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Low-temperature oxidation of isopropylbenzene mediated by the system of NHPI, $Fe(acac)_3$ and 1,10-phenanthroline



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Keywords:	Highly efficient oxidation of isopropylbenzene mediated by the system of NHPI/Fe(acac) ₃ /Phen has been carried
Oxidation	out at temperature as low as 60 °C. Significant improvement of catalysis by NHPI was associated with an
Isopropylbenzene	enhanced oxidizing ability of Fe(III) tandem with Phen, which caused the intense generation of PINO.
N-Hydroxyphthalimide	Furthermore, NMR observations revealed formation of a hydrogen-bonded NHPI-Phen adduct soluble in aceto-
Iron(III) acetylacetonate	nitrile and isopropylbenzene. Based on this phenomenon, the system was applicable for the oxidation of solvent-
1,10-Phenantroline	free isopropylbenzene. The promise of the system of NHPI/Fe(acac) ₃ /Phen for the selective synthesis of iso-
Isopropylbenzene hydroperoxide	propylbenzene hydroperoxide was demonstrated by oxidation at a low content of Fe(acac) ₃ .

1. Introduction

Liquid-phase aerobic oxidation of hydrocarbons affords industrially important chemicals such as terephthalic acid, cyclohexanone, tert-butyl and alkylbenzene hydroperoxides [1,2]. Oxidation occurs by a radical chain mechanism mediated by catalysts and initiators [3]. Recently, cyclic imides have attracted much attention as promising new catalysts. Optimal catalysis is manifested by N-hydroxyphthalimide (NHPI), which is commonly used with promoters [4,5]. Various non-metallic promoters have been used including bromine, nitrogen oxides, azo compounds, etc. [6]. Another group of promoters are single-electron carriers V(V)/V(IV), Co(III)/Co(II), Cu(II)/Cu(I) which operate together with NHPI in oxidation of organic substrates including alkanes and alkylbenzenes [7-9]. The use of Fe(III)/Fe(II) ion pair has so far been limited by high temperature and special conditions [10,11] or the presence of active additives [12]. The rare use of iron promoters is the result of the weak oxidizing ability of Fe(III) compared to Co(III) or Cu (II) ions.

Recently, we observed a positive effect of Fe(III) salts on NHPI catalyzed oxidation of cyclohexene and ethylbenzene to corresponding hydroperoxides [13]. To continue this research towards further improving oxidation, we used 1,10-phenanthroline (Phen) as a potential ligand for Fe(III)/Fe(II) ions. Here, we report on high reactivity of the triple NHPI/Fe(acac)₃/Phen mediator in oxidation of isopropylbenzene (IPB) at low temperature.

Catalysis by NHPI faces the problem of non-solubility of the polar catalyst in non-polar substrates. The problem is usually solved by diluting the substrate with a polar solvent. Other approaches have also been developed using lipophilic analogues of NHPI [14] or NHPI grafted onto solid materials [15,16]. An innovative solution is the addition of salts of organic cations (so called ionic liquids) in the absence of another polar solvent [17–20]. In the oxidation of alkylbenzenes, ionic liquids extract the NHPI and Co(II) promoter into a non-polar substrate or create micelles containing the components of the reaction mixture. By studying the properties of Phen, we realized that it could be used to dissolve NHPI in IPB. As a result, it was found that the ternary system NHPI/Fe(acac)₃/Phen was able to operate in the absence of a solvent.

2. Experimental

Oxidation of IPB was carried out in 300 mL steel reactor connected to a gas cylinder with artificial air. The required amounts of NHPI, CH_3CN , IPB, Fe(acac)₃ and Phen were loaded, and the reactor was sealed. The gas mixture was supplied to a pressure of 20 bar, and the heating was started under gentle stirring. When the temperature reached 60 °C, stirring was switched to vigorous, and this moment was considered the beginning of the reaction. The oxygen uptake during the reaction was monitored by manometer. When the pressure drop due to oxygen consumption reached 2 bar, fresh gas was supplied to maintain the oxygen partial pressure of at least 2 bar. After the oxidation was quenched, the

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Received 8 September 2020; Received in revised form 14 October 2020; Accepted 30 October 2020 Available online 5 November 2020 1566-7367/© 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). reactor was cold to $15^\circ\text{C}\text{,}$ depressurized, and solution was analyzed.

Amount of hydroperoxide was determined by iodometric titration

The oxidation products were identified by GCMS (Agilent 7000 triple quadrupole GC/MS system with a WAX20M 10 m \times 0.25 mm \times 0.25 µm column) and quantitatively determined by GC analysis (Agilent 7890B instrument with a SOLGEL-WAX 30 m \times 0.25 mm \times 1 µm column, FID and chlorobenzene standard). Prior to analysis, the solutions were treated with Ph₃P to reduce the hydroperoxide to alcohol.

NHPI was determined by HPLC on Hewlett Packard Model 1100 instrument with reversed phase Hypersil BDS-C18 250 \times 4 mm \times 5 μm silica column and UV–Vis detector.

NMR spectra were recorded at 500 MHz using Bruker AVANCE III 500 MHz spectrometer. Chemical shifts were measured relative to TMS. Standard DEPT90 and DEPT135 experiments were used for spectral editing.

Details of experiments are described in Ref. [21] and in Supplementary 1.

3. Results and discussion

3.1. Characteristic of isopropylbenzene oxidation mediated by NHPI/Fe $(acac)_3$ /Phen

It has been found before that efficiency of NHPI catalyzed oxidation of isopropylbenzene (IPB) increased under the action of $Fe(acac)_3$ [13]. As a result, intense oxidation took place in the presence of NHPI/Fe (acac)₃ at a lower temperature than required for the reaction in the presence of NHPI alone. In the present study, further improvement of the two-components catalytic system was achieved with 1,10-phenanthroline (Phen), which led to several times faster oxidation and a corresponding increase in IPB conversion over a fixed reaction time (Fig.1). As shown, the oxidation increased continuously with a gradual increase in Phen concentration until a threefold excess of Phen over $Fe(acac)_3$ was reached.

The main oxidation products were isopropylbenzene hydroperoxide (IPBHP) and 2-phenyl-2-propanol (PP), the amount of which was found to vary with the quantity of the system components (Table 1). It was observed that the increase in Phen in the range from $0.14 \cdot 10^{-3}$ to $14 \cdot 10^{-3}$ mol% ($0.3 \cdot 10^{-3} \cdot 30 \cdot 10^{-3}$ mmol) at a constant quantity of NHPI and Fe(acac)₃ (0.9 and $1.2 \cdot 10^{-3}$ mol% with respect to IPB) not only increased conversion of IPB, but also changed a selectivity for the major products toward formation of alcohol (#1–5, Table 1). A similar tendency to change the IPB conversion and selectivity for IPBHP with a



Fig. 1. Dependence of IPB conversion on Phen. Conditions: NHPI 1930 μ mol, Fe(acac)_3 2.7 μ mol, 35 ml solution of IPB/CH_3CN = 30/5 (vol), air 20 bar, 60 °C, 135 min.

Table 1

Results of IPB oxidation mediated by the system of NHPI/Fe(acac)_3/Phen in acetonitrile solution. $^{\rm a}$

#	Composition of mediator, 10 ³ ·mmol		Conversion of IPB, %	Selectivity to major products ^b , %		
	NHPI	Fe (acac) ₃ .10 ³	Phen 10 ³		IPBHP	PP
1	1930	2.70	0.30	8.5	95.7	3.8
2	1930	2.70	1.36	25.7	86.2	8.9
3	1930	2.70	2.70	40.7	84.0	12.0
4	1930	2.70	5.20	47.9	60.9	30.2
5	1930	2.70	30	58.0	50	44.8
6	400	2.70	1.36	25.0	52.0	39.0
7	400	2.70	2.70	36.0	47.5	45.2
8	200	2.70	2.70	24.0	33.9	57.8
9	1930	1.36	1.36	17.4	89.0	10.6
10	1930	1.36	10	33.0	66.7	29.6
11	1930	0.67	1.36	16.0	94.4	1.6
12	1930	0.30	1.36	14.0	98.0	< 1

 $^{\rm a}$ 1 Conditions: 215 mmol IPB in 5 ml acetonitrile, 20 bar air, 60 °C, 135 min. $^{\rm b}$ As a minor product, acetophenone ranged from 0.1 to 5% of the major products.

change in the amount of Phen was observed when using less NHPI (0.2 mol% in #6 and #7).

To understand the active role of Phen, it was important to analyze the dependence of the oxidation efficiency on the amount of other components. A decrease in the amount of NHPI by 5, and then by 10 times compared to the usual one, led only to a slight decrease in the IPB conversion (compare #2 with #6, and #3 with #7 and #8 in Table 1). As known from papers [22,23], the rate of NHPI catalyzed oxidation of IPB approaches a linear dependence on the catalyst (route A, Scheme 1), whereas lack of dependence suggests a non-catalytic chain reaction (route B) [24]. Our observations indicated that both mechanisms were involved in the oxidation of IPB mediated by NHPI/Fe(acac)₃/Phen, and a small amount of NHPI was sufficient to initiate intense oxidation.

When maximum quantity of NHPI was taken, and Fe(acac)₃ and Phen did not exceed 10^{-3} mol%, IPB was selectively oxidized to IPBHP. It accounted for 96–84% of the total products in experiments #1–3, #9 and #11–12 (Table 1). At a low quantity of NHPI, peroxy radicals ROOwere intensively accumulated under the action of highly productive NHPI/Fe(acac)₃/Phen system (1-st step of route A, Scheme 1), but slowly converted to IPBHP (2-nd step of route A), and decomposed to form alkoxy radicals RO· (route C) [25]. Further transformation of the alkoxy radicals to alcohol led to a decrease in the ratio of IPBHP to PP in the oxidation products (# 6–8, Table 1). Thus, the amount of NHPI affected the selectivity of the formation of IPBHP and PP.

Next, effect of Fe(acac)₃ on oxidation of IPB was investigated. In the absence of Fe(acac)₃, the sluggish oxidation with NHPI was barely noticeable at 60 °C, and small additions of Phen (the molar ratio of Phen/NHPI \approx 1/1000) did not provoke reaction. The oxidation was observed when NHPI was used with Fe(acac)₃/Phen promoter, and very small amount of ferric salt was acceptable (#12, Table 1). With a



Scheme 1. Principal routes responsible for oxidation of IPB to IPBHP and PP.

gradually increasing quantity of $Fe(acac)_3$ and unchanged NHPI and Phen, conversion of IPB increased, at least as long as $Fe(acac)_3$ was equimolar or slightly exceeded Phen (#11, #9 and #2). Since generation of PINO is a slow step in the mechanism of NHPI catalyzed oxidation of IPB (route A, Scheme 1) [26], observed acceleration was connected with rapid interaction of NHPI with Fe(III) to form PINO (route A in Scheme 2). The fact that this interaction was controlled by Phen could find an explanation in the formation of highly reactive complexes of Fe(III). Phen under the reaction conditions. Indeed, ligating with Phen enhances reduction potential of Fe(III)/Fe(II) redox couple from 0 0.771 to 1.14 V (vs. SHE) [27]. Well-known is a high oxidizing ability of binuclear iron-Phen complexes readily formed from Fe(III) nitrate, chloride or perchlorate in water-acetonitrile solvent [28].

Contrary to our expectations, NMR spectroscopy proved inertness of Fe(acac)₃ with respect to Phen. Indeed, a lack of the ligand exchange was evidenced from the absence of signals from free acetylacetone when Phen was added to solution of Fe(acac)₃. Rapid changes in the spectrum began after the subsequent addition of NHPI, which manifested itself in weakening the signals from Fe(acac)₃ (broad signals at -26.2 ppm (width 1240 Hz, 1H, CH) and 22.3 ppm (width 700 Hz, 6H, 2CH₃)) and appearance of signals from free acetylacetone (δ 2.14 (s, 6H, 2CH₃)), 3.60 (s, 2H, CH₂) of keto and 2.01 (s, 6H, 2CH₃) 5.60 (s, 1H, CH), 15.6 (br.s, 1H, OH) of enol tautomers). Initiated by NHPI (probably, phthalimide-N-oxyl anion), the removal of the ligand from Fe(acac)₃ was followed by the binding of Phen and inner-sphere charge transfer to form Fe (Phen)³⁺₃ complex (δ 7.60 (m, 2H, H3,8), 7.67 (d, 2H, H2,9), 8.24 (s, 2H, H5,6), 8.60 (d, 2H, 4,7)) and PINO. (More NMR data are in Supplementary 2).

Thus encouraged by Phen, the intense redox-interaction of NHPI with Fe(III) (route A in Scheme 2) was the main driving force for the rapid oxidation of IPB in the system NHPI/Fe(acac)₃/Phen. *Re*-oxidation of Fe(II) occurred under the action of isopropylbenzene peroxy radicals or IPBHP to form IPBHP in the first case and alkoxy radicals, then PP in the second case (routes B in Scheme 2). The oxidation of Fe(II) with molecular oxygen did not take place, in contrast to catalysis by NHPI/Co (II). At a small amounts of Fe(acac)₃ and Phen, PP appeared also in small amounts, which indicated reaction with ROO· to be predominant way of Fe(II) oxidation. In addition, low concentrations of Fe(acac)₃ did not cause significant decomposition of IPBHP (route C in Scheme 2), which comprised 98% of the oxidation products (#12, Table 1).

3.2. Solvent-free oxidation of IPB mediated by NHPI/Fe(acac)₃/Phen

In previous experiments, the reaction mixture contained 14% acetonitrile, which ensured almost complete dissolution of NHPI at 60 °C. Subsequently, the oxidation of IPB mediated by the system Fe (acac)₃/NHPI/Phen was tried in the absence of the polar solvent. First, a combination of IPB-soluble Fe(acac)₃ and Phen was tested. It was observed that the oxidation of IPB to predominantly IPBHP occurred without NHPI at 60 °C (#1, Table 2) which is below the typical



Scheme 2. Mediator transformations during oxidation of IPB.

temperature of catalysis by metal ions [3]. The low-temperature reaction was apparently caused by the above-discussed strong increase in the oxidizing ability of $Fe(acac)_3$ in the presence of Phen. A similar phenomenon was reported for Cu(II)/Phen catalyst [29,30]. Low rate of reaction and, accordingly, small conversion of IPB in #1corresponded to a low concentration of the active components. Addition of a solid NHPI caused a more intense oxidation of IPB under the same conditions. In the presence of NHPI/Fe(acac)₃/Phen, oxygen consumption by the reaction mixture became noticeable 30 min after start of heating of the reactor and continued at a constant rate until the reaction began to slow down at a high conversion of IPB (Fig.2).

Variation of the reaction time in several experiments showed that formation of the oxidation products grew with time, and the selectivity for IPBHP was over 82% in experiments #2-5 (Table 2) with a slight increase when conversion of IPB approached 37% in #5. The oxidation was certainly participated by NHPI. HPLC and NMR analysis showed no dissolution of NHPI in pure IPB, but NHPI did dissolve in IPB in the presence of Phen at room temperature. Addition of a solid NHPI into $0.34 \cdot 10^{-3}$ M Phen solution in IPB led to appearance of approximately equimolar amount of NHPI in solution. Associated with Phen, the solubility of NHPI suggested an interaction of two components, which was confirmed by ¹³C and ¹H NMR. Indeed, introduction of Phen caused a shift in NMR signals of NHPI in the acetonitrile solution. The spectral characteristics corresponded to formation of the hydrogen-bonded adduct of Phen and NHPI (Supplementary 3), for which the DFT calculation provided a structure shown in Fig.3. A similar phenomenon has already been established for the binding of lipophilic NHPI to acetonitrile [14].

Assisted by Phen, reaction of dissolved NHPI and Fe(acac)₃ (route A in Scheme 2) afforded PINO which, in turn, initiated oxidation of IPB. The same triple interaction is very likely to occur under the contact of Fe (acac)₃ solution with surface of the solid NHPI containing adsorbed Phen. The Phen-NHPI interaction detected in acetonitrile solution was responsible for the adsorption of Phen on solid NHPI providing an additional pathway to generation of PINO. Thus, the interaction of Fe (III) with Phen-associated NHPI in solution and on a solid surface created necessary concentration of NHPI/PINO to start the oxidation, and the concentration increased in time due to dissolution of NHPI in the products, mainly IPBHP (#2-5, Table 2). When the reaction was quenched after 160 min, only 5% of the added solid NHPI (0.04 mol% relative to IPB) was detected in the solution (#2), but after 570 min of the reaction already 50% NHPI was dissolved (#5). Note that the concentrations of NHPI were measured after the solutions were cooled to 15°C, and these quantities should have been greater at the reaction temperature of 60 °C. The gradual increase in concentration of NHPI contributed to a slight increase in selectivity for IPBHP, as would be expected according to Scheme 1.

As it turned out, the oxidation proceeded more slowly in pure IPB than in dilute one. A twofold difference in the rate was estimated from the linear part of the kinetic curves (Fig.2). It took more time, for example, to achieve an IBP conversion of 17% and lower selectivity for IPBHP was obtained in the absence than in presence of acetonitrile (#3 and #6 in Table 2). This was apparently due to the difference in concentration of NHPI in the reaction solution. Similar to the oxidation in acetonitrile solution, the oxidation without solvent showed the sensitivity of the products composition to the quantity of Fe(acac)₃ and Phen. This phenomenon is applicable to control the selectivity for each of the major products. Indeed, the formation of PP became more selective as the content of Fe(acac)₃ and Phen increased (#7 and #8, Table 2), and, conversely, IPBHP was practically the only product when using trace amount of Fe(acac)₃ (#9). Note that high selectivity for IPBHP has to be interesting in the case of targeted synthesis of hydroperoxide.

It was also important for synthetic purpose to ensure sufficient stability of NHPI. The estimates made so far have shown that more than 95% of the starting NHPI remained intact in solution after the oxidation of pure and acetonitrile diluted IPB (Supplementary 4).

Table 2

Results of IPB oxidation mediated by the system of NHPI/Fe(acac)₃/Phen.^a

#	Composition of promoter, 10 ³ ·mmol		Time, min	Conversion of IPB, %	Selectivity, %		NHPI dissolved after reaction, $mmol^{\scriptscriptstyle \mathbb{C}}$
	Fe(acac) ₃	Phen			IPBHP	PP	
1	2.70	2.70	180	0.7	87.5	10.9	0
2	1.36	1.36	160	10.8	82.1	16.5	0.1
3	1.36	1.36	225	17.4	82.6	16.2	0.17
4	1.36	1.36	340	24.0	82.7	14.5	0.23
5	1.36	1.36	570	37.4	87.8	9.3	0.56
6 (Ref.) ^b	1.36	1.36	135	17.4	89.0	10.6	0.42
7	2.70	1.36	160	13.2	81.6	16.0	0.13
8	2.70	2.70	165	17.0	75.7	22.0	0.22
9	0.67	30	225	12.1	98.0	< 1	0.18

 $^{\rm a}$ Conditions: 250 mmol IPB, 1.93 mmol (0.8 mol%) NHPI, 20 bar air, 60 $^\circ \rm C.$

^b 215 mmol IPB in 5 ml acetonitrile.

^c Amount of dissolved NHPI was determined after completion of the oxidation and cooling of the reaction solution to 15 °C.



Fig. 2. Time dependence of oxygen consumption in the presence and in the absence of acetonitrile. Conditions: NHPI 1930 µmol, Fe(acac)₃ 1.3 µmol, 35 ml of IPB or solution of IPB/CH3CN = 30/5 (vol), air 20 bar, 60 °C.



Fig. 3. Molecular structure of the hydrogen-bonded adduct of Phen and NHPI.

4. Conclusion

The presented results proved the high efficiency of the NHPI/Fe (acac)₃/Phen mediator in oxidation of IPB. Improvement of the NHPI catalyst was achieved due to combined interaction of NHPI and Phen with iron complex, which provided an easy pathway to generation of PINO. Phen was involved in two important functions. As a part of the coordination environment of Fe(III)/Fe(II) ions, Phen enhanced oxidative capacity of Fe(acac)₃. Moreover, Phen formed a hydrogen bond with NHPI, whereby equimolar amount of NHPI was dissolved in IPB. Occurrence of the hydrogen-bonded adduct initiated the oxidation of IPB without the use of other solvents. An unusual feature of the system under study is low concentration of NHPI-promoting components, which are $0.1-1.0\cdot10^{-3}$ mol% of Fe(acac)₃ and $0.1-10\cdot10^{-3}$ mol% of Phen. The use of a minimal amount of Fe(acac)₃ in combination with NHPI and Phen guaranteed IPBHP from decomposition to PP. Therefore, the system NHPI/Fe(acac)₃/Phen is of great promise for the synthesis of IPBHP under mild conditions.

Credit author statement

N.I. Kuznetsova: Ideas, formulation of research goals, presentation of the published work. D.E. Babushkin: Software, NMR study. V.N. Zudin: conducting investigation process, performing the experiments. O.S. Koscheeva: analysis by chromatography. L.I. Kuznetsova: development of methodology, preparation of the published work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106218.

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