# An Improved Catalytic Performance of Fe(III)-promoted NHPI in the Oxidation of Hydrocarbons to Hydroperoxides

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#### Abstract

N-hydroxyphthalimide (NHPI) is a promising catalyst in aerobic oxidation of hydrocarbons to corresponding hydroperoxides. We have found that a trace amount of  $Fe(benz)_3$  or  $Fe(acac)_3$  (in concentration of less than  $10^{-1}$  mmol/l and with the ratio of Fe(III): NHPI = 1:500) considerably accelerates the oxidation of cyclohexene and ethylbenzene, while retaining the selectivity to hydroperoxides at a level of 90%. As a consequence, the reaction temperature could be lowered down to 50–60 °C. The promoting effect of the additives was attributed to the ability of Fe(III) complexes to generate phthalimido-N-oxyl radicals (PINO) without participation in any transformations of hydrocarbon intermediates and hydroperoxides, thus ensuring selective formation and stability of the hydroperoxides.

#### **Graphic Abstract**



Keywords Oxidation · Cyclohexene · Ethylbenzene · N-hydroxyphthalimide · Iron(III) salt · Hydroperoxide

# **1** Introduction

The catalytic action of N-hydroxyphthalimide (NHPI) in aerobic oxidation of organic compounds has been extensively studied for several decades [1–4]. Catalysis is based on the high reactivity of the phthalimido-N-oxyl (PINO) radical, which is initially induced from NHPI and acts as an acceptor of a hydrogen atom from a hydrocarbon substrate to form alkyl and then alkyl peroxy radicals. The interaction of the latter with NHPI restores PINO, thereby completing the catalytic cycle. NHPI is often used together with various red-ox promoters that initiate formation of PINO. Apart from hydroperoxides, these can be Co(II) salts often used by Ishii [5, 6], as well as Cu, Fe, Mn, Ni and other metal ions

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of variable valence [7–18]. Some organic compounds, such as azo compounds, quinones, aldehydes [19–26] are also capable of being the radical initiators for NHPI, and have been used in oxidation of cyclic olefins [7, 12, 18, 20, 23], ethylbenzene [6, 17–20], cumene [17, 23]. The oxidation of alkanes, arylalkanes and alkenes leads to hydroperoxides as primary products, but most of the promoters cause decomposition of hydroperoxides to non-radical products. Therefore, the oxidation of hydrocarbons catalyzed by NHPI and promoters is usually purposed on producing stable oxygenates, such as alcohols, carbonyl and carboxyl compounds, but not hydroperoxides.

However, the hydroperoxides are very important reagents in organic synthesis, in particular, in production of epoxides. They are usually synthesized by hydrocarbon oxidation at elevated temperature in the absence of catalyst. Being inactive in decomposition of hydroperoxides, NHPI is applicable to synthesis of hydroperoxides in the absence of other



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radical reagents, as was first shown by Sheldon et al. [5]. High levels were achieved for the conversion in the presence of NHPI at a lower temperature (115 °C, instead of 130 °C in non-catalyzed auto-oxidation) [26]. A combination of NHPI and some organic promoters made it possible to obtain cyclohexylbenzene hydroperoxide at 95 °C [24], and isopropylarene hydroperoxides at 60 °C [25]. NHPIcatalyzed oxidation of cyclohexene occurred at 60 °C when initiated by small amount of cyclohexenyl hydroperoxide [27], and at 35 °C under photo irradiation in the presence of organic electron carriers [28]. These examples of lowtemperature oxidation stimulated us to search for a chemical promoter which would enhance catalytic action of NHPI and would be inert in decomposition of hydroperoxides. We have recently compared several transition-metal compounds in catalytic decomposition of hydroperoxides, and observed that Fe(III) benzoate is almost inert in this reaction [29]. We have now studied Fe(III) salts as possible promoters for NHPI catalyzed synthesis of hydroperoxides.

## 2 Experimental

## 2.1 Chemicals

N-hydroxiphtalimide, acetonitrile, iron(III) acetylacetonate, cobalt(II) acetylacetonate (Sigma-Aldrich), iron(III) benzoate (Reakhim) and ethylbenzene 99.8% (Acros) were used without additional purification. Cyclohexene (Aldrich) was distilled and kept cold in a tightly closed bottle.

#### 2.2 Catalytic Experiments

Oxidation of cyclohexene and ethylbenzene was carried out in a glass reactor of 28 ml internal volume supplied with water heating jacket, magnetic stirrer and two Teflon valves for gas purging, and connected to a gas burette for monitoring the gas consumption. The reactor was charged with weighted portions of hydrocarbon substrate, NHPI and Fe(benz)<sub>3</sub> or Fe(acac)<sub>3</sub> in acetonitrile solvent. Total volume of solution was 2.5 ml. The reactor and gas burette was gently purged with O<sub>2</sub> under atmospheric conditions. Heating and intensive agitation of the liquid were started simultaneously. When the reaction temperature was stabilized (1 min), monitoring of the oxygen consumption was started. After the oxidation was quenched, the reactor was rapidly cooled to~15 °C, 7.5 ml of CH<sub>3</sub>CN was introduced into reactor, and the resulting solution was sampled for analysis.

#### 2.3 Analysis

(5 ml) and 0.5 g KI was mixed with 1 ml of analyte (diluted with 7.5 ml of  $CH_3CN$  reaction solution) and allowed to stay for 30 min under argon at 60 °C. Then, 50 ml of water was added and the mixture was titrated with 0.02 N sodium thiosulfate.

Oxidation products were identified by GCMS using an Agilent 7000 triple quadrupole GC/MS system (Agilent, USA) with a WAX20 M 10 m×0.25 mm×0.25 µm column. Quantitative GC analysis was carried out using an Agilent 7890B chromatograph (Agilent, USA) with a SOLGEL-WAX 30 m×0.25 mm×1 µm column. Composition of the reaction solution was calculated using calibration curves and chlorobenzene as internal standard. The analysis was made after addition of  $Ph_3P$  to reduce cyclohexenyl or ethylbenzene hydroperoxides to corresponding alcohols.

Conversion of the substrates and selectivity to hydroperoxides was calculated according to following equations.

$$Conversion = \frac{Hydrocarbon_{init} - Hydrocarbon_{fin}}{Hydrocarbon_{init}} \cdot 100\%$$

Selectivity = 
$$\frac{\text{Hydroperoxide}}{\text{Hydrocarbon}_{\text{init}} - \text{Hydrocarbon}_{\text{fin}}} \cdot 100\%$$

where hydroperoxides were determined by iodometry  $(HP_J)$  or by GC (detected as 2-cyclohexen-1-ol or 1-phenylethanol).

Amount of NHPI after reaction was determined by HPLC using Hewlett Packard Model 1100 instrument supplied with  $250 \times 4$  mm column packed with Hypersil BDS 5 µm silica from Hewlett Packard, and UV detector. Chromatograms of the products were recorded at  $\lambda$  300 nm.

The UV–Vis spectra of solutions were recorded on a UV-2501 PC spectrometer (Shimadzu, Japan) at a room temperature using a quartz cuvette with 2 mm optical layer.

## **3** Results and Discussion

#### 3.1 Oxidation of Cyclohexene

Oxidation of cyclohexene (CH) in the presence of NHPI-Fe(III) was carried out under various temperatures and amounts of iron salt (Table 1). Cyclohexene was oxidized mainly to cyclohexenyl hydroperoxide (CHHP). The amount of CHHP determined by iodometric titration (HP<sub>J</sub>) was slightly higher than GC-determined 2-cyclohexen-1-ol (C-ol) in case of Fe(benz)<sub>3</sub> and slightly lower in case of Fe(acac)<sub>3</sub>. Such a difference is obviously caused by peroxygenation of CHHP at the second allylic position [27] and its slow decomposition to C-ol. Therefore, it is reasonable to assume that the amount of CHHP is equal to the amount of C-ol when using Fe(benz)<sub>3</sub> and to the amount of HP<sub>J</sub> in Table 1Oxidation ofcyclohexene in solutionof NHPI and Fe(benz)<sub>3</sub> orFe(acac)<sub>3</sub>

#	T ⁰C	Fe(III) salt, µmol	Conv. of CH, %	HP <sub>J</sub> , mmol	C-ol, <sup>a</sup> mmol	C-on, mmol	Sel. to CHHP, %	NHPI <sub>fin</sub> , μmol
1	60	Absent <sup>b</sup>	28	1.16	1.16	0.13	88	140
2	60	2.9 Fe(benz) <sub>3</sub>	32	1.38	1.33	0.16	88	96
3	60	2.9 $Fe(acac)_3$	33	1.32	1.33	0.12	86	144
4	60	$0.36 \text{ Fe}(\text{acac})_3$	30	1.27	1.31	0.10	93	127
5	50	0.36 Fe(benz) <sub>3</sub>	22	1.02	0.97	0.05	94	125
6	50	0.72 Fe(benz) <sub>3</sub>	22	0.98	0.95	0.05	92	105
7	50	2.9 Fe(benz) <sub>3</sub>	26	1.15	1.11	0.06	91	116
8	50	5.8 Fe(benz) <sub>3</sub>	20	0.95	0.89	0.04	91	134
9	40	2.9 Fe(benz) <sub>3</sub>	12	0.59	0.56	0.01	98	154

Cyclohexene 4.7 mmol, NHPI 180 µmol, CH<sub>3</sub>CN 2 ml, O<sub>2</sub>, 4 h, or 8 h in #1

<sup>a</sup>C-ol determined by GC after treatment with Ph<sub>3</sub>P

<sup>b</sup>CHHP was added as initiator



**Fig. 1** Volume of  $O_2$  consumed as a function of time in oxidation of cyclohexene in the presence of NHPI and initiated with CHHP (50 µmol) (1), Fe(benz)<sub>3</sub> (2), Fe(acac)<sub>3</sub> (3) and Co(acac)<sub>2</sub> (4). Conditions: NHPI 30 mg (180 µmol), metal salts 0.36 µmol, cyclohexene 4.7 mmol, CH<sub>3</sub>CN 2 ml, 60 °C

case of  $Fe(acac)_3$ . Besides, 2-cyclohexen-1-one (C-on) and epoxycyclohexane were also detected, but in very small amounts (<0.01 mmol). This indicates that the secondary transformations of CHHP are insignificant during the oxidation of cyclohexene in the presence of NHPI-Fe(III).

The addition of Fe(III) salts enhanced catalytic action of NHPI (Fig. 1). In contrast to cyclohexenyl hydroperoxide initiator, Fe(benz)<sub>3</sub> and Fe(acac)<sub>3</sub> accelerated the oxidation not only in the initial period, but during the entire reaction time. As a result, the time required for achievement of the same conversion of cyclohexene was halved in the presence of iron (#1 and #2–4, Table 1). Importantly, the selectivity to CHHP at cyclohexene conversion of 30% was about 90%, both in the absence and in the presence of iron. When

the temperature was lowered to 50 °C, the conversion for 4 h decreased to ~ 20% (#5–8 in Table 1), and was further decreased upon lowering the temperature. Nevertheless, the oxidation still proceeded with an acceptable rate and high selectivity at 40 °C in the presence of Fe(III) (# 6), whereas without iron salt the reaction did not take place at this temperature. No changes in the formation of CHHP and selectivity were detected when the amount of  $Fe(acac)_3$ and Fe(benz)<sub>3</sub> was varied (see experiments #3-4 and 5-8 in Table 1). HPLC analysis of the reaction solutions showed that partial degradation of NHPI occurs during the oxidation (Table 1). As established previously [27], the degradation of NHPI during oxidation of cyclohexene was caused by addition of PINO to the double bond. Most likely, the same process was responsible for the degradation of NHPI in the currently used conditions. Fe(III) accelerated the oxidation of cyclohexene and produced slightly greater degradation of NHPI because of an increase in concentration of PINO during reaction. Carrying out the reaction at a lower temperature simultaneously reduced the formation of CHHP and the degradation of the NHPI catalyst (#9 in Table 1).

#### 3.2 Oxidation of Ethylbenzene

Ethylbenzene (EB) is usually less reactive than cyclohexene in non-catalytic auto-oxidation. At a temperature of 60 °C, no reaction occurred under the action of either Fe(III) salt (#1 in Table 2) or NHPI (#2 in Table 2), but ethylbenzene was readily oxidized if both components were presented (Table 2, #3–6). Moreover, micro amount of Fe(benz)<sub>3</sub> was enough in the latter case. The oxidation produced mainly ethylbenzene hydroperoxide (EBHP) that was determined by iodometric titration of  $O_2^{2-}$ . Selectivity of conversion of ethylbenzene to EBHP was within 90–94%. The products determined by GC after treating the reaction solution with Ph<sub>3</sub>P were phenylethanone (P-on) and 1-phenylethanol

**Table 2**Oxidation ofethylbenzene in solution ofNHPI and Fe(benz)3

#	Fe(benz) <sub>3</sub> , µmol	Conv. of EB, %	EBHP <sub>J</sub> , mmol	P-ol, mmol <sup>a</sup>	A-on, mmol <sup>a</sup>	Sel.to EBHP %	NHPI <sub>fin</sub> , μmol
1	2	~0	0	0	0	-	0
2	No	~0	0	0	0	_	180
3	0.18	7.2	0.27	0.29	0.006	91	180
4	0.36	7.6	0.29	0.30	0.010	94	180
5	1.45	8.5	0.30	0.34	0.010	92	177
6	2.90	7.3	0.27	0.29	0.011	90	180

Ethylbenzene 4.1 mmol, NHPI 180 µmol (0 in #1), CH<sub>3</sub>CN 2 ml, O<sub>2</sub>, 60 °C, 3 h

<sup>a</sup>Data of GC after treating the solution with  $Ph_3P$ 

(P-ol). A part of P-ol determined by GC was produced during the oxidation, and another part appeared from reduction of the hydroperoxide. Therefore, total amount of the byproducts calculated as P-on plus difference between P-ol and EBHP<sub>1</sub> was within 5–10%. Unlike our results, Miao et al. reported on oxidation of ethylbenzene in the presence of NHPI and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (both at 5 mol.%) to obtain acetophenone, which was presumably explained by conversion of the hydroperoxide and alcohol under the action of nitrogen dioxide [30]. Such transformations do not occur in our experiments in the absence of redox active components other than iron. No correlation was found between the conversion of ethylbenzene achieved in a fixed reaction time and the amount of Fe(benz)<sub>3</sub>. The same phenomenon was observed in the oxidation of cyclohexene, which indicates a similar mechanism of promoting the NHPI catalyst with Fe(III) salts in the oxidation of both substrates. After the oxidation of ethylbenzene, the amount of NHPI in solution remained at the initial level, which indicates that the presence of Fe(III) does not violate stability of the NHPI catalyst.

Alkylbenzene hydroperoxides, including EBHP, are widely used in the synthesis of epoxides. The peroxides are usually obtained by high-temperature (over 100 °C) oxidation of alkylbenzenes in the absence of any solvents and catalysts. In our experiments, we had to mix ethylbenzene with acetonitrile to ensure reasonable solubility of NHPI. At the same time, it was interesting to determine capability of the NHPI-Fe(III) catalytic system at minimal dilution of ethylbenzene with acetonitrile. In the following experiments, the fraction of ethylbenzene in the reaction mixture was gradually increased. As one can see in Fig. 2, the increase of the volume fraction of ethylbenzene from 0.2 to 0.8 increased production of EBHP, while the selectivity to EBHP remained at a level of 90-93% regardless of the ethylbenzene fraction, and the solution remained homogeneous. Further increase of the volume fraction of ethylbenzene in the reaction solution led to incomplete dissolution of NHPI and corresponding lowering the EBHP yield. The solubility of NHPI was negligible in a neat ethylbenzene and, therefore, the oxidation required elevation of the temperature. After the oxidation at



**Fig. 2** Production of EBHP and selectivity to EBHP in dependence on volume part of ethylbenzene in the mixture with CH<sub>3</sub>CN. Conditions: NHPI 144  $\mu$ mol, Fe(acac)<sub>3</sub> 0.36  $\mu$ mol, 2.5 ml of solution, 5 h, 60 °C or 80 °C at EB volume part of 1

80 °C in the absence of acetonitrile, substantial part of the catalyst was found in the solid state, whereas Fe(III) salt was completely soluble both in the presence of acetonitrile and in the neat ethylbenzene. When determined 5 h after starting the reaction at 80 °C, the selectivity to EBHP was 89%, and resulting solution contained 2.8% of EBHP. Thus, the combination of NHPI-Fe(III) ensures the oxidation of concentrated solutions of ethylbenzene and even neat ethylbenzene at rather low temperatures.

## 3.3 Details of the Mechanism of Peroxidation Catalyzed by the NHPI-Fe(III)

As shown above, the NHPI-Fe(III) catalytic system with a molar ratio of NHPI:Fe(III) = 500:1 exhibited activity in oxidation of cyclohexene and ethylbenzene at the temperature above 40 and 60 °C, respectively. Based on the mechanism of catalysis by NHPI [5], the promoting effect of Fe(III) salts is probably caused by low-temperature generation of reactive PINO radicals. Analysis of UV–Vis spectra gave an idea of how this can occur in the reaction solution.

Figure 3 shows change in the spectrum of an acetonitrile solution of  $Fe(acac)_3$  and  $Fe(benz)_3$  upon the addition of NHPI. The presence of NHPI, which had no intrinsic absorption in the visible region, changed the color of the  $Fe(acac)_3$  solution to intensively orange (spectrum1, Fig. 3a), and this is reflected in the appearance of the intensive absorption band with a maximum at ~ 22,000 cm<sup>-1</sup>. Similar change in the spectrum was observed in the case of Fe(benz)<sub>3</sub> (spectrum 1 in Fig. 3b), and it was not and Fe(III) salts (Fig. 3c, d). The observed intense charge transfer bands were apparently due to the formation of Fe(III) complex with anionic form of N-hydroxyphthalimide [31] that was in equilibrium with Fe(II) complex with PINO. During the reaction with cyclohexene, a decrease in the intensity of the visible absorption occurred (spectra 2 and 3 in Fig. 3a, b), which could be associated with the reduction of a part of Fe(III) to Fe(II), as shown by the following equations.

$$[Fe^{3+}(benz)_{3}] + NHPI \longrightarrow [Fe^{3+}(benz)_{2}(>NO^{-})] \longrightarrow [Fe^{2+}(benz)_{2}(PINO)] \longrightarrow PINC - [Fe^{2+}(benz)_{2}(PINO)] \longrightarrow PINC - [Fe^{2+}(benz)_{2}(PINO)] \longrightarrow PINC - [Fe^{2+}(benz)_{2}(PINO)] - [Fe^{2+}(benz)_{2}(PINO)] \longrightarrow PINC - [Fe^{2+}(benz)_{2}(PINO)] \longrightarrow PIN$$

dependent on whether the solution contacted or not with  $O_2$  (spectrum 1 and 2 in Fig. 3b). The intensity of the absorption band increased with concentration of NHPI

The generation of PINO due to the reduction of Fe(III) compounds has been documented in [32, 33], and in our case the process can be represented as shown in upper part



**Fig.3** UV-Vis spectra of solutions of NHPI (180 µmol), and Fe(acac)<sub>3</sub> (0.36 µmol) (**a**) or Fe(benz)<sub>3</sub> (0.36 µmol) (**b**) before and after the reaction with cyclohexene ( $C_6H_{10}$  4.7 mmol, 60 °C). Optical

density versus NHPI (2.9  $\mu$ mol Fe(benz)<sub>3</sub>) (c) and versus Fe(benz)<sub>3</sub> (180  $\mu$ mol NHPI) (d). Solvent CH<sub>3</sub>CN 2 ml



Scheme 1 Plausible scheme of the oxidation of hydrocarbon to hydroperoxide in the presence of NHPI-Fe(III) catalyst

of Scheme 1. The reverse transformation of Fe(II) to Fe(III) complexes was possible due to oxidation with ethylbenzene peroxy radicals.

The specificity of the NHPI-Fe(III) catalyst is a lack of influence of the concentration of Fe(III) on selectivity to cyclohexenyl and ethylbenzene hydroperoxides and on degradation of NHPI. CHHP and EBHP were formed with high selectivity in the catalytic cycle (middle part of Scheme 1). The appearance of ketone and alcohol by-products results from the decomposition of hydroperoxides which accompanied the hydrocarbon oxidation. The formation of the by-products in the oxidation of ethylbenzene and even of the most reactive cyclohexene in the NHPI-Fe(III) system (Tables 1 and 2) remains as low as in the NHPI-catalyzed oxidation. This indicates that, while generating the active form of the catalyst, iron complex does not participate in transformation of the substrates and does not decompose the hydroperoxides. This behavior distinguishes iron salts from typical radical initiators, for instance, Co(II). The NHPI-Co(acac)<sub>2</sub> catalyst has been used in the oxidation of cyclohexane and the process was usually accompanied by the decomposition of hydroperoxides to various stable oxygenates [6].

We have compared Co(II) and Fe(III) acetylacetonates in the NHPI catalyzed oxidation of cyclohexene.  $Co(acac)_2$ induced not only rapid oxidation of cyclohexene (Fig. 1), but also conversion of CHHP to C-ol and C-on. As a result, determined at equal conversions of cyclohexene, the selectivity for CHHP was significantly lower in the presence



Fig.4 Effect of Fe(acac)\_3 and Co(acac)\_2 on production of CHHP. Conditions: cyclohexene 4.7 mmol, NHPI 180  $\mu mol,$  CH\_3CN 2 ml, 60 °C

of Co(II) than with Fe(III) acetylacetonates (Fig. 4). The behavior of Co(acac)<sub>2</sub> is associated with the formation of complexes with molecular oxygen, which facilitate Co(II) to Co(III) transformation and the generation of PINO, as well as with participation of the Co(II)/Co(III) ions in chain termination and decomposition of hydroperoxide [1, 2]. This resulted in a high rate of the oxidation and low yield of CHHP in our reaction conditions. On the contrary, iron salts showed optimal redox properties in our experiments which permitted generation of PINO, but prevented activity of Fe(II)/Fe(III) ions in the decomposition of the hydroperoxide.



**Fig. 5** Production of hydroperoxides in dependence on amount of NHPI. Conditions: cyclohexene 4.7 mmol, Fe(benz)<sub>3</sub> 2.9  $\mu$ mol, 4 h (CHHP); ethylbenzene 12.2 mmol, Fe(acac)<sub>3</sub> 0.36  $\mu$ mol, 5 h (EBHP). Volume of the CH<sub>3</sub>CN solution was 2.5 ml, 60 °C

Production of CHHP and EBHP generally increased with an increase in concentration of the NHPI catalyst, but kinetics changed in dependence on conditions and hydrocarbon nature, as shown in Fig. 5. In particular, the rate of formation of EBHP was below first order with respect to NHPI at a large fraction of ethylbenzene in the reaction solution. This indicates that more or less intensive non-catalyzed auto-oxidation accompanied the NHPI catalyzed oxidation (lower part in Scheme 1). The auto-oxidation route must be especially important for oxidation of ethylbenzene without solvent as far as concentration of NHPI was very small at the beginning of the oxidation. Accumulated with time EBHP raised the solubility of NHPI, so that the NHPI catalyzed route became predominant over auto-oxidation in the formation of the hydroperoxide. As a result, the selectivity to EBHP determined after 5 h oxidation was rather high (Fig. 2). This indicates that EBHP remains stable in the presence of Fe(III) salt even if the NHPI catalyzed reaction was accompanied by chain auto-oxidation.

# **4** Conclusion

Fe(III) salts manifest themselves as an effective promoter in the NHPI-catalyzed peroxidation of hydrocarbons, and NHPI in combination with  $Fe(acac)_3$  or  $Fe(benz)_3$  allows the oxidation of cyclohexene and ethylbenzene to corresponding hydroperoxides to be successfully performed at a lower temperature. Moreover, unlike most of existing auto-oxidation initiators, Fe(III) salts do not worsen the selectivity to peroxide. Such an efficacy is probably connected with the ability of Fe(III) to generate PINO from NHPI but to be inert to the hydroperoxide products.

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