

# Aerobic oxidation of isopropylaromatic hydrocarbons to hydroperoxides catalyzed by *N*-hydroxyphthalimide

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**Abstract** The oxidations of cumene, 4-isopropylbiphenyl, 1-methoxy-4-(1-methylethyl)benzene, 2-isopropyl-naphthalene, 2-methoxy-6-(1-methylethyl)naphthalene, 2,6-diisopropyl-naphthalene and 4,4'-diisopropylbiphenyl to the corresponding hydroperoxides with oxygen, at 60 °C, in the presence of *N*-hydroxyphthalimide (NHPI) and AIBN have been performed. Process inhibition was observed at temperatures above 60 °C resulting in lower conversion. A favorable effect of electron-donating substituents (methoxy, phenyl) on the reaction rate were described. NHPI was separated from the cumene oxidation product and recycled 5 times. It has been demonstrated that oxygen can be replaced by air.

**Keywords** Oxidation · NHPI · Isopropylaromatic hydrocarbons · Hydroperoxides

## Introduction

The industrial importance of the processes of selective oxidation of isopropyl aromatic hydrocarbons to hydroperoxides is mainly attributable to the fact that this process allows obtaining hydroxy aromatic compounds that may be useful as substrates in the synthesis of pharmaceuticals, pigments or polymers (Scheme 1) [1].

Currently, more than 7 million tons per year of phenol are obtained from cumene. In industrial systems, cumene is usually oxidized with air at 100–120 °C under

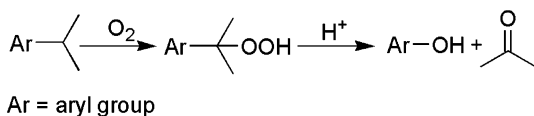
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**Scheme 1** Phenols synthesis via Hock's method



pressures of 0.5 MPa. The resulting product contains 20–30 % of cumene hydroperoxide, which then undergoes acid-catalyzed decomposition to phenol [1–3]. This method is characterized by lower energy consumption and a smaller volume of waste compared to the classic sulfonation method, hence the ongoing studies on the implementation of Hock's method for the synthesis of other hydroxyaromatic compounds.

The oxidation processes of isopropylaromatic hydrocarbons to hydroperoxides, as recently shown, can be catalyzed by *N*-hydroxyphthalimide (NHPI) [4–11] as well as its derivatives [12]. Literature data concerning the NHPI-catalyzed oxidation of isopropylarenes are collected in Table 1.

The processes studied by Ishii et al. [6–8] were usually run at 75 °C using 10 mol% of NHPI and 3 mol% of 2,2'-azobis(2-methylpropionitrile) (AIBN) as the initiator. Among the studied solvents, the best results were obtained in MeCN [6, 7]. The reaction products (the hydroperoxide contents of which were not determined) were subjected to acid-catalyzed decomposition to hydroxyarenes. For example phenol from cumene was obtained in a maximum yield of 77 % [6], whereas 2,6-dihydroxynaphthalene was obtained in 81 % yield [8]. Recently, we have described the NHPI-catalyzed oxidations of isopropylarenes with a methoxy group in the aromatic ring, i.e., of 1-methoxy-4-(1-methylethyl)benzene (**3**) [9] and 2-methoxy-6-(1-methylethyl)naphthalene (**5**) [10] to hydroperoxides. The corresponding hydroperoxides were obtained in yields of 58 and 87 % (conversion 60 and 92 %), respectively, when the processes were carried out at 60 °C in benzonitrile as a solvent. We have demonstrated that further temperature increase led to faster process inhibition resulted in lower hydrocarbons conversions and hydroperoxides yields.

Koshel' et al. [11] described the NHPI-catalyzed cumene oxidation reactions carried out without polar solvent at conditions similar to industrial process. At 120 °C, in the presence of NHPI (2.7 wt%) and AIBN, after 1 h of reaction, products containing 16.8 and 27.7 % of cumene hydroperoxide were obtained using air and oxygen, respectively. The addition of NHPI increased the oxidation rate by a factor of 2.6 making possible the industrial process intensification without modification of technology.

Novikova et al. [12] compared the oxidation of cumene in the presence of NHPI and their derivatives: 4-*tert*-butyl- and 4-carboxyl-*N*-hydroxyphthalimide, *N,N*-dihydroxypyromellitimide, *N*-acetoxyphthalimide and *N*-methoxyphthalimide. They observed that the catalytic activities of the studied catalyst decreased with the increase of the BDE values of the NO–H. The highest oxidation rate was obtained in the presence of 4-*tert*-butyl-*N*-hydroxyphthalimide.

The combination of NHPI and aldehydes or variable valence metal salts has also been reported for oxidation of isopropylarenes. The hydroperoxide in cumene oxidation reaction catalyzed by NHPI/CH<sub>3</sub>CHO system under moderate conditions at 25 °C was obtained with a yield of approximately 50 % [13].

**Table 1** NHPI-catalyzed oxidation of isopropylarenes—literature data

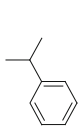
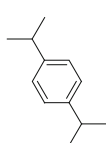
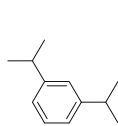
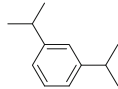
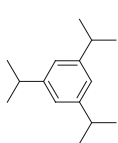
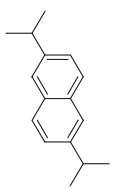
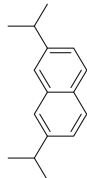
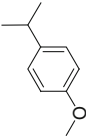
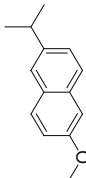
Entry	Substrate	Conversion (mol%)	Reaction conditions (studied range)			References
			Temp. (°C)	NHPI (mol%)	Solvent	
1		78	75	10	MeCN (AcOH)	6 (6–20) [6]
2		28 <sup>a</sup>	120	2	Without	1 [11]
3		99	75	10	MeCN	20 [6]
4		99	75	10	MeCN	20 [6]
5		96	75 (65–75)	10	MeCN (AcOEt, PhCN, PhCF <sub>3</sub> , AcOH)	7 (2–7) [7]
6		>99	75	10 (0–10)	MeCN	21 [8]

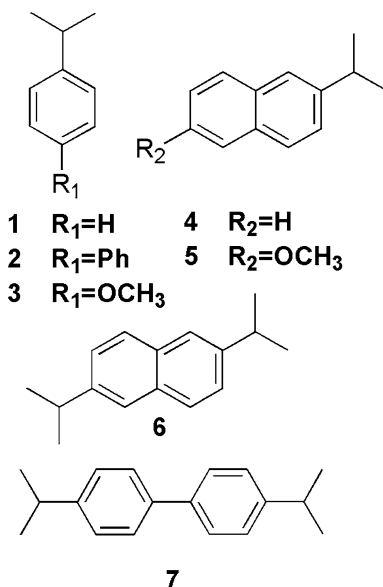
Table 1 continued

Entry	Substrate	Conversion (mol%)	Reaction conditions (studied range)			References	
			Temp. (°C)	NHPI (mol%)	Solvent		
7		>88	75	10	MeCN	21	[8]
8		60	60 (50–100)	10 (0–10)	PhCN	3	[9]
9		92	60 (50–110)	5	PhCN	3	[10]

Entries 1–9—AIBN was used as initiators

<sup>a</sup> Yield of hydroperoxide (wt %)

**Scheme 2** Isopropylarenes **1–7**



In contrast, the products of the oxidation of isopropylaromatic hydrocarbon catalyzed by NHPI and variable-valence metal salt systems primarily contained the corresponding alcohols and ketones [14–17]. The combination of NHPI and  $Co(OAc)_2$  in PEG-1000 based dication ionic liquid led even to formation of benzoic acid in the cumene oxidation reaction [18]. Therefore the processes are not useful for the synthesis of hydroperoxides.

In the present paper, the oxidation of selected mono- and diisopropylaromatic hydrocarbons **1–7**, illustrated in Scheme 2, to hydroperoxides using NHPI as the catalyst are described. The choice of substrates was based on the potential capabilities of their oxidation processes to be used in the synthesis of valuable products—hydroxyarenes.

This study complements the papers published thus far on the oxidation of isopropylarenes in the presence of NHPI [6–12] with respect to the range of the influence of temperature and the electron-donating substituents (methoxy, phenyl) on the course of the reaction as well as catalyst recovery and air application. The oxidation of hydrocarbons **2**, **4** and **7** in the presence of NHPI to hydroperoxides are reported for the first time.

## Experimental

### Materials

Cumene (Merck) and 1-methoxy-4-(1-methylethyl)benzene (Lancaster Synthesis) were purified by distillation over sodium. 2-Isopropyl-naphthalene was obtained by the crystallization of the technical product according to [19]. 2-Methoxy-6-(1-

methylethyl)naphthalene was prepared from 2,6-diisopropylnaphthalene according to the procedure described in [10]. The other starting materials and catalyst were used without further purification.

### Typical procedure

Isopropylaromatic hydrocarbon **1–7**, NHPI, initiator (2,2'-azobis(2-methylpropionitrile) (AIBN) at 50–70 °C or 1,1'-azobis(cyclohexanecarbonitrile) (ACHN) at 90 °C) and solvent (MeCN at 50–70 °C or benzonitrile (PhCN) at 90 °C) were placed in a 25 ml two-necked flask of a gasometric apparatus equipped with a magnetic stirrer (1,000 rpm), a heating bath and a gas burette filled with oxygen under atmospheric pressure. The amount of consumed oxygen was measured over the course of the reaction and used to calculate hydrocarbon conversion (after recalculation to normal conditions—273 K, 1 atm.).

$$\alpha = \frac{n_{O_2}}{n} \times 100 \%$$

$\alpha$  conversion,  $n_{O_2}$  mmols of oxygen consumed at normal conditions,  $n$  mmols of hydrocarbons 1–5 or isopropyl groups in case of hydrocarbons 6 and 7.

The amount of hydroperoxides was iodometrically determined according to the described method [20], and the result was used for calculation of selectivity.

$$S_{-OOH} = \frac{n_{-OOH}}{n_{O_2}} \times 100 \%$$

$S_{-OOH}$  hydroperoxides selectivity,  $n_{-OOH}$  mmols of hydroperoxide groups based on iodometric analysis,  $n_{O_2}$  mmols of oxygen consumed at normal conditions.

The amounts of hydroperoxides (**6a**, **6b**, **7a** and **7b**) in the oxidation products of **6** and **7** were determined by HPLC according to methods described in [21, 22] and used for calculation of yield and selectivity presented in Table 6.

A Waters Alliance 2690 HPLC equipped with an autosampler, a UV detector (Waters photodiode array), and a Nova-Pak Silica 60 Å 4 μm column (150 mm × 3.9 mm; Waters) was used with a mixture of hexane and 2-propanol as the mobile phase (99:1–97:1 v/v).

The amounts of NHPI in the reaction mixture of the cumene oxidation process (conditions are given in Table 5, entry 5) were determined by HPLC using the above mentioned apparatus and detector and Merck LiChroCART 250-2 Purospher

**Table 2** Effect of the amount of NHPI on the cumene oxidation process

Entry	Cumene (mmol)	NHPI (mmol)	Conversion (mol%)	Selectivity (mol%)
1	10	0	1.9	100
2	10	0.1	28	100
3	10	0.5	35	100
4	10	1	46	100
5	10	1.5	41	100
6	20	2	22	100

Reaction conditions: MeCN—10 ml, AIBN—3 mol%, 60 °C, 3 h, 1,000 rpm

STAR RP-18e column and a mixture of MeCN and water as a mobile phase (90:10 v/v, 1 ml/min). The amount of NHPI was compared in the samples taken after 5 min and 5 h of reaction. The presence of phenol in the cumene oxidation product were checked by GC MS analysis using Agilent 7890A chromatograph (HP5MS 30 m  $\times$  0.25 mm, helium 1 ml/min, column temperature increased from 70 to 220 °C with a rate of 7 °C/min) combined with Agilent 5975I mass spectrometer with EI ionisation (70 eV).

NHPI-catalyzed cumene oxidation in the presence of phthalic acid, phthalimide and phthalic anhydride

Cumene (10 mmol), NHPI (1 mmol), AIBN (0.3 mmol) and PhCN (10 cm<sup>3</sup>) were placed in a 25 ml two-necked flask of a described above gasometric apparatus and oxidized at 90 °C for 1 h. Then additives were introduced; after 1 h phthalic acid (0.05 mmol), after 2 h phthalimide (0.05 mmol) and after 3 h phthalic anhydride (0.05 mmol). The course of reaction was similar to that carried out without additives.

NHPI-catalyzed isopropylarenes oxidation using oxygen and air in a bubbler reactor

The oxidation was carried out in a 20 ml glass reactor supplied with a bubbler, thermometer, reflux condenser and heating jacket. Hydrocarbon and MeCN were placed in the reactor and heated to the reaction temperature. After that, NHPI and AIBN were added, and the oxygen was passed through. During the process, samples were taken, and the content of hydroperoxide was determined iodometrically [20]. The amount of hydroperoxide was used for calculation of yields.

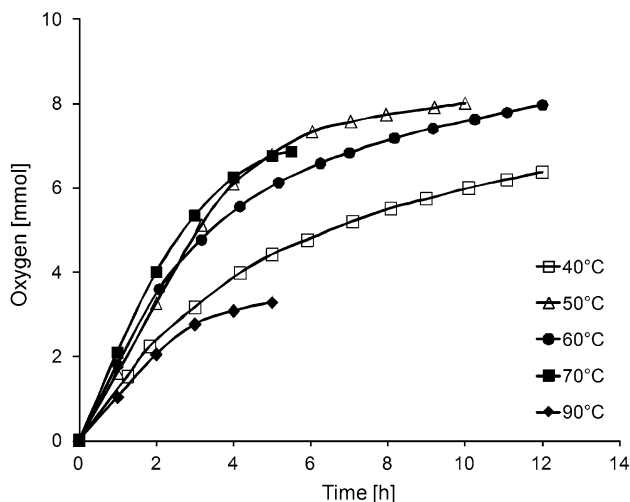
## Results and discussion

The effect of reaction conditions

Within the initial studies, the influence of the amount of NHPI, temperature and solvent on the NHPI-catalyzed oxidation reaction of isopropylarenes was studied.

Table 2 provides a comparison of the cumene conversions obtained after 3 h of reaction conducted using MeCN as the solvent and different amounts of the catalyst.

The results showed that an increase in the NHPI amount in the range of 1–10 mol% (entries 1–4) led to an increase of cumene conversion, analogous to previous results reported by Ishii for 2,6-diisopropyl-naphthalene [8]. Further increases in the amount of the catalyst are limited by its solubility in the system. With 15 mol% of NHPI, the catalyst dissolved completely only after several dozen minutes (entry 5). The use of a higher concentration of the substrate (entry 6) decreased the solubility of NHPI in the system and left a substantial portion undissolved, which, in turn, resulted in a decreased in the cumene conversion. Subsequent studies were therefore performed using 10 mol% of NHPI.



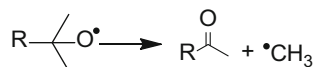
**Fig. 1** Effect of temperature on cumene oxidation catalyzed by NHPI (reaction conditions are given in Table 3)

In this study, the effect of temperature in the range of 40–90 °C on the oxidation process of **1** and diisopropylarenes **6** and **7** was examined (Fig. 1; Table 3, Supplemental Fig. S3 and S4). The aim was to indicate that the previously observed decrease in the conversion rate at temperature greater than 60 °C in the case of the oxidation of **3** and **5**, reported in our previous works [9, 10], was not a result of the presence of methoxy group in the aromatic rings of **3** and **5**.

Depending on the process temperature, different amounts of AIBN or ACHN were used as initiators, and the obtained initiation rates are also given in Table 3. An induction period of approx. 30 min was observed when compound **6** was oxidized at 40 °C. To reduce the length of this induction period at 50 and 60 °C, greater amounts of initiator were used in the case of the oxidation of **6** than in the oxidation processes of **1** and **7**.

The obtained results showed that the highest conversions to hydroperoxides in the NHPI-catalyzed oxidation of compounds **1**, **6** and **7** were obtained in the range of 50–60 °C. A temperature increase above 60 °C led to a faster process inhibition resulting in lower conversion, analogously to previous results concerning the oxidation of hydrocarbons **3** and **5** [9, 10].

The inhibition in the oxidation processes of isopropylaromatic hydrocarbons is usually related to the acid-catalyzed hydroperoxide decomposition to the corresponding phenols (even traces can retard the oxidation). Acids are known to be formed as a product of methyl-radical oxidation and methyl radicals are known to be formed in the  $\beta$ -scission reaction of 1-aryl-1-methylethoxy radicals [23].





**Table 3** Effect of temperature on isopropylaromatic oxidation catalyzed by NHPI

Entry	Substrate	Temperature (°C)	Initiation rate <sup>a</sup> (mol dm <sup>-3</sup> s <sup>-1</sup> ) × 10 <sup>6</sup>	Time (h)	Conversion <sup>b</sup> (mol%)	Selectivity (mol%)
1	1	40	0.34	12	64	100
2	1	50	0.34	10	80	100
3	1	60	0.34	12	80	100
4	1	70	1.19	5.5	69	100
5	1	90	1.64	5	33	99
6	6	40	0.32	14	52	100
7	6	50	0.67	15	89	100
8	6	60	1.19	12	80	100
9	6	70	1.19	10	61	98
10	6	90	1.64	5	19	95
11	7	40	0.34	12	58	100
12	7	50	0.34	12	77	100
13	7	60	0.34	11	81	100
14	7	70	1.19	8	51	97
15	7	90	1.64	5	23	91

Reaction condition: substrate **1–7**—10 mmol, MeCN at 40–70 °C or PhCN at 90 °C—10 ml, NHPI—1 mmol, AIBN at 40–70 °C or ACHN at 90 °C, 1,000 rpm

<sup>a</sup> Rate of initiation was calculated using the equation  $r_i = 2ek_d c_i$ , where the coefficient of effectiveness  $e = 0.6$ ,  $k_d$  is the rate constant of thermal decomposition of AIBN or ACHN calculated based on data presented in [29–31] and  $c_i$  is the concentration of the initiator

<sup>b</sup> Conversion of diisopropylarenes **6** and **7** refer to the conversion of both isopropyl groups (20 mmol)

Furthermore, the decrease in the substrate conversion rate observed at 90 °C results from the change of the solvent from MeCN to PhCN. The literature data indicate that the substitution of MeCN with PhCN results in a decrease in the substrate conversion in the case of triisopropylbenzene oxidation catalyzed by NHPI [7]. We have observed a similar effect (Table 4).

Initially, it was presumed that the conversion decrease at higher temperature could also be a result of NHPI decomposition. However, only a slight amount of NHPI was decomposed during the cumene oxidation process carried out at 90 °C (the NHPI amount decreased from 10 to 9 mol%; process conditions are given in Table 3, entry 5). It has been also demonstrated that phthalimide, phthalic anhydride

**Table 4** Oxidation processes carried out in MeCN and PhCN

Entry	Substrate	Solvent	Conversion (mol%)	Selectivity (mol%)
1	1	PhCN	29	100
2	1	MeCN	53	100
3	6	PhCN	19	100
4	6	MeCN	28	100

Reaction conditions: substrate—10 mmol, solvent—10 ml, NHPI—1 mmol (10 mol%), AIBN—0.3 mmol (3 mol%), 1,000 rpm, 3 h, 70 °C

and phthalic acid, known as a products of NHPI or PINO decomposition [5], had no negative influence the NHPI catalyzed cumene oxidation at 90 °C.

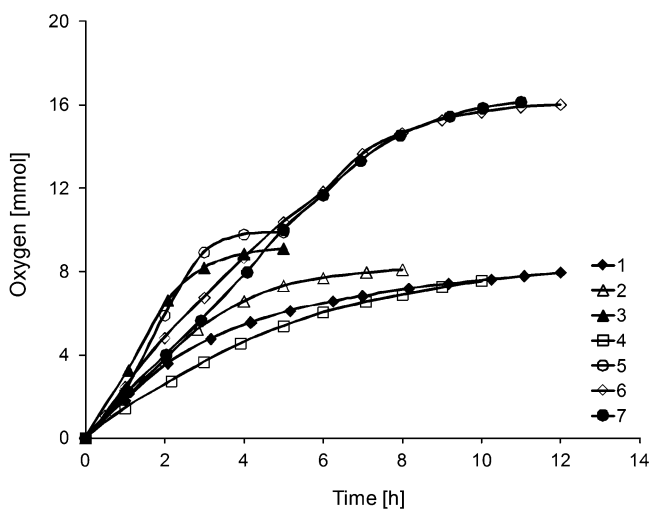
Although GC MS analysis of cumene oxidation product obtained at 90 °C (reaction conditions are given in Table 3 entry 5) did not confirm the presence of phenol, its formation and negative impact on the process is still taken under the consideration. The formed phenol was probably consumed in subsequent reactions e.g. with free radicals and retarded the process.

### Oxidation processes of hydrocarbons 1–7

Having established the conditions for the NHPI-catalyzed oxidation of isopropylarenes to the corresponding hydroperoxides (50–60 °C, 10 mol% NHPI, MeCN as a solvent), we then examined the reaction for a wider range of substrate. Fig. 2 presents a comparison of the oxidation processes of compounds 1–7, whereas Table 5 lists the obtained conversions and hydroperoxide selectivities.

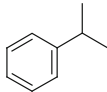
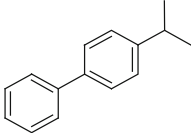
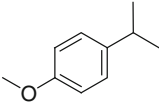
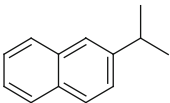
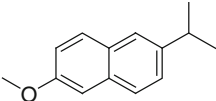
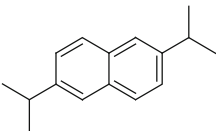
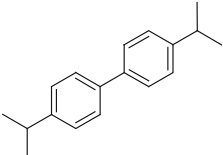
The results showed that the isopropylarenes 1–7 were oxidized to corresponding hydroperoxides with high conversions and selectivities. The yields of hydroperoxides obtained within the study are higher than those previously reported in literature. The reported lower yields obtained in the NHPI-catalyzed oxidation processes of 1, 3 and 5 [6, 9, 10] most likely result from the use of higher temperatures (75 °C) [6] or PhCN as the solvent [9, 10]. Our research indicates that such conditions are less favorable.

The presented data indicate a favourable influence of methoxy and phenyl substituent in the aromatic ring of compounds 2, 3 and 5 on the NHPI-catalyzed oxidation process, resulted in an acceleration of the reaction rates. The presence of the electron-donating group in the aromatic ring most likely stabilizes the partial positive charge on the tertiary carbon atom in the transition state during the



**Fig. 2** Comparison of the oxidations of isopropylarenes 1–7 catalyzed by NHPI at 60 °C (reaction conditions are given in Table 5)

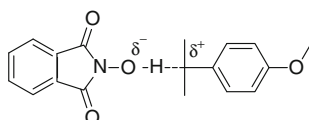
**Table 5** Conversion of hydrocarbons and selectivity of the hydroperoxides obtained in the oxidation processes catalyzed by NHPI

Entry	Substrate	Time (h)	Conversion (mol%) <sup>a</sup>	Selectivity (mol%)
1		12	80	100
2		8	80	100
3		5	91	100
4		10	76	100
5		5	99	100
6		12	80	100
7		11	81	100

Reaction conditions: substrate **1–7**—10 mmol, MeCN—10 ml, NHPI—1 mmol, AIBN was used in the amounts given in Table 3, 60 °C, 1,000 rpm

<sup>a</sup> Conversion of diisopropylarenes **6** and **7** refer to the conversion of both isopropyl groups (20 mmol)

abstraction of the atom by the electrophilic PINO radical, which accelerates the propagation rate.



A similar influence of electron-donating substituents on the NHPI-catalyzed oxidation has been reported for toluene and ethylbenzene derivatives [24–26]. However, to the best of our knowledge, no such data are available for isopropylarenes.

### Oxidation processes of hydrocarbons **6** and **7** oxidation

The studies showed that the products of the NHPI-catalyzed oxidation of compounds **6** and **7** contained only the corresponding mono- and dihydroperoxides (Table 6).

The analysis of the composition of the oxidation products of **6** and **7** revealed that it is possible to obtain the corresponding dihydroperoxides **6b** and **7b** in high yields and with high selectivities when the NHPI-catalyzed process is run at 50 °C for

**Table 6** Yield and selectivity of the corresponding mono- and dihydroperoxides obtained from the oxidation of diisopropylarenes **6** and **7** in the presence of NHPI

**6 Ar = 2,6-naphthalenyl**  
**7 Ar = 4,4'-biphenyl**

Entry	Temp. (°C)	Time (h)	<b>6a</b>		<b>6b</b>	
			Yield <sup>a</sup> (mol%)	Sel. (mol%)	Yield <sup>a</sup> (mol%)	Sel. (mo %)
1	50	3	32	68	15	32
2	50	6	38	48	41	52
3	50	9	19	22	68	78
4	50	12	9	10	79	90
5	50	15	6	7	85	93
6	60	3	43	76	13	24
7	60	12	20	22	70	78
8	70	3	44	88	6	12
9	70	10	53	61	34	39
			<b>7a</b>		<b>7b</b>	
10	50	3	22	46	26	54
11	50	12	12	14	72	86
12	60	3	19	42	26	58
13	60	11	19	21	71	79
14	70	3	33	87	5	13
15	70	8	46	62	26	35

Reaction conditions: substrate **6** or **7**—10 mmol, MeCN—10 ml, NHPI—1 mmol, 1,000 rpm, the amounts of AIBN used depends on the process temperature and are given in Table 3

<sup>a</sup> Yield was calculated based on HPLC determination of content of **6a**, **6b**, **7a** and **7b**

**Table 7** Cumene oxidation in the presence of recycled NHPI

Entry	Recycling	Recycled NHPI (mmol)	Fresh NHPI (mmol)	Cumene (mmol)	Conversion (mol%)	Selectivity (mol%)
1	0	0.0	1.0	10	61	100
2	1	0.86	0.14	10	44	100
3	2	0.80	0.20	10	65	100
4	3	0.80	0.20	10	54	100
5	4	0.86	0.14	10	57	100
6	5	0.74	0.26	10	59	100
7	0	0.0	0.0	10	64	100
8	1	0.86	0.0	8.6	51	100
9	2	0.61	0.0	6.1	57	100
10	3	0.49	0.0	4.9	51	100
11	4	0.40	0.0	4.0	50	100

MeCN—10 ml, AIBN—0.3 mmol, 5 h, 1,000 rpm, 60 °C

12–15 h. It was also established that the corresponding monohydroperoxides **6a** and **7a** can be obtained with similarly high selectivities but in lower yields if the process is run at 70 °C for 3 h.

Our previous studies described the methods of separation of the mixtures of mono- and dihydroperoxides obtained in the uncatalyzed oxidation of **6** and **7** [27, 28]. The oxidation of hydrocarbons **6** and **7** in the presence of NHPI, combined with the previously developed separation method based on differences in their acidity, are a promising approach to the synthesis of corresponding mono- and dihydroperoxides as intermediates for the synthesis of valuable mono- and dihydroxyarenes.

#### NHPI recovery and recycling

The studies on the catalyst separation and recycling were carried out for the process of cumene oxidation. After the process was completed, the MeCN was distilled off, and the NHPI was filtered and washing with hexane. The separated NHPI was used in the subsequent reaction with or without refilled of fresh catalyst.

The results presented in Table 7 showed that about 80 % of NHPI was recovered by this method and can be recycled without meaningful loss in the hydroperoxide yield.

#### Cumene oxidation using air under atmospheric pressure

The processes of NHPI-catalyzed oxidation of cumene using oxygen and air were compared (Table 8 entries 1 and 2, Supplemental Fig. S5). The processes were carried out in a bubbler reactor under atmospheric pressure.

Although the rate of cumene oxidation using air was lower in the initial stages of the processes high yields of cumene hydroperoxide were obtained using both oxidizing agent. Therefore hydrocarbons **2–7** were also oxidized using air and

**Table 8** NHPI-catalyzed isopropylarenes oxidation using air and oxygen under atmospheric pressure

Entry	Substrate	Oxidising agent	Hydroperoxide yield (mol%)
1	1	Oxygen	71
2	1	Air	70
3	2	Air	85
4	3	Air	70
5	4	Air	88
6	5	Air	92
7	6	Air	86
8	7	Air	78

Reaction condition: substrate—20 mmol, MeCN—20 ml, NHPI—2 mmol, AIBN—0.61 mmol, gas flow—15 dm<sup>3</sup>/h, 60 °C, 8 h, 1 atm.

respective hydroperoxides were obtained in high yields (Table 8, entries 3–8). The slight differences in hydroperoxides yields obtained using oxygen (Table 5) and air (Table 8) were probably the results of different process conditions (time of reaction, type of apparatus). Previously, the application of air in the NHPI-catalyzed isopropylarenes oxidation has been reported only in the papers [8, 11]. However Ishii [8] oxidized hydrocarbon **6** using air under pressure of 20 atm., while Koshel' et al. [11] oxidized cumene under the conditions similar to the industrial process (120 °C, without polar solvent, 2.7 % NHPI) and obtained lower hydroperoxide yield in process with air than with oxygen (17 and 28 wt%, resp. after 1 h of reaction).

## Conclusions

- It has been shown that in order to obtain high yields of hydroperoxides, the oxidation reactions of the corresponding isopropylaromatic hydrocarbons with oxygen should be performed in the presence of 10 mol% NHPI using MeCN as the solvent at temperature of 50–60 °C. These results are in good agreement with previous works [6–10] and confirm that the reaction temperatures above 60 °C adversely affect the NHPI-catalyzed oxidation processes.
- The yields of hydroperoxides obtained within this study under the above mentioned conditions were higher than those previously reported in the literature [6, 9, 10]. The oxidation of hydrocarbons **1**, **4** and **7** to hydroperoxides in the presence of NHPI was reported first time.
- The NHPI-catalyzed oxidation reactions of diisopropylarenes **6** and **7** to mono- and dihydroperoxides, as described herein, in combination with the separation method that we have previously reported [27, 28], appears to be a promising approach to their synthesis as intermediates in the production of mono- and dihydroxyarenes.
- The favorable effect of electron-donating substituents (methoxy, phenyl groups) on the oxidation processes of isopropylarenes in the presence of NHPI was observed.

- It has been demonstrated that NHPI can be easily separated from the product of cumene oxidation and used in subsequent reaction.
- It has been indicated for the first time that hydroperoxides could be obtained in high yields in the NHPI-catalyzed isopropylarenes **1–7** oxidation processes using air in place of oxygen under atmospheric pressure.

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