenol C_6H_5OH in time grows non-linearly with acceleration (Figure 1e), which, according to the kinetic scheme used by us, can only be explained by the accumulation of formic acid in the reaction system, which catalyzes the cumene hydroperoxide decomposition according to reactions (42,43).



Figure 3. The dependencies of cumene hydroperoxide accumulation versus time. Without catalyst **Ca Sr Ba**. G = 0.6 L/min, T = 393 K, P = 1 atm, $[RH]_0 = 6.19 \text{ mol/L}$, $[ROOH]_0 = 0.15 \text{ mol/L}$, $[ROH]_0 = 0.08 \text{ mol/L}$, $[HCOOH]_0 = 0.018 \text{ mol/L}$, $[C_6H_5C(O)CH_3]_0 = 0.024 \text{ mol/L}$, and $[Cat]_0 = 1 \text{ mmol/L}$.

This maximum value in the case of the presence of Sr and Ca is reached much earlier compared to the non-catalytic process and that in the presence of Ba, and after an increase of the cumene oxidation temperature, the time to reach the maximum concentration of cumene hydroperoxide decreases (Figures 3 and 4).



Figure 4. Time to reach the maximum concentration of cumene hydroperoxide depending on the temperature of cumene oxidation. Without catalyst Ca Sr Ba. G = 0.6 L/min, P = 1 atm, $[RH]_0 = 6.19 \text{ mol/L}$, $[ROOH]_0 = 0.15 \text{ mol/L}$, $[ROH]_0 = 0.08 \text{ mol/L}$, $[HCOOH]_0 = 0.018 \text{ mol/L}$, $[C_6H_5C(O)CH_3]_0 = 0.024 \text{ mol/L}$, and $[Cat]_0 = 1 \text{ mmol/L}$.

Obviously, it is expedient to carry out the industrial cumene oxidation to the maximum achievable concentration of cumene hydroperoxide. Moreover, to ensure reasonable times for reaching the maximum concentration of cumene hydroperoxide, the cumene oxidation must be carried out at fairly high temperatures (under the process conditions shown in Figure 4, for a process in the presence of Sr or Ca, these are temperatures of 393–403 K, for a non-catalytic process and a process in the presence of Ba these are temperatures of 403–407 K).

The following criterion was used as a criterion reflecting the productivity of cumene oxidation at the moment of reaching the maximum concentration of cumene hydroperoxide and taking into account the cumene conversion and selectivity achieved in this case:

$$C = \frac{[\text{ROOH}]_{\text{max}}}{t_{\text{max}}} \left(1 - ([\text{RH}]_{t_{\text{max}}} / [\text{RH}]_0)\right) \frac{[\text{ROOH}]_{\text{max}} - [\text{ROOH}]_0}{[\text{RH}]_0 - [\text{RH}]_{t_{\text{max}}}},$$
(51)

where [ROOH]_{max} is the maximum concentration of cumene hydroperoxide, mol/L; t_{max} is the time to reach the maximum concentration of cumene hydroperoxide, h; [ROOH]₀ is the initial concentration of cumene hydroperoxide, mol/L; [RH]_{tmax} is the cumene concentration at time t_{max} , mol/L; [RH]₀ is the initial concentration of cumene, mol/L; $1 - ([RH]_{tmax}/[RH]_0)$ is the cumene conversion at time t_{max} ; ([ROOH]_{max} – [ROOH]₀)/([RH]₀ – [RH]_{tmax}) is the selectivity.

When the temperature increases, the *C* criterion grows to a maximum value (the maximum lies in the region of 393–413 K), after which it falls (Figure 5a). Catalysts, based on the value of the maximum criterion *C*, can be arranged in the following order (in the order of growth of this criterion): 1. Without the catalyst, Sr, and Ca; 2. Ba (Figure 5a). [ROOH]_{max} and cumene conversion also pass through a maximum in the range of 393–413 K. Catalysts based on the value of the maximum [ROOH]_{max} can be arranged in the following order (in the order (in the order of growth of this criterion): 1. Ba; 2. Ca; 3. Sr; 4. Without catalyst (Figure 5b). Catalysts based on the value of the maximum conversion of cumene can be placed in the following order (in the order of growth of this criterion): 1. Ba, Ca; 2. Without catalyst; 3. Sr (Figure 5c).

The temperature dependence of the selectivity in the range of 393–413 K has the form of a plateau. Catalysts based on the value of selectivity at the peak of this plateau can be placed in the following order (in the order of growth of the selectivity): 1. Without catalyst; 2. Ca; 3. Ba, Sr (Figure 5d).

At a constant temperature (406 K) chosen from the range of 393–413 K, at low initial concentrations of the $[Cat]_0$ catalyst (<2 mmol/L), criterion C is maximum and falls in the row Sr > Ca > Ba (Figure 6a). At $[Cat]_0 > 2 \text{ mmol/L}$ (Figure 6a):

- (1) criterion *C* for Sr has a minimum in the range $[Cat]_0 = 2-4 \text{ mmol/L}$, and at $[Cat]_0 > 4 \text{ mmol/L}$ it reaches a plateau, the value of which is comparable to the value of criterion *C* at $[Cat]_0 < 2 \text{ mmol/L}$;
- (2) criterion C for Ca and Ba falls with growing [Cat]₀ and reaches a plateau at [Cat]₀ = 7 mmol/L;
- (3) criterion *C* falls in the row $Sr \gg Ca \gg Ba$.



Figure 5. The dependencies of criterion C (**a**), $[\text{ROOH}]_{\text{max}}$ (**b**), cumene conversion at t_{max} (**c**), and selectivity at t_{max} (**d**) versus cumene oxidation temperature. Without catalyst Ca Sr Ba. G = 0.6 L/min, P = 1 atm, $[\text{RH}]_0 = 6.19 \text{ mol/L}$, $[\text{ROOH}]_0 = 0.15 \text{ mol/L}$, $[\text{ROH}]_0 = 0.08 \text{ mol/L}$, $[\text{HCOOH}]_0 = 0.018 \text{ mol/L}$, $[C_6H_5C(O)CH_3]_0 = 0.024 \text{ mol/L}$, and $[Cat]_0 = 1 \text{ mmol/L}$.

The time to reach the maximum concentration of cumene hydroperoxide at $[Cat]_0 < 2 \text{ mmol/L}$ lies in the range of 7–8 h. Catalysts based on the time to reach the maximum concentration of cumene hydroperoxide can be arranged in the following order (in the order of growth of this indicator): 1. Ca, Sr; 2. Ba (Figure 6b). At concentrations $[Cat]_0 > 2 \text{ mmol/L}$, the t_{max} for Ba is the same as at $[Cat]_0 < 2 \text{ mmol/L}$, and t_{max} for Sr decreases with the growth of $[Cat]_0$ reaching the plateau at $[Cat]_0 = 5-6 \text{ mmol/L}$; t_{max} for Ca monotonically decreases with the growth of $[Cat]_0$.

[ROOH]_{max} for Ca and Ba reduces with the growth of $[Cat]_0$ from 0 to 10 mmol/L, and $[ROOH]_{max}$ for Sr reduces with the growth of $[Cat]_0$ up to 3 mmol/L and reaches a plateau (Figure 6c).







Figure 6. The dependencies of criterion *C* (**a**), t_{max} (**b**), [ROOH]_{max} (**c**), cumene conversion at t_{max} (**d**), and selectivity at t_{max} (**e**) versus initial catalyst concentration.

The cumene conversion for Ca with the growth of $[Cat]_0$ to 7 mmol/L holds on a plateau (about 55%), after which it reduces; the cumene conversion for Ba with the growth of $[Cat]_0$ from 0 to 10 mmol/L reduces from 55% to 40%; the cumene conversion for Sr first

grows with the growth of $[Cat]_0$, passing through a maximum (70%) at $[Cat]_0 = 2 \text{ mmol/L}$, after which it reduces until reaching the plateau (50%) at $[Cat]_0 = 6 \text{ mmol/L}$ (Figure 6d). The dependencies of the selectivity for Ca and Sr versus $[Cat]_0$ are mirror-like with respect to the similar dependence of the conversion; the dependence of the selectivity for Ba is the same as the similar dependence of the cumene conversion (Figure 6e,d). To ensure selectivity comparable with the selectivity of a non-catalytic process, it is necessary to carry out the catalytic process at the lowest possible initial concentration of any of the considered catalysts (Figure 6e).

5. Conclusions

Using kinetic modeling, a study was performed on the effect of Ca, Sr, and Ba chloride complexes with dibenzo-18-crown-6 ether as catalysts on the process criteria of the efficiency of industrial cumene oxidation using kinetic modeling. It is the first stage in the process chain of polymer composite production: (1) cumene oxidation (obtained by alkylation of benzene with propylene) with air oxygen is the production of cumene hydroperoxide; (2) cumene hydroperoxide decomposition into phenol and acetone; (3) production of precursors from phenol; (4) production of oligomers and polymers from precursors; (5) composite production based on oligomers and polymers. The kinetic scheme of the process is made of classical reactions of the radical chain mechanism (reactions of initiation, chain propagation, and chain termination), molecular reactions, reactions of formation of intermediate adducts "component of the reaction mixture-catalyst" and their decomposition, and reactions that take into account the specifics of the catalyst used: (1) formation of planar catalyst complexes with various substances; (2) formation of acetophenone along the catalytic path; (3) hydration of the intermediate adduct " α -methylstyrene—catalyst" to the required alcohol. It is shown that the kinetic model reproduces the experimental time dependencies of the cumene hydroperoxide concentration in the cumene oxidation and of cumene hydroperoxide decomposition within the error (25%). Using the kinetic model, computational experiments were carried out, as a result of which the following conclusions were made: (1) among the considered catalysts, the complex of Sr chloride with dibenzo-18-crown-6 ether should be recognized as the best, provided that it is used at temperatures of 393–413 K and an initial concentration < 2 mmol/L since the maximum value of the criterion reflecting the productivity of cumene oxidation at the moment of reaching the maximum concentration of cumene hydroperoxide and taking into account the cumene conversion and selectivity achieved in this case is reached in a relatively short time (7–8 h) with a cumene conversion of 60–70% and selectivity of 40–60%; (2) to ensure selectivity comparable to the selectivity of a non-catalytic process, it is necessary to conduct the catalytic process at a lowest possible initial concentration of any of the considered catalysts. Further research involves a more detailed study of the kinetic patterns and mechanism of the process under consideration (identification of limiting stages and reaction paths that make the greatest contribution to the kinetics of the process).

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