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RESEARCH ARTICLE

Para-tert-butylcumene synthesis

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Abstract

Objectives. *This study describes a new approach to obtain para-tert-butylcumene by alkylation of cumene with isobutylene in the presence of catalysts, such as Amberlyst 36 Dry, KU-2-8, aluminum chloride, and tert-butyl alcohol and concentrated sulfuric acid.*
Methods. *To determine the qualitative and quantitative composition of the compounds and reaction masses, the following analysis methods were used: gas–liquid chromatography (on the Kristall 2000M hardware-software complex), chromatomass spectrometry on an Agilent 6850 instrument equipped with an Agilent 19091S-433E capillary column (30 m × 250 µm × 0.25 µm), and nuclear magnetic resonance spectroscopy (on a Bruker DRX 400 instrument with an operating frequency of 400 MHz).*
Results. *A significant quantity of meta-tert-butylcumene was obtained by the alkylation of cumene with isobutylene using several catalysts, along with para-tert-butylcumene. This study also showed that the use of the catalysts Amberlyst 36 Dry and KU-2-8 during alkylation in a closed system (autoclave) led to the formation of isobutylene oligomers, often in quantity greater than the target reaction product. Simultaneously, the alkylation of cumene with tert-butyl alcohol in the presence of concentrated sulfuric acid enabled the obtainment of only one isomer, para-tert-butylcumene, which is essential for the further production of high-purity para-tert-butyl phenol.*
Conclusions. *Sulfuric acid alkylation of cumene with tert-butyl alcohol enabled the obtainment of an individual para-isomer of tert-butylcumene with a yield of 87–89% for the loaded tert-butyl-alcohol with a cumene conversion of ~30%.*

Keywords: *para-tert-butylcumene, isobutylene, tert-butyl alcohol, alkylation*

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НАУЧНАЯ СТАТЬЯ

Синтез *пара-трет*-бутилкумола

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Аннотация

Цели. *В статье рассматривается возможность получения пара-трет-бутилкумола алкилированием кумола изобутиленом в присутствии таких катализаторов, как Amberlyst 36 Dry, КУ-2-8, хлористый алюминий, и трет-бутиловым спиртом в присутствии концентрированной серной кислоты.*
Методы. *Для определения качественного и количественного состава веществ и реакционных масс использованы следующие методы анализа: газожидкостная хроматография (на аппаратно-программном комплексе «Кристалл 2000М»), хромато-масс-спектрометрия (на приборе Agilent 6850, оснащенном капиллярной колонкой Agilent 19091S-433E (30 м × 250 мкм × 0.25 мкм) и спектроскопия ядерного магнитного резонанса (на приборе «Bruker DRX 400» с рабочими частотами 400 МГц).*
Результаты. *Установлено, что в процессе алкилирования кумола изобутиленом с использованием перечисленных катализаторов наряду с пара-трет-бутилкумолом образуется значительное количество мета-трет-бутилкумола. Также исследования показали, что применение катализаторов Amberlyst 36 Dry и КУ-2-8 при алкилировании в замкнутой системе (автоклав) приводит к образованию олигомеров изобутилена, количество которых многократно преобладает над целевым продуктом реакции. В то же время установлено, что алкилирование кумола трет-бутиловым спиртом в присутствии концентрированной серной кислоты позволяет получать только один изомер – пара-трет-бутилкумол, что имеет важное практическое значение для дальнейшего получения пара-трет-бутилфенола с высокой степенью чистоты.*
Выводы. *Сернокислотное алкилирование кумола трет-бутиловым спиртом позволяет получить индивидуальный пара-изомер трет-бутилкумола с выходом 87–89% на загруженный трет-бутиловый спирт при конверсии кумола около 30%.*

Ключевые слова: *пара-трет-бутилкумол, изобутилен, трет-бутиловый спирт, алкилирование*

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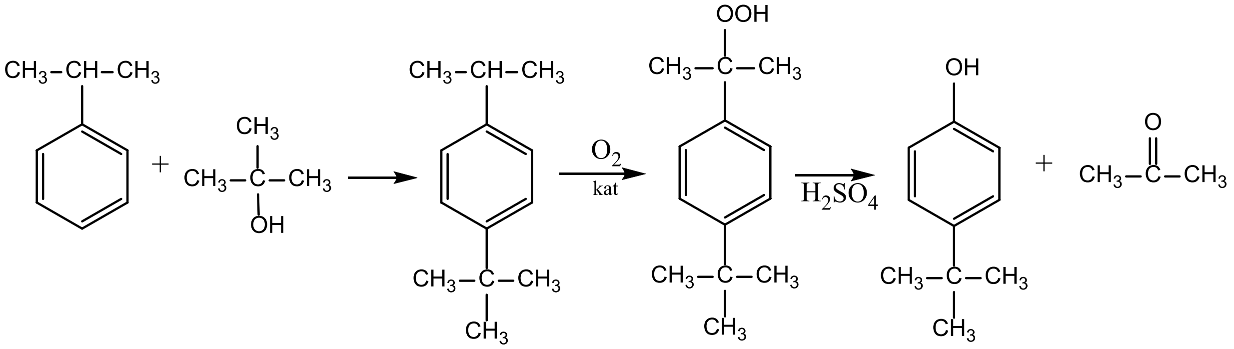
INTRODUCTION

Alkyl- and dialkylaromatic hydrocarbons containing an isopropyl fragment in their structures are valuable products in the petrochemical synthesis. The oxidative transformations of these hydrocarbons underlie the synthesis of various (alkyl)phenols [1–6], among which *para-tert*-butylphenol is of particular interest. Its scope of application is constantly expanding, covering the production of antioxidants, pesticides, rubbers, lacquers, paints, and pharmaceuticals [8–13]. The most promising areas of the *para-tert*-butylphenol use are the production of phenolic resin used in glued leather products, and the production of calixarenes based on it [14, 15].

Currently, *para-tert*-butylphenol is industrially obtained by the alkylation of phenol with isobutylene in the presence of ion-exchange resins or macroporous sulfocationites of the Amberlyst type [16]. However, the main limitation of this method is the low selectivity



Scheme. Method for the obtainment of *para-tert*-butylphenol.

of the *para-tert*-butylphenol formation (70–75%). Along with *para-tert*-butylphenol, *ortho*- and *meta*-isomers are also formed owing to the similar boiling points of these species, which significantly complicates the separation of *para-tert*-butylphenol from the reaction mixture with a sufficiently high degree of purity.

An alternative method for the synthesis of *para-tert*-butylphenol based on the selective preparation of *para-tert*-butylcumene (*para*-TBC) is proposed, which excludes the formation of *ortho*- and *meta*-isomers of *tert*-butylphenol [17]. The subsequent liquid-phase oxidation of *para*-TBC into tertiary hydroperoxide and its acid decomposition leads to the production of *para-tert*-butylphenol and acetone (Scheme).

In this study, the issues related to the investigation of several regularities in the synthesis of *para*-TBC by alkylation of cumene with isobutylene and *tert*-butyl alcohol in the presence of various catalysts are discussed.

MATERIALS AND METHODS

The reagents *tert*-butyl alcohol (AR, TU 2632-127-44493179-08) produced by *ECOS-1* (Russia), sulfuric acid (CP, GOST 4204-77) produced by *Sigma Tech* (Russia), cumene 99.9% extra pure produced by *Acros Organics* (USA) were used. Isobutylene (99.95% (mass), grade “A”), the sulfocationites KU-2-8 and Amberlyst 36 Dry, and the $AlCl_3$ catalyst (99.0% (mass)) were provided by *NNK* (Russia).

The main method for the reaction mixture analysis was gas–liquid chromatography. The chromatographic analysis was performed on a Kristall 2000M device (*Chromatec*, Russia) with Chromatec-Analyst hardware and software complex, equipped with a flame ionization detector, a gas flow divider, and a quartz capillary column (60 m × 250 µm × 0.25 µm) with a grafted stationary phase SE-30. Helium was used as the carrier gas. The carrier gas pressure at the column inlet was 3 atm, and the pressure stability was ensured by double reduction. The temperature profile was as follows: isotherm 333 K-10 min, temperature rise 20 K/min, isotherm 413 K-40 min. The temperatures of the evaporator and detector were 230°C and 260°C, respectively.

The components of the alkylation reaction mixtures were identified by gas chromatography combined with mass spectrometry (GC–MS). GC–MS analysis was performed on an Agilent 6850 gas chromatograph (*Agilent*, USA) equipped with an Agilent 19091S-433E capillary column (30 m × 250 µm × 0.25 µm) with a fixed phase of HP-5MS (5% diphenylpolysiloxane + 95% dimethylpolysiloxane) and an Agilent 5975C VL MSD mass-selective detector at an ionizing voltage of 70 eV. The identification of the reaction products was performed through the analysis of the mass spectra of the compounds using the rules and approaches described by Lebedev [18], and also the data from the NIST2017 library [19].

The nuclear magnetic resonance (NMR) spectra were recorded using a Bruker DRX 400 NMR spectrometer (*Bruker*, USA; 400 MHz frequency). A mixture of DMSO-d_6-CCl_4 was used as a solvent. Tetramethylsilane was used as the internal standard.

EXPERIMENTAL

Obtaining para-tert-butilcumene

Method 1. Alkylation of cumene with *tert*-butyl alcohol in the presence of concentrated sulfuric acid

The alkylation was performed in a round-bottomed three-necked flask equipped with a stirrer, a thermometer, and immersed in a water bath. The calculated quantity of concentrated sulfuric acid was slowly added to the loaded hydrocarbon. Next, *tert*-butyl alcohol was added drop by drop at a given temperature and continuous stirring (the rotation speed of the agitator was 250 rpm) using a separating funnel. After the reaction mixture was transferred to a separating funnel and sulfuric acid layer separated from the hydrocarbon layer, the latter was washed with distilled water until a neutral environment was achieved and dried over calcium chloride. The resulting alkylate was analyzed on a Crystal 2000M gas–liquid chromatograph and subjected to rectification under vacuum.

The synthesized *para*-TBC showed the following constants: $T_{boil} = 217°C$ [19]. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 7.28 d (2H (arom.), H-2, H-6, $3J = 8.1$), 7.14 d (2H (arom.), H-3, H-5, $3J = 8.1$), 2.8–2.9 septet (1H, CH (isopropyl), $3J = 6.8$); 1.25 c (9H, $C(CH_3)_3$), 1.18 d (6H, $2CN_3$ (isopropyl), $3J = 6.8$).

Method 2. Alkylation of cumene with isobutylene

The first method was a liquid-phase alkylation performed in a closed-type reactor (autoclave) using two grades of sulfocationites—KU-2-8 and Amberlyst 36 Dry (A36Dry) as catalysts.

In this method, alkylation was performed in reactors of the "glass ampoule with a screw cap" type manufactured by SamSTU glass-blowing workshop. The diagram is shown below (Fig. 1). Sealed cylindrical batch reactors were fabricated using molybdenum glass with a volume of 4–5 mL, internal diameter of 6 mm, and a wall thickness of 2 mm.

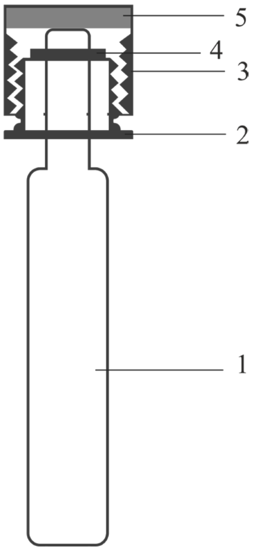


Fig. 1. Alkylation reactor:
(1) molybdenum glass reactor, (2) metal bearing,
(3) swivel nut, (4) copper ring, (5) gasket seal.

The second method was a gas-phase alkylation performed in a tubular flow-type reactor manufactured in the SamSTU glass-blowing workshop (Fig. 2). Cumene was added to the top of the reactor ($\nu_{vol} = 5$ mL/min) from a graduated separation funnel, and isobutylene was added to the bottom of the gas cylinder through a rheometer and a calibrated capillary ($\nu_{vol} = 120$ mL/min). A tank for collecting the alkylation product was also provided in the lower part of the reactor. The process was performed at atmospheric pressure, and the unreacted isobutylene was removed using a reverse refrigerator installed in the upper part of the reactor. The volume of the reaction zone filled with the A36Dry catalyst was 5 cm^3.

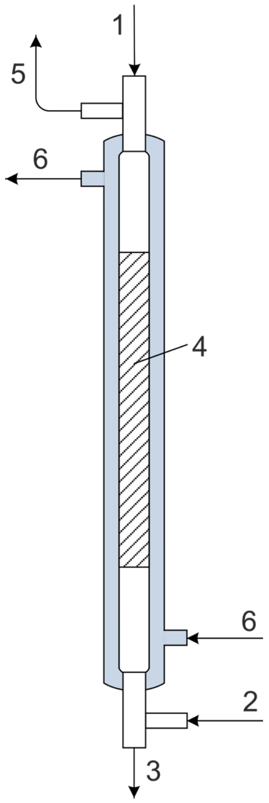


Fig. 2. Scheme of flow tubular reactor:
(1) IPB feeding, (2) isobutylene feeding,
(3) alkylate to receiver, (4) catalyst bed, (5) vent gas,
(6) heat carrier.

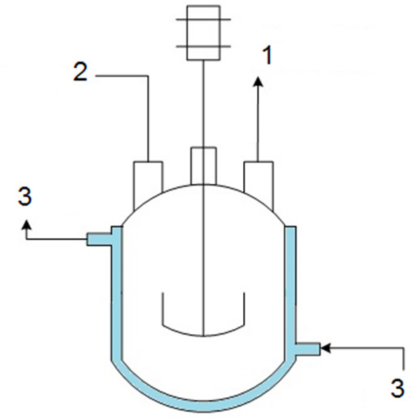


Fig. 3. Scheme of the jacketed reactor with stirrer:
(1) to reflux condenser, (2) for samples collection,
(3) heat carrier.

Method 3. The third method was liquid-phase alkylation of cumene with isobutylene in the presence of aluminum chloride in a reactor containing a stirrer and a jacket for the coolant, also manufactured in the SamSTU glass-blowing workshop (Fig. 3). The process was performed at atmospheric pressure, and the unreacted isobutylene was removed through a return cooler installed in the upper part of the reactor.

RESULTS AND DISCUSSION

Although extensive information is available on the regularities of the alkylation of aromatic hydrocarbons by olefins or alcohols, insufficient data on the synthesis of *para*-TBC have been reported. A method for the alkylation of cumene with isobutylene on tableted montmorillonite clay at elevated pressure and temperature of 135°C was described, and the product yield was 71.1% under these conditions [20]. An alternative method using alkylation of cumene with 1-butene or 2-butene on HZSM-12 zeolite at 200°C and pressure of 20 atm was also described, achieving 95% of selectivity for the alkylating agent in the *para*-position, the remaining 5% was alkylated in the *meta*-position [21]. The formation of a large number of by-products, (i.e., *ortho-tert*-butylcumene, *meta-tert*-butylcumene, diisopropylbenzene, isopropyltoluene, among others) along with *para*-TBC, makes necessary the use of complex systems for isolating the target product. Therefore, the search for selective methods to synthesize *para*-TBC is important, aiming for further implementation of the technology for the joint production of *para*-TBC and acetone.

In this regard, initial attempts were made to obtain *para*-TBC by alkylation of cumene with isobutylene. As can be seen from Table 1, the alkylation of cumene with isobutylene, in open and closed systems in the presence of the A36Dry catalyst, was not selective and was accompanied by the formation of the *meta*-TBC and *para*-TBC. The ratio of *meta*- and *para*-isomers was 0.12–0.17. The use of aluminum chloride as a catalyst contributed to an even more intensive formation of *meta*-TBC and led to an increase in the ratio of *meta*- and *para*-isomers of TBC up to 0.72.

The alkylation in a closed system using A36Dry and KU-2-8 catalysts was followed by a substantial formation of isobutylene oligomers. The analysis of the reaction products demonstrated that the content of oligomers significantly exceeds the content of the *para*-TBC target product. The transition to gas-phase alkylation in a tubular flow-type reactor using an A36Dry catalyst and liquid-phase alkylation in a stirrer reactor using $AlCl_3$ reduced the formation of

Table 1. Alkylation of cumene with isobutylene in the presence of various catalysts

Catalyst	Temperature, K	Catalyst concentration, wt %	Reaction time, min	The ratio of *m*- and *p*-isomers of TBC
A36Dry* (closed system – autoclave)	353	5.0	60	no alkylation
	373	5.0	5/10/15/30/90	0.12–0.17
	393	5.0	15/30/60/90/120	
	393	25.0	30/60/90/120	
КУ-2-8* (closed system)	393	5.0	30/60/90/120	0.12–0.15
	393	25.0	30/60/90/120	
A36Dry** (flow system)	393	–	1	0.12–0.15
	373	–	1	
$AlCl_3$** (liquid-phase alkylation, open system)	303	0.25	90	0.41
			150	0.41
			180	0.40
	303	0.5	40	0.68
			80	0.68
	303	0.75	40	0.72
			100	0.72
			140	0.67

*active formation of isobutylene oligomers;

**oligomers of isobutylene are formed in small amounts, which is ensured by the short residence time of isobutylene in the reaction zone.

isobutylene oligomers to insignificant quantities, which can be explained by the short residence time of isobutylene in the reaction zone.

According to the conducted studies, the obtainment of an individual *para*-isomer of TBC was not possible through the alkylation of cumene with isobutylene in open and closed systems in the presence of A36Dry, KU-2-8, and $AlCl_3$ catalysts.

Simultaneously, the alkylation of cumene with *tert*-butyl alcohol (TBA) in the presence of concentrated sulfuric acid practically eliminated all the formation of the *meta*-isomer of TBC (Table 2). Therefore, these investigations revealed that this reaction does not follow the usual rules of orientation, despite the mild conditions of the process. This can be explained by the appearance of the steric effect associated with the size of the functional group and the resulting spatial difficulty. According to previously reported, the ratio of *ortho*-and *para*-isomers in the alkylation of alkylphenols depends on the size of the incoming alkyl group. For example, the ratio of *o*- and *p*-isomers in the alkylation of toluene CH_3Br is 1.9 : 1; $(CH_3)_2CHBr$—1.2 : 1; $C_6H_5CH_2Cl$—0.82 : 1; no *ortho*-substitution product was detected during alkylation with *tert*-butyl bromide [22].

Accordingly, when the cumene was alkylated with *tert*-butyl alcohol in a 30 min reaction at 35°C with molar ratio cumene : TBA : H_2SO_4 3 : 1 : 3, it was possible to synthesize *para*-TBC with a yield of 87–89% on the loaded TBA with a cumene conversion of ~30%. Table 3 shows the material balance of the process.

The *para*-TBC isolated from the reaction mixture can be oxidized to tertiary hydroperoxide, which can be decomposed to produce *para*-*tert*-butylphenol together with acetone [23].

Table 2. Influence of various parameters on the alkylation of cumene with *tert*-butyl alcohol (TBA) in the presence of sulfuric acid. Cumene : TBA : H_2SO_4 ratio is 3 : 1 : 3

Temperature, °C	Reaction time, h	Cumene conversion, %	*para*-TBC concentration, wt %	*para*-TBC yield for the taken *tert*-butyl alcohol, %
20	**0.5**	**23.6**	**16.8**	**71.1**
25	0.5	28.2	23.4	82.9
30	0.5	32.9	34.8	89.4
35	0.5	49.0	42.7	87.1
30*	0.5	35.5	14.4	49.0
15	0.25	19.2	12.1	63.0
15	1.0	20.1	12.5	62.0
15	2.0	21.3	13.3	62.4
15	3.0	30.4	13.7	45.0

*the ratio of cumene : TBA : H_2SO_4 is 2 : 1 : 2.

Table 3. Material balance of the process of alkylation of cumene with *tert*-butyl alcohol (TBA) in the presence of concentrated sulfuric acid

Compound	Molar mass, g/mol	Taken		Obtained	
		g	wt %	g	wt %
Cumene	120.19	49.5	49.50	35.37	35.37
TBA	74.12	10.17	10.17	0.00	0.00
H_2SO_4	98.08	40.33	40.33	39.53*	39.53*
para-TBC	176.30	0	0.00	20.47	20.47
di-TBC	233.41	0	0.00	2.33	2.33
Losses	–	0	0.00	2.30	2.30
Total	–	100.00	100.00	100.00	100.00

*mass of acidic layer after reaction.

CONCLUSIONS

In summary, the regularities of the alkylation of cumene reaction with isobutylene in the presence of catalysts such as Amberlyst 36 Dry, KU-2-8, aluminum chloride, and TBA, and concentrated sulfuric acid were investigated. The sulfuric acid alkylation of cumene with TBA produced an individual *para*-isomer of *tert*-butylcumene with a yield of 87–89% on the loaded TBA with a cumene conversion of ~30%. These results confirmed that high-purity *para-tert*-butylphenol can be obtained using the hydroperoxide method based on the aerobic liquid-phase oxidation of *para*-TBC.

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Authors' contribution

E.M. Yarkina – development of the study concepts, development and execution of the experiments, discussion of the results, writing the text of the manuscript;

E.A. Kurganova – development of the study concepts, development of the experiments, data processing, discussion of the results, writing the text of the manuscript;

A.S. Frolov – gas chromatography and mass spectrometry experiment, writing the text of the manuscript;

G.N. Koshel – development of the study concepts, development of the experiments, discussion of the results, writing the text of the manuscript;

T.N. Nesterova – development of the study concepts, development of the experiments, data processing, discussion of the results, writing of the manuscript;

V.A. Shakun – gas chromatography and mass spectrometry experiments, data processing, discussion of the results, writing the text of the manuscript;

S.A. Spiridonov – execution of the experiments, discussion of the results, writing the text of the manuscript.

The authors declare no conflicts of interest.

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