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Acid Decomposition of *p-tert*-Butylcumene Hydroperoxide to *p-tert*-Butylphenol and Acetone

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Abstract—*p-tert*-Butyphenol is a valuable product of basic organic synthesis, widely used in various branches of industry. The relationships of acid decomposition of *p-tert*-butylcumene hydroperoxide to *p-tert*-butylphenol and acetone as one of the key steps of the alternative method for *p-tert*-butylphenol synthesis were studied. The influence exerted by temperature, catalyst concentration, and initial concentration of *p-tert*-butylcumene hydroperoxide on its acid decomposition was examined. Conditions ensuring preparation of *p-tert*-butylphenol in 92% yield were found. A kinetic model of the acid decomposition of *p-tert*-butylcumene hydroperoxide in the presence of concentrated sulfuric acid was constructed; it adequately describes the experimental data and allows substantiation of the reaction mechanism.

Keywords: *p-tert*-butylcumene, *p-tert*-butylcumene hydroperoxide, acid decomposition, *p-tert*-butylphenol, kinetic model

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p-tert-Butylphenol is one of the main phenol homologs; it is used as an intermediate in basic organic synthesis. Its application sphere steadily expands, covering the production of antioxidants, pesticides, rubbers, varnishes, paints, and in the recent time also pharmaceuticals [1]. Promising applications fields of *p-tert*-butylphenol include production of phenolic resin 2402 used in glued leather items and of macrocylic compounds, calixarenes [2].

In industry, *p-tert*-butylphenol is synthesized by alkylation of phenol with isobutylene in the presence of KU-type ion-exchange resins and, in the recent time, of Amberlyst macroporous sulfonic cation-exchange resins at 100–110°C [3]. The drawback of this method of low selectivity (70–75%) of *p-tert*-butylphenol formation: ortho and meta isomers of tert-butylphenol are also formed. The boiling points of these isomers are close to that of *p-tert*-butylphenol, which considerably complicates isolation of sufficiently pure *p-tert*-butylphenol from the reaction mixture.

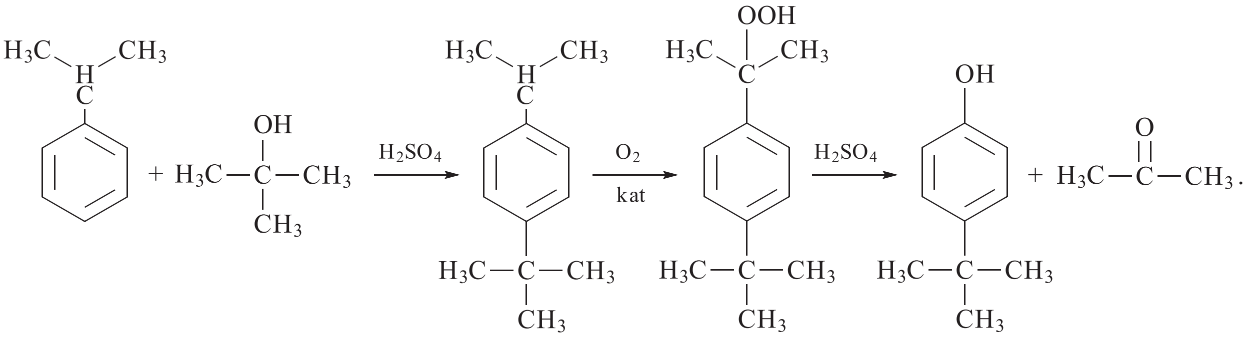
The problem can be solved by using an alternative method for preparing *p-tert*-butylphenol jointly with acetone, consisting of three main steps: synthesis of *p-tert*-butylcumene by alkylation of cumene with tert-butyl alcohol, oxidation of *p-tert*-butylcumene to hydroperoxide, and subsequent acid decomposition of the hydroperoxide to *p-tert*-butylphenol and acetone (Scheme 1).

The key step of the joint synthesis of *p-tert*-butylphenol and acetone is acid decomposition of *p-tert*-butylcumene hydroperoxide. Despite available ample data on the relationships of the acid decomposition of *sec*-alkylarene hydroperoxides, including cumene hydroperoxide [4], into phenol and carbonyl compounds, the relevant data concerning *p-tert*-butylcumene hydroperoxide are lacking. Therefore, it is topical to examine the relationships of the acid decomposition of *p-tert*-butylcumene hydroperoxide. That was the subject of this study.

EXPERIMENTAL

p-tert-Butylcumene hydroperoxide was prepared by aerobic oxidation of *p-tert*-butylcumene by the

Scheme 1.



procedure described in [5]. The product precipitated on cooling the oxidate was filtered off and dried in air at room temperature; purity 98.5%, T_m = 72°C. The structure of *p-tert*-butylcumene hydroperoxide was confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR spectrum (400 MHz), δ, ppm: 1.35 m (9H, $3CH_3{}^{t\text{-Bu}}$), 1.63 m (6H, $2CH_3{}^{i\text{-Pr}}$), 7.28 s (1H, O–O–H), 7.42 m (4H, $4CH^{arom}$).

Acid decomposition of *p-tert*-butylcumene hydroperoxide was performed in acetone in a reactor equipped with a stirrer and a sampler. The reactor design allowed the loss of the reactants to be virtually fully excluded. A mixture of the hydroperoxide and acetone was heated to the preset temperature maintained with a water bath. When the required temperature was reached, a calculated amount of 98% H_2SO_4 was added to the reaction mixture with continuous stirring. Samples (0.2–0.3 g each) were taken at 5-min intervals to determine the residual content of *p-tert*-butylcumene hydroperoxide by iodometric titration. After the reaction completion, the products were analyzed chromatographically for the content of *p-tert*-butylphenol and acetone. Chromatographic analysis was performed with a Khromatek-Kristall 5000.2 chromatograph under the following conditions: flame ionization detector; SK-5 capillary column 30 m long and 0.32 mm in diameter, coated with 5% phenyl–95% dimethylpolysloxane; carrier gas nitrogen, flow rate 2 cm^3 min^{-1}; programmed heating from 80 to 200°C at a rate of 8 deg min^{-1}. The quantitative analysis of the acid decomposition products was performed using an internal reference. *p-tert*-Butylphenol and acetone were isolated from the products by fractional distillation. Figure 1 shows the chromatogram of the products obtained by acid decomposition of *p-tert*-butylcumene hydroperoxide.

The synthesized *p-tert*-butylphenol was 99.3% pure and had T_m = 97.6°C. Its structure was confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.01 s (^{1}H, OH), 7.18 d ($2H^{arom}$, ^3J = 6.71), 6.68 d ($2H^{arom}$, ^3J = 6.71), 1.2 m (9H, CH_3). The ^{1}H NMR spectrum was recorded with a Bruker DRX 400 NMR spectrometer (400.4 MHz). A DMSO-d_6–CCl_4 mixture was used as a solvent, and tetramethysilane, as an internal reference.

RESULTS AND DISCUSSION

Experiments on studying the influence of the main process parameters on the acid decomposition of *p-tert*-

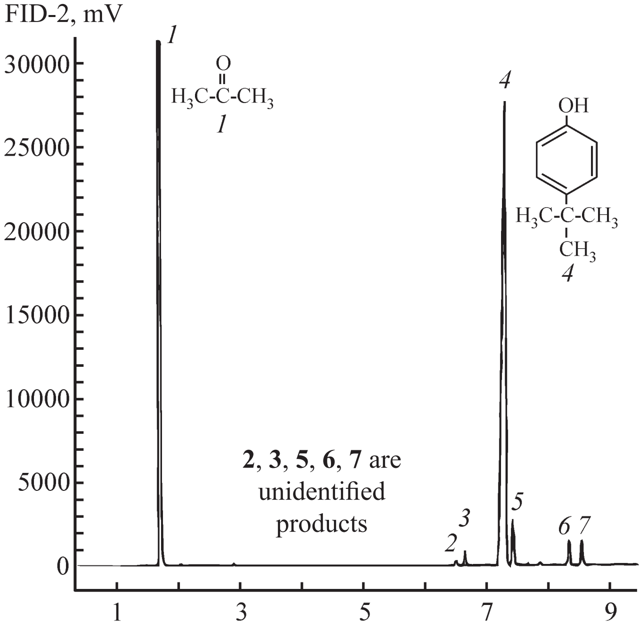


Fig. 1. Chromatogram of the products formed by acid decomposition of *p-tert*-butylcumene hydroperoxide at 40°C, catalyst content of 0.6 wt %, and initial *p-tert*-butylcumene hydroperoxide concentration of 30 wt %.

Table 1. Influence of process parameters on the acid decomposition of *p-tert*-butylcumene hydroperoxide to *p-tert*-butylphenol and acetone

Initial *p-tert*-butylcumene hydroperoxide concentration, M	Temperature, °C	Catalyst (concentrated H_2SO_4) concentration, wt % relative to the loaded hydroperoxide	Time, min	Initial reaction rate $W_0 \times 10^2$, mol L^{-1} min^{-1}	*p-tert*-Butylcumene hydroperoxide conversion, %	*p-tert*-Butylphenol formation selectivity, %
0.065	30	0.6	35	0.28	84.6	87.1
	40		35	1.03	99.0	88.3
	50		15	2.31	98.7	89.5
0.065	40	0.3	55	0.53	98.7	89.7
		0.6	55	1.02	100.0	89.4
		0.9	20	1.56	98.7	87.9
		1.5	15	2.64	99.3	87.3
0.026	40	0.6	35	0.26	97.1	89.6
0.065				0.96	99.3	89.3
0.132				1.91	95.0	91.0

butylcumene hydroperoxide to *p-tert*-butylphenol and acetone was performed in the temperature interval 30–50°C in acetone; the initial hydroperoxide concentration was varied from 0.026 to 0.132 M. Concentrated sulfuric acid was used as the decomposition catalyst; its concentration was varied from 0.3 to 1.5 wt % relative to the loaded *p-tert*-butylcumene hydroperoxide. The reaction progress was monitored by determining the unchanged *p-tert*-butylcumene hydroperoxide by iodometric titration.

The *p-tert*-butylcumene hydroperoxide conversion under these conditions reaches virtually 100%, and the *p-tert*-butylphenol formation selectivity is approximately 90% (Table 1).

The kinetic curves of the acid decomposition of *p-tert*-butylcumene hydroperoxide (Fig. 2) have a complex shape and cannot be described by any of equations for simple reactions. The kinetics was evaluated by the initial rates W_0, because in the initial period the concentration of reaction products is low and their effect on the decomposition rate is insignificant. The initial rates were determined from the slope of the tangent to the kinetic curve at the initial time moment.

With an increase in the temperature from 30 to 50°C, the initial rate of the acid decomposition of *p-tert*-butylcumene hydroperoxide increased by a factor of approximately 8. The preferable temperature for performing acid decomposition of *p-tert*-butylcumene hydroperoxide is 40°C.

An increase in the catalyst amount from 0.3 to 1.5 wt % relative to the loaded hydroperoxide leads to an increase in the initial reaction rate by a factor of 5, but does not noticeably influence the *p-tert*-butylphenol yield.

An important factor influencing the acid decomposition is the initial concentration of *p-tert*-butylphenol hydroperoxide. As seen from Table 1, with an increase in the initial concentration of the hydroperoxide from 0.026 to 0.132 M the initial rate of the acid decomposition increases by a factor of approximately 7. The initial concentration of *p-tert*-butylcumene hydroperoxide of 0.132 M is preferable. Because the acid decomposition of *p-tert*-bnutylcumene hydroperoxide occurs with large heat release, further increase in the initial hydroperoxide concentration is unsafe.

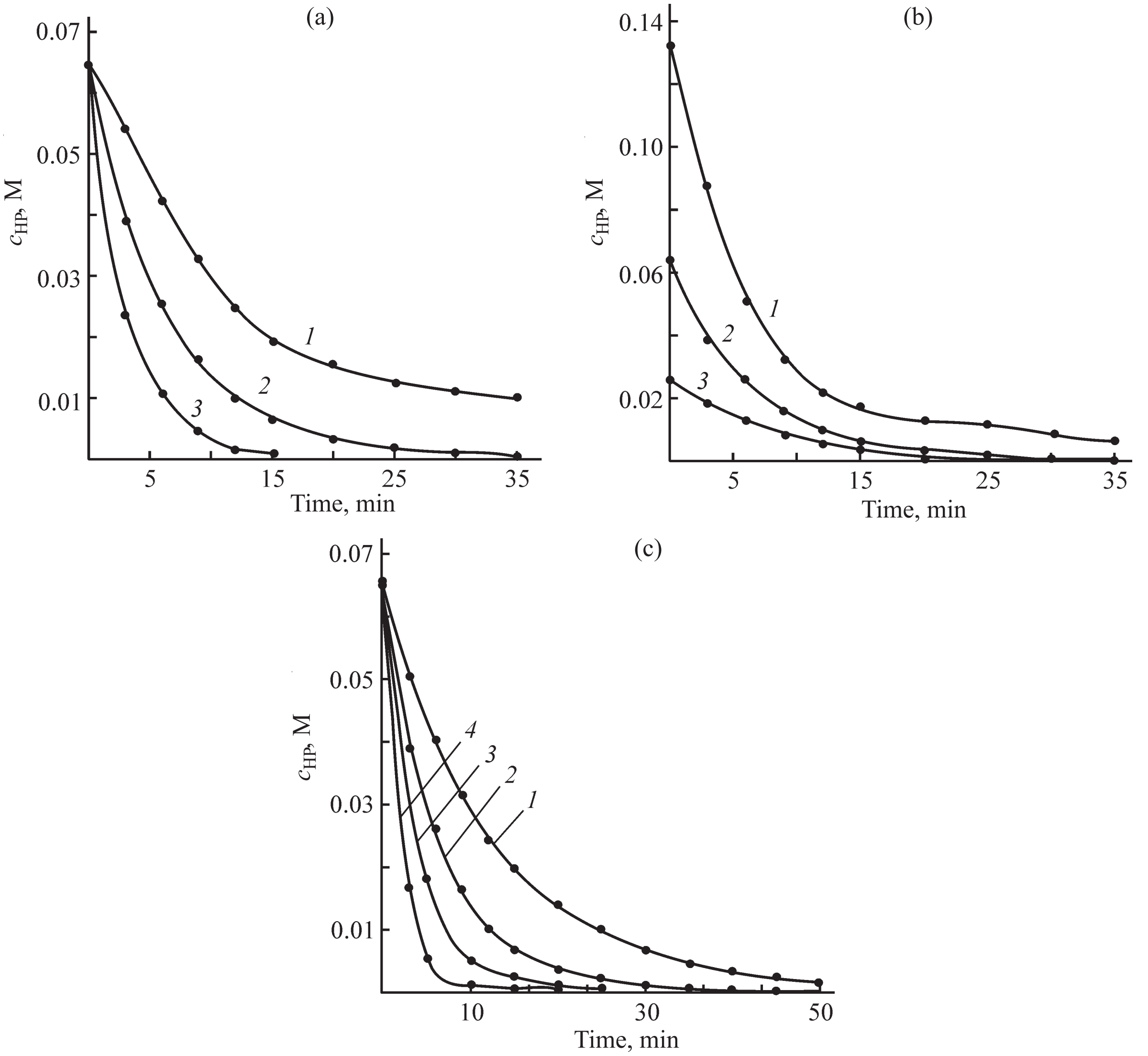


Fig. 2. Kinetic relationships of the acid decomposition of *p-tert*-butylcumene hydroperoxide under various conditions. (a) Temperature, °C: (*1*) 30, (*2*) 40, and (*3*) 50; catalyst concentration 0.6 wt %. (b) Initial hydroperoxide concentration, M: (*1*) 0.132, (*2*) 0.065, and (*3*) 0.026; temperature 40°C; catalyst concentration 0.6 wt %. (c) Catalyst concentration, wt %: (*1*) 0.3, (*2*) 0.6, (*3*) 0.9, and (*4*) 1.5; temperature 40°C.

Based on the data obtained, the following conditions for *p-tert*-butylcumene hydroperoxide decomposition can be recommended: reaction time of 45 min, temperature of 40°C, and initial concentration of *p-tert*-butylcumene hydroperoxide in acetone of 0.132 M. Under the chosen conditions, we performed a balance experiment and constructed the material balance of the acid decomposition of *p-tert*-butylcumene hydroperoxide. It confirmed the formation of *p-tert*-butylphenol in 92.8% yield at 100% conversion of *p-tert*-butylcumene hydroperoxide (Table 2).

To substantiate the mechanism, we constructed a kinetic model of the acid decomposition of *p-tert*-butylcumene hydroperoxide. It included the steps of the formation of the hydroperoxide dimer and of complexes of the hydroperoxide with *p-tert*-butylphenol and acetone. The probability of the formation of such complexes and their higher reactivity compared to the individual hydroperoxide were proved in numerous studies [4, 6–9]. The sulfuric acid decomposition of the hydroperoxide involves parallel occurrence of the decomposition of the hydroperoxide proper, its dimer,

Table 2. Material balance of the acid decomposition of *p-tert*-butylcumene hydroperoxide in acetone. Conditions: initial hydroperoxide concentration 0.132 M, reaction time 45 min, temperature 40°C, catalyst amount 0.6 wt % relative to the loaded hydroperoxide

Substance	Molar mass, g mol^{-1}	Initial mixture		Products	
		g	wt %	g	wt %
p-tert-Butylcumene hydroperoxide	208	23.70	30.00	0.00	0.29
Sulfuric acid	98	0.14	0.18	0.14	0.18
Acetone	58	55.15	69.82	60.10	75.86
p-tert-Butylphenol	150	0.00	0.00	15.80	19.94
By-products	–	0.00	0.00	2.05	2.59
Loss	–	0.00	0.00	0.90	1.14
Total	–	78.99	100.00	78.99	100.00

and complexes with decomposition products. The overall reaction is a complex process characterized both by autocatalysis and by inhibition with the reaction product.

Thus, the kinetic model of the *p-tert*-butylcumene hydroperoxide decomposition can be presented as follows:

$$\mathrm{HP + OH} K_1 \mathrm{HP\ldots OH},$$

$$\mathrm{HP + A} K_2 \mathrm{HP\ldots A},$$

$$\mathrm{HP + HP} K_3 \mathrm{HP\ldots HP},$$

$$\mathrm{H_2SO_4 + A} K_4 \mathrm{H_2SO_4\ldots A},$$

$$\mathrm{HPH^+} k_1 \mathrm{OH + A},$$

$$\mathrm{IH^+} k_2 \mathrm{OH + A},$$

$$\mathrm{IIH^+} k_3 \mathrm{OH + A},$$

$$\mathrm{IIIH^+} k_4 \mathrm{OH + A},$$

where K_1, K_2, K_3, and K_4 are the equilibrium constants of the formation of complexes I–III and IV; k_1, k_2, k_3, and k_4 are the rate constants of the decomposition of the hydroperoxide and complexes I, II, and III; HP is hydroperoxide; OH is *p-tert*-butylphenol; and A is acetone.

Because of low equilibrium constants of formation of complexes I–III [6], it can be assumed that their concentration is considerably lower than the initial concentration of the hydroperoxide; then, the material balance equation with respect to the hydroperoxide will have the form

$$c_{0\mathrm{HP}} = c_{\mathrm{HP}} + (c_{\mathrm{OH}} + c_{\mathrm{A}})/2, \quad c_{\mathrm{OH}} = c_{\mathrm{A}}, \tag{1}$$

$$c_{0\mathrm{K}} = c_{\mathrm{K}} + c_{\mathrm{IV}}, \tag{2}$$

$$c_{\mathrm{I}} = K_1 c_{\mathrm{HP}} c_{\mathrm{OH}}, \tag{3}$$

$$c_{\mathrm{II}} = K_2 c_{\mathrm{HP}} c_{\mathrm{A}}, \tag{4}$$

$$c_{\mathrm{III}} = K_3 c_{\mathrm{HP}}{}^2, \tag{5}$$

$$c_{\mathrm{IV}} = K_4 c_{\mathrm{K}} c_{\mathrm{A}}, \tag{6}$$

where c_{C} is the running catalyst concentration; $c_{0\mathrm{C}}$, initial catalyst concentration; c_{I}, c_{II}, c_{III}, c_{IV}, running concentrations of complexes I, II, III, and IV; $c_{0\mathrm{HP}}$, initial hydroperoxide concentration; and c_{HP}, c_{OH}, c_{A}, running concentrations of hydroperoxide, *p-tert*-butylphenol, and acetone.

The overall reaction rate is the sum of the decomposition rates of the hydroperoxide and its complexes with reaction products, which are proportional to the catalyst concentration raised to *n*th power and concentrations of hydroperoxide and the respective complexes:

$$-\frac{\partial c_{\mathrm{HP}}}{\partial t} = c_{\mathrm{C}}^{n}(k_1 c_{\mathrm{HP}} + k_2 c_{\mathrm{I}} + k_3 c_{\mathrm{II}} + k_4 c_{\mathrm{III}}),$$

where *n* is the reaction order with respect to the catalyst. Taking into account Eqs. (1)–(6), we finally obtain

$$-\frac{\partial c_{\mathrm{HP}}}{\partial t} = k_1 \left(\frac{c_{0\mathrm{C}}}{K_4(c_{0\mathrm{HP}} - c_{\mathrm{HP}}) + 1} \right)^{n} c_{\mathrm{HP}}[1 + a(c_{0\mathrm{HP}} - c_{\mathrm{HP}}) + b c_{\mathrm{HP}}], \tag{7}$$

Table 3. Constants of Eq. (7) describing the acid decomposition of *p-tert*-butylcumene hydroperoxide at 40°C

k_1	k_2	k_3	k_4	K_4	a	b	n
L mol^{-1} s^{-1}							
10.1	33.4	269.8	11.5	0.1	11.9	14.2	1

where $a = \dfrac{K_1k_2 + K_2k_3}{k_1}$, $b = \dfrac{K_3k_4}{k_1}$.

The differential equation was solved using numerical methods, and the $c_{\mathrm{HP}} = f(\tau)$ dependence was obtained (Fig. 3). The rate constants of the acid decomposition of *p-tert*-butylcumene hydroperoxide are given in Table 3. The reaction is first-order with respect to the catalyst. The reaction order was determined graphically from the slope of the logarithmic plot of the initial reaction rate vs. catalyst concentration.

As seen from Fig. 3, Eq. (7) adequately describes the acid decomposition of *p-tert*-butylcumene hydroperoxide. The approximation reliability for each kinetic curve was $R^2 \approx 0.99$. The error of measuring the constants did not exceed ±4%.

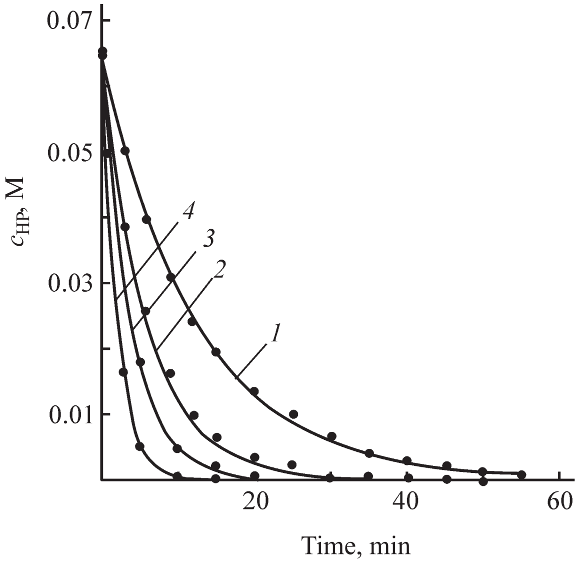


Fig. 3. Kinetic curves of acid decomposition of *p-tert*-butylcumene hydroperoxide at various catalyst concentrations. Curves: calculation using Eq. (7); points: experimental data. Catalyst (concentrated H_2SO_4) concentration, wt %: (*1*) 0.3, (*2*) 0.6, (*3*) 0.9, and (*4*) 1.5.

CONCLUSIONS

The results of studying the influence of various process parameters on sulfuric acid decomposition of *p-tert*-butylcumene hydroperoxide to *p-tert*-butylphenol and acetone show that the optimum reaction conditions are as follows: temperature of 40°C, reaction time of 45 min, initial concentration of *p-tert*-butylcumene hydroperoxide in acetone of 0.132 M, and sulfuric acid concentration of 0.6 wt %. Under these conditions, *p-tert*-butylphenol can be obtained in a yield exceeding 90%.

The results of mathematical modeling suggest that *p-tert*-butylphenol is mainly formed by decomposition of the complex of *p-tert*-butylcumene hydroperoxide with acetone, as indicated by high rate constant of the decomposition of this complex (k_3). This conclusion agrees with the conclusions made previously in [6, 7] when studying the relationships of the acid decomposition of cyclohexylbenzene hydroperoxide, and also in [9].

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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