

N-Hydroxyphthalimide as a Catalyst of Cumene Oxidation with Hydroperoxide

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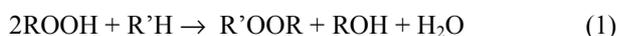
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Abstract: Cumene oxidation with 1-methyl-1-phenylethyl hydroperoxide catalyzed by *N*-hydroxyphthalimide or its derivatives and transition metal salts has been studied. Effects of the type of metal compound (Co(II), Mn(II) or Cu(II) chloride, acetate or acetylacetonate), amounts of *N*-hydroxyphthalimide and metal salt as well as temperature were established. The highest yields of dicumyl peroxide (48-54%) were obtained, when reaction was performed at 60-70°C, in the presence of the NHPI/CuCl₂ catalytic system, in acetonitrile as a solvent. Similar yield of dicumyl peroxide (43%) was obtained in solvent-free medium.

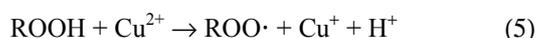
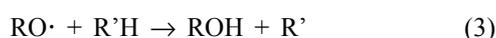
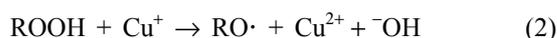
Keywords: Oxidation, *N*-Hydroxyphthalimide, Cumene Hydroperoxide, Dicumyl Peroxide, Cumene, Copper(II) Chloride

1. Introduction

Organic peroxides play very important role in many industrial technologies. Their oxidative capacity and reactivity is utilized especially in free radical processes such as polymerization or oxidation. They can be synthesized from different substrates, by oxidation with oxygen, hydrogen peroxide or other peroxides. [1] One of the methods involves oxidation of hydrocarbons possessing active hydrogen atom with alkyl hydroperoxides (Eq. 1).



The reaction proceeds via free radical mechanism, mostly in the presence of transition metal salts as catalysts (Mechanism described by Kharash is depicted in Eq 2-7). [2-3]



where $\text{R}=(\text{CH}_3)_3\text{C}-$ and $\text{R}'=\text{Ph}(\text{CH}_3)_2\text{C}-$; Ox is Cu^{2+} or hydroperoxide.

Copper organic and inorganic compounds are applied very often as catalysts in such reactions. It was found that systems composed of copper salts together with phase transfer catalysts, such as onium salts or crown ethers, allow to obtain dialkyl peroxides in higher yields and under milder conditions. [4-7] Unfortunately, in the discussed reaction, from two molecules of hydroperoxide only one molecule of peroxide is formed. This is the drawback of utilizing such reaction in the production of e.g. dicumyl peroxide. However, this problem can be overcome by applying two stage process, where the post-reaction mixture containing peroxide and alcohol is directed to the second step where alcohol reacts with hydroperoxide forming additional amounts of desired peroxide (Figure 1). [8]

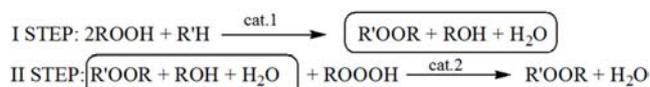


Figure 1. Production of dicumyl peroxide in two-steps process, where R, R' = 1-methyl-1-phenylethyl [8].

Recently, *N*-hydroxyphthalimide (NHPI) has been widely applied as an active catalyst of many free radical oxidation processes using oxygen. [9-12] NHPI-catalyzed oxidation of hydrocarbons, (including cumene oxidation with oxygen), have been performed under mild conditions, and high yields as well as high selectivities of products have been achieved. In oxidation processes, PINO radical which is formed in-situ from NHPI, abstracts hydrogen atom from oxidized hydrocarbon much faster, than alkylperoxy radicals in non-catalytic processes (Figure 2). [12]

According to our best knowledge, there has been no research on the possibility of utilizing NHPI in the free radical process of cumene oxidation with cumene hydroperoxide. One can assume that in such oxidation reaction, PINO radical will be also formed and it will abstract hydrogen from cumene faster than alkylperoxyl radicals in reaction (6) proposed by Kharash.

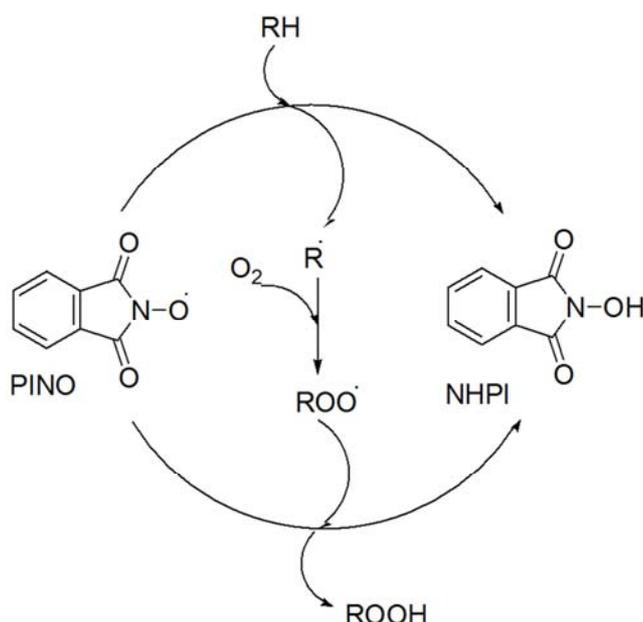


Figure 2. NHPI-catalyzed hydrocarbons oxidation with oxygen [12].

In this paper we present results of our investigation on NHPI catalyzed synthesis of DCP. Catalytic systems consisted of transition metal salts (copper, manganese, cobalt, iron) together with NHPI were applied. Additionally NDHPI, having two hydroxyimide were also investigated. The possibility of performing discussed reaction at lower temperatures was also checked. For safety reason, the reaction was carried out in semi-batch system, where hydroperoxide was added dropwise to the reaction mixture.

2. Experimental

2.1. Materials

1-Methyl-1-phenylethyl hydroperoxide (CHP) was purchased as 80% solution in cumene from Aldrich. Cumene was purchased from Merck and washed with concentrated sulfuric acid, neutralized, dried with anhydrous magnesium

sulfate, and distilled (62-65°C/20 mm Hg). Other reagents and catalysts were purchased either from Merck, Sigma Aldrich or Avantor (former POCH, Poland) and used as received.

2.2. Oxidation of Cumene with CHP

In a typical procedure 80% solution of 1-methyl-1-phenylethyl hydroperoxide (20 mmol) in cumene was added dropwise (~2 h) to a mixture of cumene (10 mmol), metal salt (0.015-0.30 mmol), NHPI (1mmol) and, in some cases MeCN (10 cm³). The mixture was stirred for additional 1 h. The reaction was carried out at 30-70°C for 3 h (total reaction time). The reaction course as well as the CHP and DCP content in post-reaction mixture were analysed using the iodometric (CHP and DCP) [13] and HPLC (2-phenyl-2-propanol - PhPr and acetophenone - AcPh) methods. HPLC analysis conditions: apparatus - Waters Alliance 2690 HPLC, equipped with Nova-Pak Silica column (60 Å, 3.9x150 mm, 4 µm; Waters); hexane:isopropanol (99:1 v/v; flow rate 1.0 cm³/min); wavelength 210 nm for PhPr and 240 nm for AcPh.

2.3. Synthesis of NDHPI and C12-NHPI

4-Dodecyloxycarbonyl-*N*-hydroxyphthalimide (C12-NHPI) was obtained using trimellitic anhydride chloride and dodecyl alcohol according to the previously described method. [14]

N,N'-Dihydroxypyromelitimide, NDHPI, was obtained from 1,2,4,5-benzenetetracarboxylic anhydride and hydroxylamine hydrochloride according to the reported method. [15]

3. Results

N-hydroxyphthalimide (NHPI) and its derivatives, together with salts of transition metals, were used as catalysts in the reaction of cumene oxidation with cumene hydroperoxide (CHP) (Figure 3). Acetonitrile was used as a solvent in order to overcome poor solubility of NHPI in non-polar systems. When the oxidation was performed without solvent, lipophilic NHPI derivatives or systems of NHPI with alkylammonium salts were used.

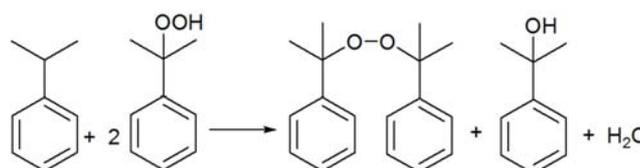


Figure 3. Cumene oxidation with cumene hydroperoxide.

3.1. The Influence of NHPI and NDHPI

The influence of NHPI on the yield of DCP obtained in the catalytic oxidation of cumene with CHP was determined. The reaction was performed at 70°C, in the presence of CuCl₂·2H₂O, in MeCN, using 2.5-15 mol% of NHPI (calc. on

cumene). The results are presented in Table 1.

Table 1. Effect of NHPI on dicumyl peroxide yield in the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

	NHPI [mol %]	DCP yield [%]	CHP conversion [%]
1	0	41	97
2	2.5	45	99
3	5.0	48	96
4	10	48	99
5	15	41	97

CHP 20 mmol, cumene 10 mmol, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.15 mmol, MeCN 10 ml; 70°C; 3 h.

The results presented in Table 1 show, that the best DCP yield was obtained when 5-10 mol% of NHPI (calc. on cumene) was used. The yield increased from 41% without NHPI to 48%. The best selectivity was obtained for 5 mol% of NHPI.

NHPI does not change the conversion of CHP. It can be explained by the high activity of Cu(II) salt in catalyzing decomposition of CHP.

It has been reported, that NHPI derivatives, such as *N,N'*-dihydroxypyromellitimide (NDHPI) were more active in the oxidation of *p*-xylene or nitrotoluenes with oxygen, especially at the initial stages. [16, 17] It was assumed, that because NDHPI possessed two hydroxyimide moieties in the molecule, it provided even more effective catalyst. The study revealed that catalysts consisting of NDHPI and Co(II) were also more stable than those with NHPI. In our investigation, we used NDHPI/Cu(II) system (0.5 mmol of NDHPI was applied, in order to compare results with those obtained in the presence of 1 mmol of NHPI). The application of *N,N'*-dihydroxypyromellitimide (NDHPI) led to lower DCP yield in comparison with NHPI. However, the selectivity of DCP formation was higher than in the reaction with Cu(II) chloride (41% for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 46% for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ + NDHPI) (Table 2). Such results are consistent with the data discussed by I. O. Opeida. [18]

Table 2. Effect of type of catalytic system on dicumyl peroxide yield.

	Catalyst	DCP yield [%]	CHP conversion [%]
1	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	40	98
2	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ + NHPI	46	98
3	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ + NDHPI	39	84

CHP 20 mmol, cumene 10 mmol, NHPI 1 mmol, NDHPI 0.5 mmol, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.3 mmol, MeCN 10 ml; 70°C; 3 h.

3.2. The Influence of Transition Metal Salt

Chosen salts of transition metals were tested for catalytic activity in the reaction of cumene oxidation with CHP. The catalytic system contained metal salt (0.30 mmol) and NHPI (1 mmol). Chlorides, acetates, acetylacetonates of copper(II), manganese(II), cobalt(II) and iron(III) were selected. The obtained results are shown in Table 3.

Table 3. Effect of metal salt on dicumyl peroxide synthesis in the presence of NHPI.

	Metal salt	DCP yield [%]	CHP conversion [%]
1	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	46	98
2	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	21	19
3	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	30	29
4	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	35	82
5	$\text{Mn}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$	26	52
6	$\text{Co}(\text{OAc})_2$	41	90
7	$\text{Cu}(\text{acac})_2$	37	79
8	$\text{Mn}(\text{acac})_2$	43	80
9	$\text{Co}(\text{acac})_2$	39	91
10	$\text{Fe}(\text{acac})_3$	7	8

CHP 20 mmol, cumene 10 mmol, NHPI 1 mmol, metal salt 0.30 mmol, MeCN 10 ml; 70°C; 3 h.

The results presented in Table 3 indicate, that the best yields of DCP were obtained for systems consisting of NHPI and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{OAc})_2$ or $\text{Mn}(\text{acac})_2$ (46%, 41% and 43% respectively). It can be concluded, that type of transition metal plays much more important role than type of anion in catalyst. In our experiments, high conversion of CHP was also observed. As can be calculated from yield and conversion values, the selectivity of DCP was rather low (~50%). In the post reaction mixture, besides 2-phenyl-2-propanol, other byproducts such as acetophenone (AcPh) were identified. The presence of acetophenone indicates that β -scission of 1-methyl-1-phenylethyl radical occurred. The major components (DCP, PhPr, AcPh) of post reaction mixture are presented in Table 4.

Table 4. Major components of the post-reaction mixture after catalytic oxidation of cumene with CHP.

Catalytic system	DCP	PhPr	AcPh
	[mmol]		
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	4.0	7.2	6.4
1 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ + NHPI	4.7	7.1	5.4
2 $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ + NHPI	3.5	8.4	5.2
3 $\text{Cu}(\text{acac})_2$ + NHPI	3.7	8.8	3.7
4 $\text{Mn}(\text{acac})_2$ + NHPI	4.3	6.6	3.8
5 $\text{Co}(\text{acac})_2$ + NHPI	3.9	9.0	4.2

CHP 20 mmol, cumene 10 mmol, NHPI 1 mmol, metal salt 0.30 mmol, MeCN 10 ml; 70°C; 3 h.

The results revealed, that depending on the transition metal salt, different amounts as well as alcohol: ketone molar ratio could be obtained. The anion in metal salt also matters. The highest PhPr:AcPh ratios were obtained for acetylacetonates of Cu, Mn and Co (2.4: 1; 1.7: 1; 2.1: 1 respectively, compared to 1.1:1 for copper(II) chloride).

The influence of the amount of copper chloride on the DCP yield was determined for the system NHPI/ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Table 5).

Table 5. Effect of amounts of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ on dicumyl peroxide synthesis in the presence of NHPI.

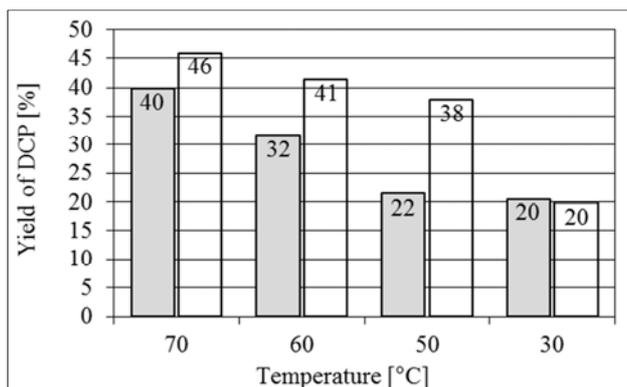
	NHPI [mmol]	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ [mmol]	Yield DCP [%]	Conversion CHP [%]
1	-	0.15	41	97
2	-	0.30	40	98
3	1	0.015	30	52
4	1	0.03	43	98
5	1	0.15	48	99
6	1	0.30	46	98

CHP 20 mmol, cumene 10 mmol, NHPI 1 mmol, MeCN – 10 ml; 70°C; 3 h.

The best DCP yields (46–48%) were obtained for 1.5 – 3.0 mol% of Cu(II) (calc. on cumene).

3.3. The Influence of Temperature

The catalytic oxidation of cumene with CHP was performed at different temperatures from the range of 30 – 70°C. Copper(II) chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was applied as a catalyst. In some experiments NHPI was also added. DCP yields obtained at different temperatures with and without NHPI were compared (Figure 4).

**Figure 4.** Effect of temperature on DCP yield CHP 20 mmol, cumene 10 mmol, NHPI 1 mmol (white), without NHPI (grey), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.30 mmol, MeCN – 10 ml, 3 h.

Conversion of CHP was ~90% in the entire studied range of temperatures. Since CHP and DCP are very thermally unstable molecules, one can assume that lowering temperature as much as possible, should significantly improve safety of the process. However, our study revealed, that at 30°C, CHP accumulated in the reaction mixture, followed by its uncontrolled decomposition and temperature increase (up to solvent boiling temperature). Because of that, further experiments were not performed below 50°C for the safety reasons. The best yields of DCP were obtained at 70°C, in the presence of NHPI. The most significant influence of NHPI on the DCP yield was observed at 50°C (22% without and 38% with NHPI).

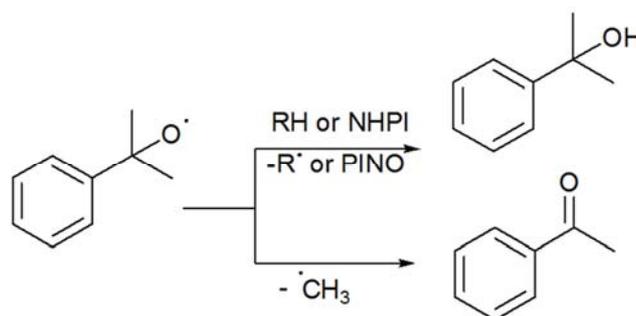
Additionally, the influence of NHPI on the content of AcPh and PhPr in post-reaction mixtures obtained at 50°C and 70°C was determined (Table 6).

Table 6. The influence of NHPI on the content of DCP, 2-phenyl-2-propanol (PhPr) and acetophenone (AcPh) in the products of cumene oxidation with CHP in the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

	Temp. [°C]	NHPI [mmol]	DCP	PhPr	AcPh
			[mmol]		
1	50	-	2.2	10.0	5.5
2	50	1	3.8	9.0	5.2
3	70	-	4.0	7.2	6.4
4	70	1	4.7	7.1	5.4

CHP 20 mmol, cumene 10 mmol, MeCN – 10 ml; 70°C; 3 h.

Data presented in Table 6 show, that the amount of AcPh increases with temperature, while PhPr:AcPh ratio decreases (from 1.7:1 to 1.3:1 at 50 and 70°C respectively). The β -scission reaction is more concurrent to the reaction of hydrogen with alkoxy radicals at higher temperatures, leading to the decrease of alcohol: ketone ratio in products. It is assumed that in the presence of NHPI alcohol can be formed in reaction of alkoxy radicals with hydrocarbon as well as with NHPI as presented in Figure 5. However slightly increase of the alcohol: ketone ratio in the presence of NHPI was observed only at 70°C.

**Figure 5.** Formation of alcohol PhPr and ketone AcPh from alkoxy radical.

The same tendency was observed for other processes in the literature. Acetophenone formation is less favourable than 2-phenyl-2-propanol, since the post reaction mixture containing alcohol can be used without separation in the second step of the dicumyl technology (Figure 1).

3.4. The Influence of Cumene: CHP Ratio

The studied reaction was performed using cumene: CHP in ratios 1: 2 and 1: 1 (Table 7). It was observed that higher yield of DCP was obtained when cumene was used in excess. It was particularly interesting, that in the presence of NHPI/Cu(II) system, 53% yield of DCP was obtained, at relatively low temperature 60°C (without NHPI the yield was only 41%). The possibility of lowering temperature of this process is very important for safety reasons.

Table 7. Effect of cumene: CHP ratio on on dicumyl peroxide synthesis in the presence of NHPI and CuCl₂·2H₂O.

	Cumene:CHP [mol/mol]	Temp. [°C]	NHPI [mmol]	DCP yield [%]	CHP conversion [%]
1	1: 2	60	-	32	91
2	1: 2	60	1	41	90
3	1: 1	60	-	46	90
3	1: 1	60	1	53	92
3	1: 2	70	-	41	97
3	1: 2	70	1	48	99
3	1: 1	70	-	54	97
4	1: 1	70	1	54	97

Cumene 10 mmol, NHPI 1 mmol, CuCl₂·2H₂O 0.30 mmol (60°C) or 0.15 mmol (70°C), MeCN 10 ml; 3 h.

3.5. Oxidation of Cumene with CHP in a Solvent-Free Medium

The solubility of NHPI in non-polar, alkyl aromatic hydrocarbons is known to be very poor. In the studied process acetonitrile was added to improve the solubility. Taking into account that polar CHP is introduced to the reaction medium and that polar products are formed, we tried to perform the reaction without any additional solvent. The DCP yield was compared with that obtained in the presence of CuCl₂ as well as CuCl₂·2H₂O/TBAB system. Additionally, experiments with more lipophilic NHPI derivative - 4-dodecyloxycarbonylo-N-hydroxyphthalimide (C12-NHPI) were performed, in order to increase solubility of catalytic system in the reaction medium (Table 8).

Table 8. Comparison of DCP yield obtained in solvent-free medium.

	Catalyst	Amount of catalyst [% mol]	DCP yield [%]	CHP conversion [%]
1	CuCl ₂ ·2H ₂ O	1.5	10	46
2	CuCl ₂ ·2H ₂ O + TBAB	1.5, 0.037	59	93
3	CuCl ₂ ·2H ₂ O + NHPI	1.5, 2.5	43	83
4	CuCl ₂ ·2H ₂ O + C12-NHPI	1.5, 2.5	36	90

CHP 60 mmol, cumene 60 mmol, 70°C; 3 h.

CHP 16 mmol, cumene 16 mmol, 70°C; 3 h.

C12-NHPI 4-dodecyloxycarbonylo-N-hydroxyphthalimide.

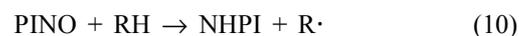
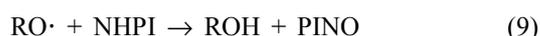
The DCP yield obtained in the presence of CuCl₂·2H₂O/NHPI in a solvent-free medium (43%) is lower than that with CuCl₂·2H₂O/TBAB catalytic system (59%). However, when CuCl₂·2H₂O/NHPI catalyst is considered, only slight decrease in DCP yield was observed in solvent-free medium (46% in the presence of MeCN and 43% without solvent). Slightly lower DCP yield (36%) was obtained when lipophilic derivative of NHPI (C12-NHPI) was applied. Such results show, that the presence of polar CHP and products in reaction mixture, allow to dissolve sufficient amount of NHPI. The influence of polar products formed in the reaction, on the increase of NHPI solubility has been observed previously by us in the reactions of oxidation of several hydrocarbons with oxygen. [14]

4. Conclusion

It has been demonstrated that catalytic system composed of NHPI and transition metal salt can be applied in cumene oxidation with hydroperoxide. Reactions were carried out in polar solvent, similarly to other NHPI-catalyzed processes, due to catalyst insolubility in non-polar media. When reactions were performed in acetonitrile as solvent the maximum yield of DCP, obtained in the presence of catalytic system composed of NHPI and CuCl₂·2H₂O was 53% at 60°C (without NHPI the yield was 46% under the same conditions). Therefore addition of NHPI allowed to perform this reaction at lower temperature. Since hydroperoxide is a very strong oxidizing agent, which may react explosively, lowering temperature of the process is one of the most important safety issues.

It has also been demonstrated, that studied process can be performed without additional of solvent. Presence of polar hydroperoxide CHP together with products formed, allowed to dissolve NHPI. When reaction was performed without solvent, DCP was obtained in yield of 43% at 70°C. We believe that process optimization can lead to further improvement.

It can be assumed, that in the presence of NHPI, the following reactions should be added to the mechanism proposed by Kharash:



where R=Ph(CH₃)₂C.

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