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Aerobic oxidation of cumene catalysed by 4-alkyloxycarbonyl-*N*-hydroxyphthalimide

Research Article

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Abstract: 4-Hexyloxycarbonyl-, 4-dodecyloxycarbonyl- and 4-hexadecyloxycarbonyl-*N*-hydroxyphthalimides were synthesised using trimellitic anhydride chloride as the starting material. The obtained lipophilic derivatives of *N*-hydroxyphthalimide were applied as catalysts of the cumene oxidation reaction with oxygen performed in polar acetonitrile, in non-polar tert-butylbenzene and in the absence of a solvent. The courses of reactions catalysed by *N*-hydroxyphthalimide and its derivatives were compared.

Keywords: *N-Hydroxyphthalimide derivatives • Cumene • Oxidation*

1. Introduction

The oxidation of cumene to hydroperoxide is an important industrial process [1]. Hydroperoxide is used for the synthesis of phenol (*via* the Hock method) and used as an oxidising agent of propylene in Sumitomo's PO-only process [2]. The Hock method can also be applied to the synthesis of other valuable hydroxyaromatic compounds from isopropylarenes.

Recently, *N*-hydroxyphthalimide (NHPI) has been shown to be an effective catalyst in many oxidation processes [3,4], including the oxidation of isopropylaromatics. In these processes, NHPI acts as a precursor of phthalimide-*N*-oxyl radical PINO, which effectively abstracts the hydrogen atom from substrate. Many methods of PINO generation have been reported including electrocatalytic, biocatalytic as well as chemocatalytic systems [4,5]. The most often used co-catalysts are transition-metal compounds. However, when NHPI, in combination with transition metal compounds, has been used in the isopropylaromatics oxidation processes, the selectivities to hydroperoxides were low and products contained mainly respective alcohols and ketones [6,7]. Therefore in order to obtain hydroperoxides with high selectivity, metal-free systems are required. In 2001, Ishii reported that cumene could be oxidised in the presence of NHPI (10 mol%) and an azo-initiator (3 mol%) to hydroperoxide with a high yield of 77% when the process was performed at 75°C for 6 h in acetonitrile (MeCN) as the solvent [8]. Several other isopropylaromatics were oxidised under the same conditions, including 1,3- and 1,4-diisopropylbenzenes [8], 2,6- and 2,7-diisopropylnaphthalenes [9], and 1,3,5-triisopropylbenzene [10]. Recently, we reported the oxidation of other mono- and diisopropylaromatics (*e.g.* 4-isopropylbiphenyl, 1-isopropyl-4-methoxybenzene, 2-isopropylnaphthalene, 2-isopropyl-6-methoxynaphthalene, and 4,4'-diisopropylbiphenyl) to hydroperoxides with a high yield (76-99%) using the NHPI/AIBN catalytic system, even at a milder temperature of 60°C, using both oxygen and air under atmospheric pressure and MeCN as the solvent [11]. The combination of NHPI and aldehyde has been reported by Melone *et al*. [5,12]. Cumene hydroperoxide was obtained with selectivity of 81% when cumene was oxidised at 25°C for 6 h using NHPI (10 mol%) and CH_3CHO (10 mol%) in MeCN as a solvent (cumene conversion 36%).

The use of NHPI as an organocatalyst in the isopropylaromatics oxidation processes has many advantages, such as higher conversion and selectivity to hydroperoxides and milder reaction conditions compared with non-catalysed and transition metal

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catalysed processes. However, due to the low solubility of NHPI in hydrocarbons, a polar solvent is necessary. It can limit the possibility of NHPI implementation for industrial application [13]. Additionally, solvents such as acetonitrile or acetic acid are hydrogen-bond acceptors and form complexes with NHPI, resulting in decreased catalytic activity [14,15].

To the best of our knowledge, cumene has been oxidised in the presence of NHPI and in the absence of solvent only by Koshel *et al.* [16]. The authors observed an increase in the reaction rate in the presence of NHPI under conditions similar to those used in industry (120°C). However, most likely due to the use of smaller amounts of NHPI and its unwanted decomposition at the high temperature of 120°C, the obtained hydroperoxide yield was lower compared with those achieved in the processes performed at lower temperature using 10 mol% of NHPI and polar solvents [8-11].

To eliminate the solvents Ishii *et al.* used in the oxidation process of cyclohexane, lipophilic derivatives of NHPI, such as 4-alkyloxycarbonyl-*N*-hydroxyphthalimides [17] and its fluorinated derivatives [18], were used as catalysts. The processes were performed at 100°C under an air pressure of 1 MPa for 14 h in the presence of Co(II) and Mn(II) salts and 0.08 mol% of the NHPI derivatives. Among 4-hexyloxycarbonyl-, 4-dodecyloxycarbonyl- and 4-tetradecyloxycarbonyl-*N*-hydroxyphthalimides, the last two showed the highest activity. The NHPI derivatives containing long, fluorinated alkyl chains as substituents were also active, but their synthesis was more complex.

The influence of the introduction of a substituent to the NHPI aromatic ring on the catalytic activity has been described previously. Wentzel *et al.* [19] and Annunziatini *et al.* [20] observed an increase in the rate of the oxidation reaction of ethylbenzene and benzyl alcohol by increasing the electron-withdrawing properties of the substituent. In contrast, Novikova *et al.* [21] and Kushch [22] observed that the rate of cumene oxidation decreased due to the introduction of an electron-withdrawing carboxyl group (4-COO-). The influence of the electron-withdrawing substituent on the increase in the BDE value of NO-H and the stabilisation of the transition state of the hydrogen abstraction reaction by the *N*-oxyl radical was discussed in previous publications [19-22].

In this study, the 4-alkyloxycarbonyl-*N*-hydroxyphthalimides were synthesised and used as catalysts of the cumene oxidation processes to hydroperoxide performed in polar and non-polar media under mild reaction conditions.

2. Experimental procedure

Cumene (Merck) was purified by extraction with concentrated sulphuric acid and distillation over sodium. Crystallisation of 2,2'-azobis(2-methylpropionitrile) (AIBN) from ethanol was performed. Pyridine was boiled with potassium hydroxide and distilled. The other starting materials were commercially available and used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO-d6) with a Varian Unity Inova-300 spectrometer. HRMS data were recorded using a Waters Xevo G2 QTof Mass Spectrometer. Melting points were determined in capillary tubes on an Electrothermal Melting Point Apparatus. 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 (150×3.9 mm; Waters) was used with a mixture of hexane and 2-propanol as the mobile phase (99:1 v/v) at a flow rate of 1.0 mL min^{-1}.

2.1. Typical procedure for cumene oxidation

The cumene oxidations were performed in a gasometric apparatus as shown in Fig. 1.

The cumene, the catalyst, AIBN and, in some cases, the solvent (*tert*-butylbenzene or acetonitrile) were placed in a 10 mL flask connected to a gas burette filled with oxygen under atmospheric pressure. The oxygen uptake was measured and used to calculate the cumene conversion (after recalculation to standard conditions of 273 K and 1 atm).

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

α – conversion, n_{O2} – mmols of oxygen consumed at normal conditions, n – mmols of hydrocarbon

The amount of cumene hydroperoxide was determined iodometrically according to the described method [23], and the result was used for calculation of selectivity.

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

S_{-OOH} – hydroperoxide selectivity, n_{-OOH} – mmols of hydroperoxide groups based on iodometric analysis, n_{O2} – mmols of oxygen consumed at normal conditions.

The amounts of 2-phenyl-2-propanol and acetophenone were determined by HPLC according to the method described in [24].

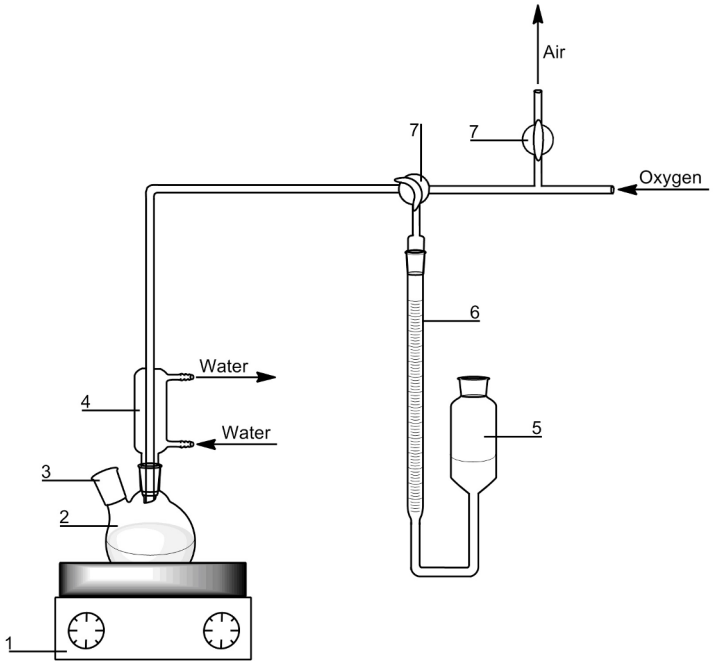


Figure 1. Gasometric apparatus: (1) magnetic stirrer (2) flask (3) rubber stopper (4) Liebig condenser (5) levelling bulb (6) gas burette (7) valve.

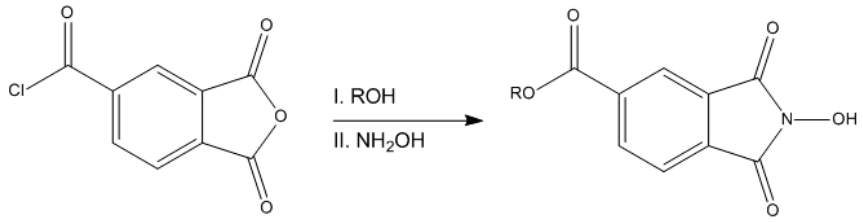
2.2. Synthesis of 4-alkyloxylcarbonyl-N-hydroxyphthalimide using trimellitic anhydride chloride

Pyridine (20 mmol, 1.5 mL) was added in a few portions to a stirred mixture of trimellitic anhydride chloride (20 mmol, 4.2 g) in toluene (10 mL) at 0ºC. Next, a solution of hexyl, dodecyl or hexadecyl alcohol (20 mmol) in toluene (10 mL) was added dropwise over 30 min. The mixture was stirred for 4 h at room temperature, then for 10 h at 85ºC and for 7 h at 100ºC. Toluene was evaporated, and product in form of white paste was obtained. Dried pyridine (25 mL) and hydroxylamine hydrochloride (22 mmol, 1.52 g) were added and the reaction mixture was stirred at 90ºC for 15 h. A portion of the pyridine (approximately 15 mL) was evaporated, and the product was poured to 10 mL of water and acidified by hydrochloric acid (11 M) to pH 1. The precipitate was filtered, and poured into water, and acidified again. The product was recrystallised twice from benzene (compound 1) or methanol (compounds 2 and 3).

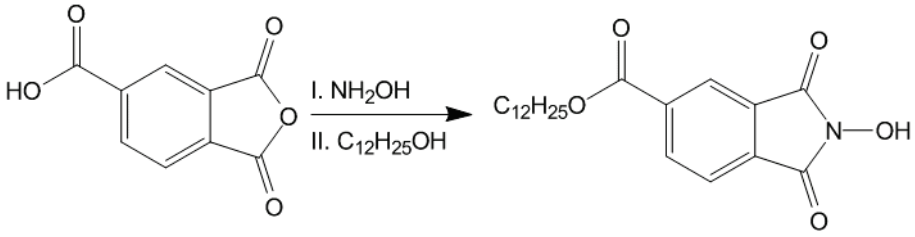
1: ^{1}H NMR (300 MHz DMSO-d6): δ 11.00 (s, 1H, N-OH), 8.33 (dd, J = 7.8, 1.4 Hz, 1H, Ar-H), 8.15 (s, 1H, Ar-H), 7.95 (dd, J = 7.8, 0.6 Hz, 1H, Ar-H), 4.31 (t, J = 6.5 Hz, 2H, CO-OCH_2-), 1.67 - 1.76 (m, 2H, OCH_2-CH_2-), 1.27 - 1.39 (m, 6H, -CH_2-), 0.85 (t, J = 3.5 Hz, 3H, -CH_3), ^{13}C NMR (75 MHz DMSO-d6): δ 175.6 (Ar-COOCH_2), 165.0 (Ar-CO-N), 163.9 (Ar-CO-N), 135.9 (Ar), 135.7 (Ar), 133.2 (Ar), 130.1 (Ar), 124.2 (Ar), 123.3 (Ar), 66.3 (COO-CH_2-), 31.6 (OCH_2-CH_2-), 28.7 (-CH_2-), 25.8 (-CH_2-), 22.7 (-CH_2CH_3), 14.6 (-CH_3); HRMS (ESI) calc. for $C_{15}H_{16}NO_5$ [M-H]$^-$ 290.1029, found 290.1021; mp 80÷82°C (benzene); 19% yield.

2: ^{1}H NMR (300 MHz DMSO-d6): δ 11.01 (s, 1H, N-OH), 8.33 (dd, J = 7.8, 1.5 Hz, 1H, Ar-H), 8.16 (s, 1H, Ar-H), 7.95 (d, J = 7.8 Hz, 1H, Ar-H), 4.31 (t, J = 6.5 Hz, 2H, CO-OCH_2-), 1.67 - 1.74 (m, 2H, OCH_2-CH_2-), 1.21 - 1.38 (m, 18H, -CH_2-), 0.83 (t, J = 6.9 Hz, 3H, -CH_3), ^{13}C NMR (75 MHz DMSO-d6): δ 164.9 (Ar-CO-N), 163.9 (Ar-CO-N), 135.9 (Ar), 135.7 (Ar), 133.2 (Ar), 130.1 (Ar), 124.2 (Ar), 123.3 (Ar), 66.3 (COO-CH2-), 32.0 (OCH2-CH2-), 29.7 (-CH2-) 29.6 (-CH2-), 29.5 (-CH2-), 29.4 (-CH2-), 28.7 (-CH2-), 26.1 (-CH2-), 22.8 (-CH2CH3), 14.6 (-CH3); HRMS (ESI) calc. for $C_{21}H_{28}NO_5$ [M-H]$^-$ 374.1968, found 374.1973; mp 102÷104.5°C (MeOH); 67% yield.

3: ^{1}H NMR (300 MHz DMSO-d6): δ 11.02 (s, 1H, N-OH), 8.35 (d, J = 7.7 Hz, 1H, Ar-H), 8.16 (s, 1H, Ar-H), 7.96 (d, J = 7.8 Hz, 1H, Ar-H), 4.31 (t, J = 6.3 Hz, 2H, CO-OCH_2-), 1.68 - 1.77 (m, 2H, OCH_2-CH_2-), 1.20 - 1.38 (m, 26H, -CH_2-), 0.83 (t, J = 6.6 Hz, 3H, -CH_3), ^{13}C NMR (75 MHz DMSO-d6): δ 164.9 (Ar-CO-N), 163.9 (Ar-CO-N), 135.9 (Ar), 133.2 (Ar), 130.1 (Ar), 124.2 (Ar), 123.3 (Ar), 66.3 (COO-CH_2-), 32.0 (OCH_2-CH_2-), 29.7 (-CH_2-) 29.4 (-CH_2-), 29.3 (-CH_2-), 28.7 (-CH_2-), 26.1 (-CH_2-), 22.8 (-CH_2CH_3), 14.6 (-CH_3); HRMS (ESI) calc. for $C_{25}H_{36}NO_5$ [M-H]$^-$ 430.2595, found 430.2619; mp 110.7÷111.2°C (MeOH); 16% yield.



Scheme 1. Preparation of 4-alkyloxycarbonyl-*N*-hydroxyphthalimides. Reagents and conditions: (I) alcohol, toluene, 4 h - rt, 10 h - 85°C, 7 h - 100°C; (II) hydroxylamine hydrochloride, pyridine, 90°C, 15 h.



Scheme 2. Preparation of 4-dodecyloxycarbonyl-*N*-hydroxyphthalimide. Reagents and conditions: (I) hydroxylamine hydrochloride, pyridine, 90°C, 15 h; (II) dodecyl alcohol, *p*-toluenesulphonic acid, hexane, 6-10 h, 70°C.

2.3. Synthesis of N-hydroxyphthalimide-4-carboxylic acid from trimellitic anhydride

Trimellitic anhydride (200 mmol, 38.4 g) and hydroxylamine hydrochloride (220 mmol, 13.9 g) were added to 250 mL of pyridine and stirred at 90°C for 15 h. The product was poured into water (400 mL), acidified with 11 M hydrochloric acid (55 mL) and maintained at 5°C for 16 h. The precipitate was filtered, poured into to 20 mL of water and acidified by 11 M hydrochloric acid (2.5 mL) again. The product was dried under vacuum. ^{1}H NMR (300 MHz DMSO-d6): δ 10.98 (s, 1H, N-OH), 8.32 (ddd, J = 7.7, 2.4, 1.5 Hz, 1H, Ar-H), 8.14 (dd, J = 1.4, 0.7 Hz, 1H, Ar-H), 7.92 (dd, J = 7.7, 0.7 Hz, 1H, Ar-H), ^{13}C NMR (75 MHz DMSO-d6): δ 166.4 (Ar-CO-N), 164.0 (Ar-CO-N), 136.9 (Ar), 136.0 (Ar), 132.9 (Ar), 129.92 (Ar), 124.0 (Ar),123.5 (Ar); mp 230-231°C; 33.1% yield.

2.4. Synthesis of 4-dodecyloxylcarbonyl-N-hydroxyphthalimide using N-hydroxyphthalimide-4-carboxylic acid

N-hydroxyphthalimide-4-carboxylic acid (10 mmol, 2.1 g), dodecyl alcohol (20 mmol, 3.72 g) and *p*-toluenesulphonic acid (1 mmol, 0.2 g) were added to 40 mL of hexane. The reaction mixture was refluxed for 10 h, and the precipitate was filtered. The product contained unreacted *N*-hydroxyphthalimide-4-carboxylic acid, as revealed by TLC analysis (using aluminium plates coated with silica gel 60 F254 (Merck) and a methanol/chloroform 3:2 v/v solvent system). The ^{1}H NMR spectra determined a negligible amount of 4-dodecyloxycarbonyl-*N*-hydroxyphthalimide.

3. Results and discussion

3.1. Synthesis of the lipophilic derivatives of NHPI

The 4-hexyloxycarbonyl- (1), 4-dodecyloxycarbonyl- (2) and 4-hexadecyloxycarbonyl-*N*-hydroxyphthalimides (3) were synthesised by a two-step method using trimellitic anhydride chloride as the starting material (Scheme 1). Compound 3 has not been synthesised before. The properties of compounds 1 and 2 that were not given in a previous paper [17] were determined.

We attempted also to synthesise 4-dodecyloxycarbonyl-*N*-hydroxyphthalimide using trimellitic anhydride as the starting material, in accordance with a previous study [17] (Scheme 2). However, this method was found to be less effective. A reaction of anhydride with hydroxylamine produced 4-carboxyl-*N*-hydroxyphthalimide; however, in the subsequent step consisting of a reaction with alcohol, a mixture of unreacted acid and a small amount of ester was obtained.

Table 1. Oxidation of cumene with NHPI derivatives in polar and non-polar solvents.

N°	Catalyst	Conversion [%]	Selectivity[a] [%]	Solvent
1.	Non	5	100	MeCN
2.	NHPI	50	100	MeCN
3.	**1**	49	100	MeCN
4.	**2**	40	100	MeCN
5.	**3**	40	100	MeCN
6.	Non	2	100	*t*-BuPh
7.	NHPI	11	100	*t*-BuPh
8.	**1**	30	100	*t*-BuPh
9.	**2**	32	100	*t*-BuPh
10.	**3**	35	100	*t*-BuPh

60°C; 1 atm.; 1000 rpm; 6 h. Cumene (0.7 mL, 5 mmol); catalyst (5 mol%); AIBN (0.025 g); solvent (5 mL).
[a] Calculated based on oxygen consumption and iodometric analysis.

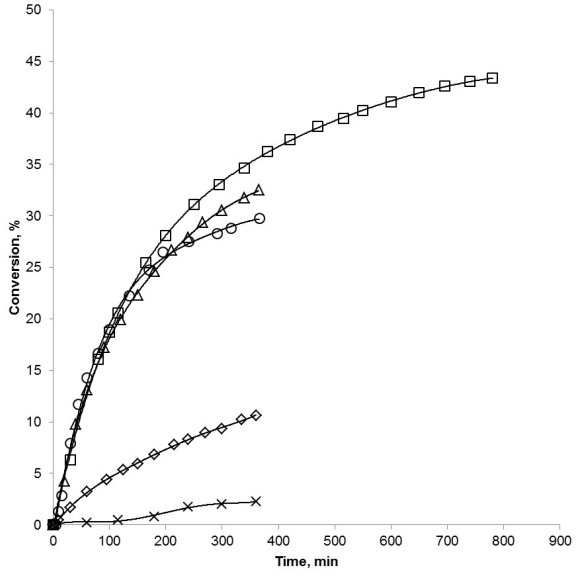


Figure 2. Oxidation of cumene with NHPI derivatives in a non-polar solvent. (□) 5.0 mol% C16-NHPI; (△) 5.0 mol% C12-NHPI; (○) 5.0 mol% C6-NHPI; (◇) 5.0 mol% NHPI; (×) 0.0 mol% NHPI

3.2. Catalytic cumene oxidation in polar and non-polar solvents

The lipophilic NHPI derivatives 1-3 in an amount of 5 mol% were used as catalysts in the cumene oxidation processes performed both in polar acetonitrile and in non-polar *tert*-butylbenzene as solvents under mild reaction conditions (60°C, 0.1 MPa). It has been reported previously [11] that hydroperoxide and NHPI were stable at these conditions. The processes were compared with those catalysed by NHPI (Table 1).

Catalysts 1-3 were soluble in the reaction mixture within 10-15 min of the reaction time when both MeCN and *tert*-butylbenzene were used. In contrast, a large portion of NHPI remained insoluble in the reaction using *tert*-butylbenzene, and, therefore, a lower conversion of cumene was obtained (entry 7). The comparison of the processes catalysed by 1-3 performed in *tert*-butylbenzene and MeCN showed that the oxidation reaction rates were lower in the non-polar conditions. To obtain a higher conversion of cumene in a non-polar solvent (48%), the process using catalyst 3 was performed for 13 h (Fig. 2).

The cumene conversion slightly decreased with the length of the alkyl group in the processes performed in MeCN and increased in those performed in *tert*-butylbenzene. This result suggests that the observed effects resulted from the small differences in the catalyst solubility in the mixture.

3.3. Catalytic cumene oxidation in the absence of a solvent

The cumene oxidation processes in the presence of compounds 1-3 were also performed in the absence of a solvent. The influence of the catalyst amount on the course of the oxidation reaction was studied using the most lipophilic derivative, catalyst 3.

The results presented in Fig. 3 demonstrated that the highest reaction rate was obtained when 1 mol% of compound 3 was used. When higher amounts of catalyst were applied, a portion of the catalyst remained insoluble in the mixture and negatively influenced the process.

Therefore, the processes using 1 mol% of compounds 1-3 and NHPI as catalysts were compared (Table 2, Fig. 4).

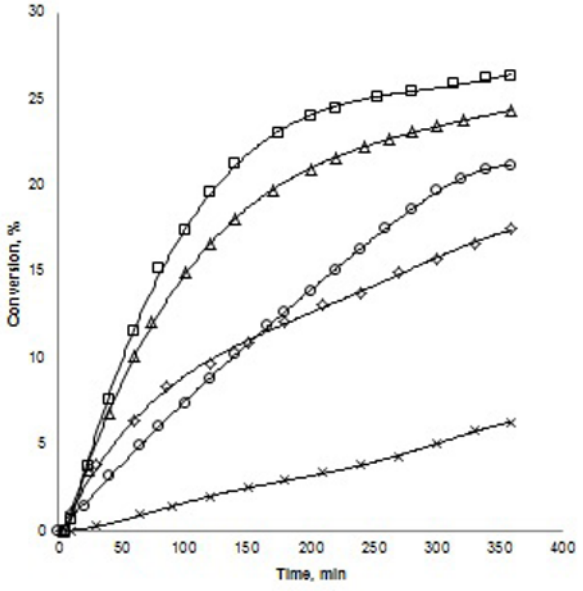


Figure 3. Oxidation of cumene with different amounts of C16-NHPI in the absence of solvent. (◇) 0.1 mol%; (△) 0.5 mol%; (□) 1.0 mol%; (○) 2.0 mol%; (×) 2.5 mol%.

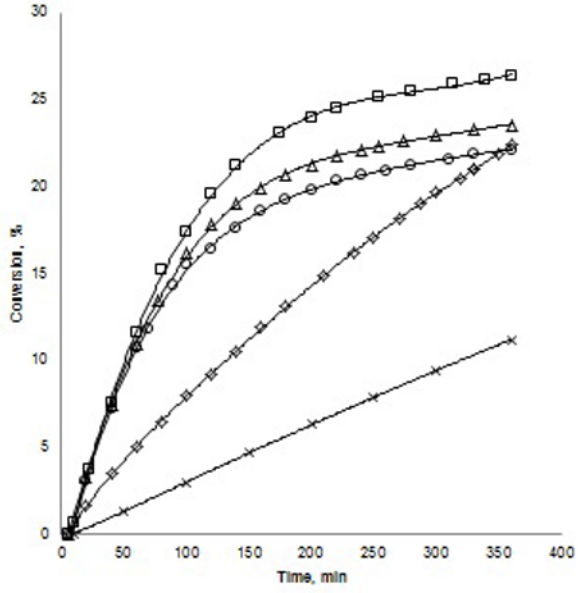


Figure 4. Oxidation of cumene with NHPI derivatives in the absence of a solvent. (□) 1.0 mol% C16-NHPI; (△) 1.0 mol% C12-NHPI; (○) 1.0 mol% C6-NHPI; (◇) 1.0 mol% NHPI; (×) 0.0 mol% NHPI.

Table 2. Oxidation of cumene with NHPI derivatives in the absence of a solvent.

N°	Catalyst	Conversion [%]	Selectivity[a] [%]
1.	Non	11	100
2.	NHPI	22	100
3.	**1**	22	100
4.	**2**	23	100[b]
5.	**3**	26	100[c]

60°C; 1 atm.; 1000 rpm; 6 h. Cumene (2.0 mL, 14.3 mmol); catalyst (1 mol%); AIBN (0.025 g).
[a] *Calculated based on oxygen consumption and iodometric analysis.*
[b] *The HPLC analysis demonstrated that the selectivity to hydroperoxide was slightly lower. The presence of 2-phenyl-2-propanol in the mixture was observed (acetophenone was not detected); the selectivity to 2-phenyl-2-propanol calculated based on HPLC was 2.1%.*
[c] *The HPLC analysis demonstrated that the selectivity to hydroperoxide was slightly lower. The presence of 2-phenyl-2-propanol in the mixture was observed (acetophenone was not detected); the selectivity to 2-phenyl-2-propanol calculated based on HPLC was 1.8%.*

Similar to the processes performed in non-polar *tert*-butylbenzene, the highest conversion was obtained using the most lipophilic derivative, compound 3, as the catalyst. The slight increase in the conversion with increasing alkyl chain length was also observed. This result is in accordance with the results reported by Ishii et al. for cyclohexane oxidation [17].

The courses of the reactions catalysed by compounds 1-3 and NHPI differed significantly. The rates of the oxidation reactions using compounds 1-3 were initially significantly higher than those using NHPI because of their higher solubility in the studied system. However, the rates changed after approximately 2 h of reaction. The observed decrease in the reaction rates in the processes using compounds 1-3 could be a result of inhibitor formation and/or catalyst decomposition. However, further studies are needed to explain this phenomenon. It is known that *N*-oxyl radicals can be unstable at higher temperature and decompose to inactive compounds. For example, Ishii et al. have reported that a portion of the lipophilic derivatives of NHPI was changed to the corresponding phthalimide in the studied cyclohexane oxidation at 100°C under a pressure of 1 MPa. On the other hand, we demonstrated previously [11] that NHPI was stable under mild conditions (60°C, 0.1 MPa), which were applied in present studies. The cumene oxidation is typically autoinhibited by the phenol that is formed in the acid catalysed rearrangement reaction of hydroperoxide [25]. The high selectivity to hydroperoxide that was found in this study implied that autoinhibition did not occur. However, even traces of phenol can retard the free radical processes.

Valuable results were also obtained using NHPI as the catalyst in the absence of a solvent. At the beginning of the reaction, a portion of the NHPI remained insoluble in the mixture, but its solubility steadily increased with the progress of the reaction (the mixture became transparent after approximately 110 minutes). The increase in solubility was a result of the hydroperoxide

formation that caused an increase in the polarity of the reaction mixture. This result was confirmed by the comparison of the solubility of NHPI in cumene and its solubility in a solution of cumene hydroperoxide (10 weight %) and cumene. At 60°C, the NHPI solubility was 0.03 and 0.055 g cm^{-3} in cumene and in the hydroperoxide solution, respectively.

4. Conclusions

The derivatives of NHPI, 4-hexyloxycarbonyl-, 4-dodecyloxycarbonyl- and 4-hexadecyloxycarbonyl-*N*-hydroxyphthalimides, were synthesised using trimellitic anhydride chloride as starting material. The synthesis was more effective compared with the described previously method using trimellitic anhydride as a substrate [17].

The lipophilic derivatives 1-3 showed catalytic activity in the cumene oxidation processes performed in polar (MeCN) and non-polar (*tert*-butylbenzene) solvents as well as in the absence of solvents. Their catalytic activity in MeCN was comparable to NHPI. However, the rates of cumene oxidation reactions performed in *tert*-butylbenzene were higher in the presence of catalysts 1-3 than NHPI because their higher solubility in non-polar media (*e.g.* the cumene conversion of 11 and 35% were achieve using NHPI and compound 3 as catalyst, respectively; 60°C, 6 h).

Valuable results were obtained in the processes performed in the absence of a solvent. As expected, the rates of oxidation reactions using compounds 1-3 were initially significantly higher than those using NHPI because of their higher solubility in the studied system. However, the solubility of NHPI in the system steadily increased as a result of polarity increase caused by hydroperoxide formation. Therefore, the conversions obtained after 6 h of oxidation reaction catalysed by NHPI and lipophilic derivatives were similar.

Acknowledgements

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