J. Chem. Sci.
DOI 10.1007/s12039-017-1373-4

REGULAR ARTICLE

Special Issue on Recent Trends in the Design and Development of Catalysts and their Applications

Iron(II) and copper(II) phthalocyanine-catalyzed synthesis of 2-nitro-4-methylsulfonylbenzoic acid under mild conditions

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MS received 23 May 2017; revised 22 August 2017; accepted 30 August 2017

Abstract. A novel method was developed to produce 2-nitro-4-methylsulfonylbenzoic acid (NMSBA) from the oxidation of 2-nitro-4-methylsulfonyltoluene (NMST) by oxygen catalyzed by iron(II) phthalocyanine (FePc) and copper(II) phthalocyanine (CuPc). The order of activity for oxidation of NMST was found to be: FePc > CuPc. Meanwhile, major reaction parameters such as concentrations of catalyst and NaOH, reaction temperature and oxygen pressure have been investigated. Through optimization of the reaction parameters, the highest yield of NMSBA and conversion of NMST (up to 53%, 89.3%, respectively) were achieved with oxygen (2.0 MPa), FePc (1.0×10^{-4} mol L^{-1}), NaOH (0.6 mol L^{-1}), in methanol at 55°C for 8 h. A plausible mechanism for this catalytic process is proposed which involved deprotonation and radical pathways.

Keywords. 2-Nitro-4-methylsulfonyltoluene; 2-nitro-4-methylsulfonylbenzoic acid; aero oxidation; metal phthalocyanines.

1. Introduction

Mesotrione, namely 2-(4-mesyl-2-nitrobenzoyl)-1,3-cyclohexanedione, is a commercial cornfield herbicide developed by Syngenta company. It is widely produced and utilized due to its safety, low toxicity, strong miscibility and high efficiency.[1] Along with the global market demand of mesotrione increased rapidly, it has been widely researched in recent years. In the production of mesotrione, 2-nitro-4-methylsulfonylbenzoic acid (NMSBA) as a key intermediate of mesotrione is usually oxidized from 2-nitro-4-methylsulfonyltoluene (NMST).

In the chemical structure of NMST, there are two strong electron-withdrawing substituents ($-NO_2$ and $-SO_2CH_3$) attached to the benzene ring, which increase the difficulty of oxidizing NMST to NMSBA. To oxidize methyl group on benzene rings with strong electron-withdrawing substituents attached, traditionally, stoichiometric oxidants such as potassium permanganate,[2] sodium hypochlorite,[3] or organic peroxides[4] are necessary for effective conversion. However, these stoichiometric oxidants are not only relatively expensive but also generate significant amounts of waste. From both an economic and environmental point of view, the effective catalytic oxidation processes using clean and inexpensive oxidants, such as molecular oxygen for converting aryl methyl group to carboxylic acid group on an industrial scale, is the most gratifying route. In recent years, significant progress has been made in oxidizing aryl methyl group with molecular oxygen as oxidant, and Co^{2+}/Mn^{2+} salts as catalysts.[5,6] Due to the low oxidizing capability of oxygen, the reaction condition in these catalytic systems is very harsh, especially when strong electron-withdrawing groups such as $-NO_2$ and $-SO_2CH_3$ are attached on the benzene, even under high reaction temperature and high pressure of air/oxygen. Meanwhile, the catalytic system may bring undesirable side reactions, such as the decarboxylation of the resulting carboxylic acid and decomposition of acetic acid solvent.[7]

To avoid these drawbacks, it is very challenging and significant to explore an efficient and green catalyst to activate molecular oxygen and produce reactive oxygen species which induce oxidation of aryl methyl groups. Recently, metal phthalocyanines (MPc) have been widely used in the oxidation of aryl methyl groups, which have attracted much interest due to their high catalytic activity.[8] The oxidation process is attributed to the ability of MPcs, which could excite

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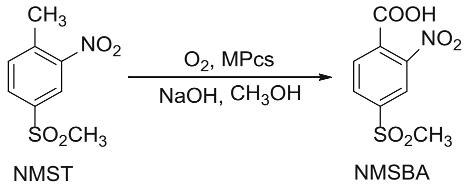


Scheme 1. Catalytic oxidation of NMST to NMSBA.

ground-state molecular oxygen ($^3O_2$) to highly active singlet oxygen ($^1O_2$).[9,10] Song and co-authors[11] investigated the bromide-free and acetic acid-free aerobic oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid in high yield by using MPcs as catalysts under mild conditions in alkali-methanol solution. Up to 88.8% isolated yield of *p*-nitrobenzoic acid was obtained. Shan and co-authors[12] reported a method for oxidation of nitrotoluenes to nitrobenzoic acids with molecular oxygen and ionic liquid [omim][BF_4] containing the iron phthalocyanine complex with the isolated yield of 93%. All these previous studies indicate that MPcs exhibited excellent performance in catalytic oxidation by oxygen under mild condition. In particular, iron(II) phthalocyanine (FePc) and copper(II) phthalocyanine (CuPc) showed high selective catalytic oxidation of aryl methyl group to carboxylic acid group, which are preferred catalysts in the catalytic oxidation reaction.

On the other hand, oxidants are also major contributors in NMST selective oxidation to NMSBA. For oxidation of NMST as a critical procedure in mesotrione production, many ways have been tried. According to the literature,[13,14] some researchers reported the oxidation of NSMT with concentrated nitric acid. However, there were some disadvantages which included more acid-containing waste water and nitro-compounds. Jary and Cheng[15,16] put forward that NMST could be oxidized to NMSBA by hydrogen peroxide and different metal catalysts in sulfuric acid solution. However, using hydrogen peroxide as oxidant, the actual dosage of hydrogen peroxide will be relatively large. As a well-known green oxidant, oxygen is preferred to make the oxidation of NMST to NMSBA, inexpensively and efficiently.[17] Long and co-authors[18] developed a method to oxidize NMST to afford NMSBA with oxygen coupled with a homogeneous catalyst system consisting of $H_3PW_{12}O_{40}$/Co(II)/Mn(II)/Br. This technology used bromine as a promoter and it had a serious impact on the environment, but compared with the previous methods, this process demonstrated that oxygen can be used as a green oxidant in oxidation of NMST.

In this work, we report a catalytic system with efficient MPc catalysts and green oxidant oxygen for oxidation of NMST to NMSBA. The synthetic routes is shown in Scheme 1. This work was aimed at optimizing the synthesis of NMSBA to decrease the economic cost and reduce the pollution. These results would provide an important guidance for industrial production of mesotrione.

2. Experimental

2.1 *Materials*

Copper(II) phthalocyanine and iron(II) phthalocyanine were purchased from the J&K Chemical Co., Ltd. (Beijing, China). NMSBA was purchased from Energy Chemicals Co., Ltd. (Shanghai, China). NMST was obtained from Changqing Agrochemical Co., Ltd. (Jiangsu, China). Spectrophotmetric grade solvents were used for spectroscopic studies and were purchased from Alfa Aesar Company. All the other reagents and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification.

2.2 *General procedure for the oxidation*

The aerobic oxidation was carried out in the following steps. Firstly, 1000 mL autoclave was charged with mixtures of substrate (20 mmol) and methanol (200 mL), proposed amount of NaOH and MPc. Secondly, high purity O_2 was introduced into the autoclave to replace the air for three times and then raise the pressure in the reactor to proposed pressure and the stirring was started. The agitation speed was maintained at 250 rpm. Thirdly, the reactor was heated by an electric heating jacket. At last, the temperature reached to the scheduled values and reacted for 8 h. The reaction solution was diluted with the solvent to a certain volume to be quantitatively analyzed the NMST conversion and NMSBA yield by high-performance liquid chromatography (HPLC).

2.3 *Analytical methods*

The concentration of NMST and NMSBA was analyzed by HPLC (Dionex, USA) equipped with Hypersil C18 ODS2 (4.6×150 mm, 5 μm) column and UV-detector set at λ = 254 nm. A solution of 60% deionized water and 40% acetonitrile was used as a mobile phase with a flow rate of 1.0 mL min^{-1}. The column temperature and injection volume were set at 25°C and 20 μL, respectively. The calibration curves of NMST and NMSBA were obtained by using standard solutions. Least-squares fits to the data yield standard equations shown in Table 1. *A* stands for peak area and *C* means the concentration with NMST or NMSBA.

The NMST conversion and NMSBA yield were determined by Eqs. (1) and (2) respectively.[18]

Table 1. Standard equations of NMST and NMSBA.

Sample	Linear Equation	R^2
NMST	$C_{NMST} = 0.369A_{NMST} + 0.02$	0.996
NMSBA	$C_{NMSBA} = 0.479A_{NMSBA} + 0.025$	0.997

$$\alpha_{NMST}(\%) = \frac{C^0_{NMST} - C^e_{NMST}}{C^0_{NMST}} \times 100 \qquad (1)$$

where α_{NMST} stands for the conversion of NMST, C^0_{NMST} for the initial NMST concentration and C^e_{NMST} for the NMST concentration (g mL^{-1}) at the end of reaction in the solution.

$$Y_{NMSBA}(\%) = \frac{C^e_{NMSBA}}{\frac{M_{NMSBA}}{M_{NMST}} C^0_{NMST}} \times 100 \qquad (2)$$

where Y_{NMSBA} is the yield of NMSBA, M_{NMST} and M_{NMSBA} are the molecular weights of NMST and NMSBA, C^e_{NMSBA} is the NMSBA concentration (g mL^{-1}) at the end of reaction in the solution.

3. Results and Discussion

3.1 *Catalytic studies*

3.1a *Oxidation of different toluene derivatives with MPcs*: In order to test the catalytic activities of MPcs, the oxidation of toluene derivatives with electron-withdrawing substitute was utilized for model reaction. The reactions were performed in the presence of the Cu(II) and Fe(II) phthalocyanine catalysts (Table 2).

The results in Table 2 show that MPc catalysts possess high catalytic efficiency in the oxidation of toluene derivatives with an electron-withdrawing substitute. As an example, nitrobenzoic acid was obtained in a high yield under oxygen using a very low concentration of catalyst. However, the conversion of nitrotoluene and yield of nitrobenzoic acids are very low when the air was used as the oxidant. The reason for the low conversion is that air exhibits lower oxidation efficiency than pure oxygen. Additionally, the position of a substituent on the toluene has also great influence on the conversion. Since toluene is substituted by an electron-withdrawing group at its para position, the C-H bond length of the methyl group on the benzene ring will be longer than that at its ortho position.[19] Generally, a longer bond length represents a weaker bond.[20] In other words, the oxidation of *o*-nitrotoluene is difficult than *p*-nitrotoluene. Oxidation of chloro-substituted toluene was also examined, and the acid yield reached nearly 62%. The results of the model reaction indicate the MPcs possess high activity in the oxidation of toluene derivatives with electron-withdrawing substitute and can be used in the oxidation of NMST.

3.1b *Effect of MPc concentration on NMST oxidation*: It is necessary to measure the effect of MPcs on the oxidation of NMSBA from NMST because it is an important component of this catalytic system. A series of experiments were conducted with CuPc and FePc for a concentration of 1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4}, 5.0×10^{-4} mol L^{-1}, respectively. The results are shown in Table 3, which indicate that as the concentration of CuPc/FePc increased from 1.0×10^{-5} to 1.0×10^{-4} mol L^{-1}, the conversion of NMST increased from 10.8 to 89.3% and the yield of NMSBA also increased from 5 to 53%. Upon further increasing

Table 2. Oxidation of different toluene derivatives with MPc catalysts[a].

Entry	Substrate	Catalyst	Oxidant	Time (h)	Conversion[b] (%)	Yield of acid[b] (%)
1[c]	*p*-Nitrotoluene	CuPc	Air	24	3.4	3
2[c]	*p*-Nitrotoluene	FePc	Air	24	3.8	3
3	*p*-Nitrotoluene	CuPc	O_2	8	91.3	65
4	*p*-Nitrotoluene	FePc	O_2	8	92.6	73
5	*o*-Nitrotoluene	CuPc	O_2	8	85.3	55
6	*o*-Nitrotoluene	FePc	O_2	8	89.3	61
7	2-Chlorotoluene	CuPc	O_2	12	70.9	53
8	2-Chlorotoluene	FePc	O_2	12	71.3	58
9	4-Chlorotoluene	CuPc	O_2	12	81.4	58
10	4-Chlorotoluene	FePc	O_2	12	87.0	62

[a] Reaction conditions: $M_{NaOH} = 0.6$ mol L^{-1}, $M_{MPc} = 1.0 \times 10^{-4}$ mol L^{-1}, 55°C, O_2 (2.0 MPa).
[b] Determined by high performance liquid chromatography (HPLC).
[c] Air bubbling.

Table 3. Effect of MPcs concentration on NMST oxidation with CuPc and FePc[a].

Entry	Catalyst	M_{MPc} (molL^{-1})	Conversion[b] (%)	Yield[b] (%)	TON[c]	TOF[d] (h^{-1})
1	CuPc	1.0×10^{-5}	10.8	5	581	73
2	FePc	1.0×10^{-5}	12.4	8	877	110
3	CuPc	5.0×10^{-5}	43.3	23	526	66
4	FePc	5.0×10^{-5}	73.5	37	839	105
5	CuPc	1.0×10^{-4}	81.6	43	495	62
6	FePc	1.0×10^{-4}	89.3	53	604	75
7	CuPc	5.0×10^{-4}	51.8	27	62	8
8	FePc	5.0×10^{-4}	53.7	30	68	9

[a] Reaction conditions: $M_{NaOH} = 0.6$ mol L^{-1}, 55°C, 8 h, O_2 (2.0 MPa).
[b] Determined by high-performance liquid chromatography (HPLC).
[c] TON = mole of product/mole of catalyst.
[d] TOF = mole of product/mole of catalyst × time (h).

the concentration of CuPc/FePc (5.0×10^{-4} mol L^{-1}), the yield of NMSBA and the conversion of NMST decreased. This is due to the tendency of MPcs molecule to aggregate, leading to decrease in the active sites for oxidation of NMST to NMSBA, which has also been proven previously.[21] Meanwhile, it was observed that the final products contained some other products such as the corresponding alcohol and aldehyde.[11] In addition, taking reaction pathway and conditions into consideration, the byproducts may also contain the dimeric product.[22] The results in Table 3 indicate that the optimal MPc concentration in this catalytic system may be 1.0×10^{-4} mol L^{-1}.

We found for the same concentration of MPc, the conversion of NMST and yield of NMSBA for FePc were higher than the corresponding results for CuPc. Meanwhile, the higher turnover number (TON) and turnover frequency (TOF) obtained for FePc suggested that the catalytic activity of FePc in NMST oxidation reaction is better than that of CuPc. Catalytic oxidation of MPcs may be assumed to be accompanied by coordination of the oxygen to the central metal of the catalyst, in a similar manner to porphyrins.[23] MPcs with different central metal ions may have varying coordination abilities, which could result in varying modes and rates of cleavage of the oxygen-MPc bonds hence resulting in different product yields.[24] For this reason, Fe(II)Pc could easily react with oxygen to give PcFe(III)O-O complex to improve the catalytic activity of FePc. However, invariant valence CuPc has a lower capacity for the activation of oxygen, which leads to its catalytic activity lower than that of FePc.[25]

Compared with the model reaction (Table 2), the yield of NMSBA is lower than these corresponding acids under identical experimental conditions. In general, for more electron-withdrawing groups on the benzene ring, the methyl becomes more difficult to oxidize. These might explain why the yield of NMSBA is lower than those of monosubstituted corresponding acids.

3.1c *Effect of NaOH concentration on NMST oxidation*: The above reaction occurs only when a large amount of strong alkali such as NaOH-methanol exists in the reaction system. The hydrogen of methyl is abstracted by NaOH-methanol, and then completes the catalytic oxidation of NMST to NMSBA. Experiments were performed with the NaOH concentration of 1.0, 1.5, 2.0, 2.5 mol L^{-1} respectively, while keeping all other conditions the same. The results are summarized in Table 4.

From Table 4, it can be observed that the conversion of NMST and yield of NMSBA increase with NaOH concentration from 1.0 to 2.5 mol L^{-1}. For example, when the NaOH concentration increases from 1.0 to 2.5 mol L^{-1}, the conversion of NMST increases from 44.8% to 90.4%. It is also noted that trace conversion of NMST was obtained if NaOH was not utilized in the oxidation, which indicates that NaOH played an important role in the formation of NMSBA. The NMSBA yield increases from 20% to 54% when the concentration of NaOH increases from 1.0 to 2.5 mol L^{-1}. These results suggested that the increase of NaOH concentration could promote the oxidation of NMST.[11] However, when the concentration of NaOH increased above 2.0 mol L^{-1}, the conversion of NMST, as well as the yield of NMSBA, increased only slightly. In terms of cost in post-processing and waste water discharge, the best NaOH concentration is 2.0 mol L^{-1}.

Table 4. Effect of NaOH concentration on NMST oxidation[a].

Entry	Catalyst	M_{NaOH} (mol L^{-1})	Conversion[b] (%)	Yield[b] (%)	TON[c]	TOF[d] (h^{-1})
1	CuPc	1.0	44.8	20	232	29
2	FePc	1.0	70.2	36	406	51
3	CuPc	1.5	67.6	32	368	46
4	FePc	1.5	84.2	42	478	60
5	CuPc	2.0	81.6	43	495	62
6	FePc	2.0	89.3	53	604	75
7	CuPc	2.5	83.3	45	515	64
8	FePc	2.5	90.4	54	619	77
9	CuPc/FePc	0	Trace	Trace	-	-

[a] Reaction conditions: $M_{MPc} = 1.0 \times 10^{-4}$ mol L^{-1}, 55°C, 8 h, O_2 (2.0 MPa).
[b] Determined by high-performance liquid chromatography (HPLC).
[c] TON = mole of product/mole of catalyst.
[d] TOF = mole of product/mole of catalyst × time (h).

Table 5. Temperature effect of NMST oxidation with CuPc and FePc[a].

Entry	Catalyst	T(°C)	Conversion[b](%)	Yield[b](%)	TON[c]	TOF[d] (h^{-1})
1	CuPc	35	28.5	14	160	20
2	FePc	35	28.3	13	150	19
3	CuPc	45	54.3	33	376	47
4	FePc	45	63.3	39	441	55
5	CuPc	55	81.6	43	495	62
6	FePc	55	89.3	53	604	75
7	CuPc	65	84.6	42	475	59
8	FePc	65	91.2	50	573	72

[a] Reaction conditions: $M_{NaOH} = 0.6$ mol L^{-1}, $M_{MPc} = 1.0 \times 10^{-4}$ mol L^{-1}, 8 h, O_2 (2.0 MPa).
[b] Determined by high performance liquid chromatography (HPLC).
[c] TON = mole of product/mole of catalyst.
[d] TOF = mole of product/mole of catalyst × time (h).

3.2 *Effect of other reaction parameters on the NMST oxidation*

3.2a *Effect of reaction temperature and time on NMST oxidation*: To examine the influence of temperature on the oxidation of NMST, the reactions were carried out at a range of temperatures by using CuPc and FePc as catalysts. Table 5 shows a significant effect of the temperature on the conversion of NMST. The conversion of NMST increases from 28.3% to 89.3% with the increase of reaction temperature from 35 to 55°C. Meanwhile, the yield of NMSBA increases from 13% to 53% in this temperature range. The highest yield reaches 43% for CuPc and 53% for FePc at 55°C with the highest TON and TOF values (495, 62 for CuPc and 604, 75 for FePc). However, further increase of reaction temperature to 65°C, results in slight decreasing of the yield of NMSBA 50% while NMST conversion remains nearly quantitative. This yield loss of NMSBA at 65°C may be due to the decrease of selectivity to NMSBA with increasing temperature, which suggests that the catalysts may facilitate the reaction toward an undesired pathway by higher reaction temperatures.

Meanwhile, the conversion of NMST and the yield of NMSBA increased with the reaction processing and reached the highest point after 8 h by using FePc (Figure 1). However, only a slight decrease in yield of NMSBA when the reaction time was prolonged to 10 h. Based on the results of conversion and yield, 8 h was selected as the optimal reaction time.

3.2b *Effect of oxygen pressure on NMST oxidation*: The influence of the pressure of oxygen was also investigated, as illustrated in Table 6. A series of experiments were carried out with the initial oxygen partial pressure of 0.1 MPa, 1.0 MPa, 2.0 MPa, 2.5 MPa and 3.0 MPa, respectively.

Table 6 indicates the yield of NMSBA increases sharply from 13% to 53% with the increase of oxygen pressure from 0.1 MPa to 2.0 MPa. These results

Table 6. Effect of oxygen pressure on NMST oxidation[a].

Entry	Catalyst	Pressure(MPa)	Conversion[b] (%)	Yield[b] (%)
1	CuPc	0.1	3.2	2
2	FePc	0.1	3.9	3
3	CuPc	1.0	67.4	35
4	FePc	1.0	61.9	31
5	CuPc	2.0	81.6	43
6	FePc	2.0	89.3	53
7	CuPc	2.5	82.2	44
8	FePc	2.5	90.1	53
9	CuPc	3.0	82.6	44
10	FePc	3.0	89.8	54

[a]Reaction conditions: $M_{NaOH} = 0.6\,mol\,L^{-1}$, $M_{MPc} = 1.0 \times 10^{-4}\,mol\,L^{-1}$, 55°C, 8 h.

[b]Determined by high performance liquid chromatography (HPLC).

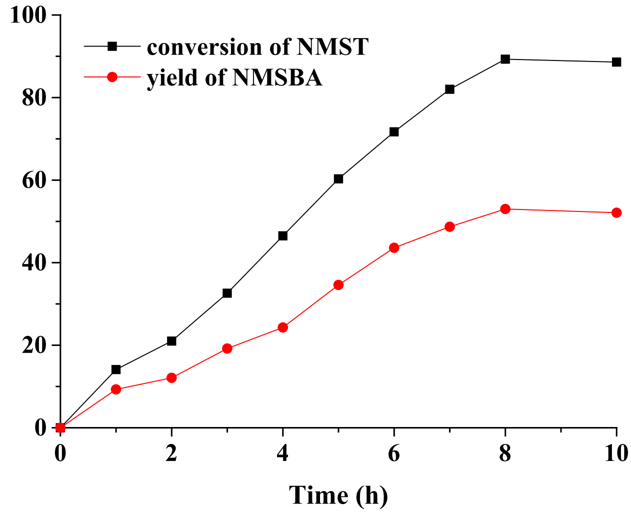


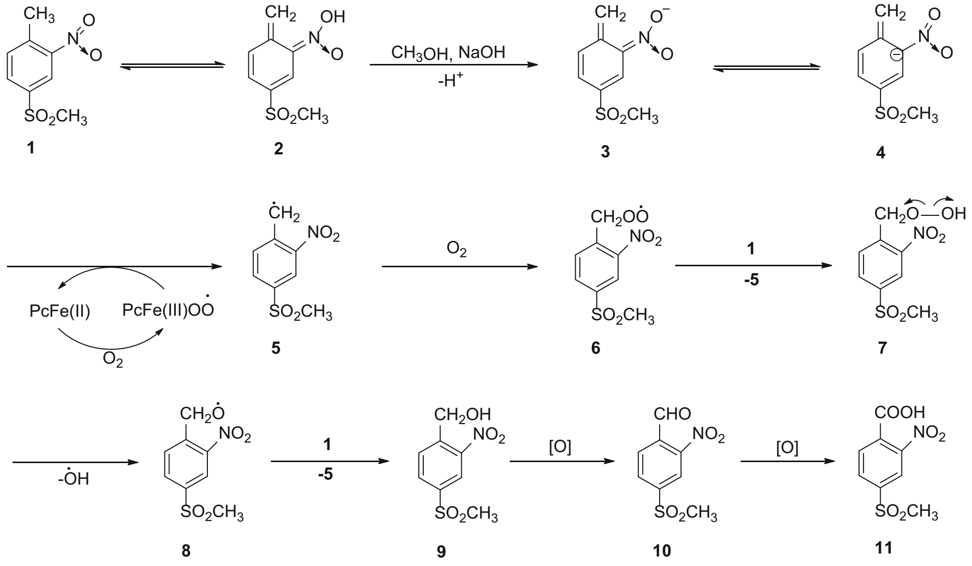
Figure 1. Time-dependent curve of conversion and yield under the optimum conditions, Reaction conditions: $M_{NaOH} = 0.6\,mol\,L^{-1}$, $M_{FePc} = 1.0 \times 10^{-4}\,mol\,L^{-1}$, O_2 (2.0 MPa), 55°C, 8 h.

suggest that the yield and oxygen pressure are closely correlated. Adsorption of oxygen to the phthalocyanine would be very fast, and 0.1 MPa of oxygen would be sufficient to fully form the metal-oxygen complex.[26] However, only 0.1 MPa of oxygen could not provide enough molecular oxygen into the solvent. The yield of NMSBA increases with the oxygen pressure increase, in that oxygen concentration increases in the solvent and eventually the increase of reaction rate. When the oxygen pressure further increases to 2.5 MPa, the yield of NMSBA only slightly increased with an oxygen pressure increasing of 0.5 MPa. This phenomenon could be mainly attributed to the dissolved amount of the oxygen in the reaction solvent which almost reaches the maximum and the extra increase in the pressure of oxygen has less influence on the increase in the concentration of oxygen.[12] Hence, the yields of NMSBA and conversions of NMST were almost unchanged, when the oxygen pressure is above 2.5 MPa (Table 6, entries 9–10).

3.3 *Plausible mechanism*

According to results of this work and the literature reports previously,[27,28] we propose a possible mechanism of the catalytic oxidation (Scheme 2). The catalytic procedure is confirmed to be initiated in a two-step process. In the first step, NaOH-methanol could capture an H^+ from the methyl on the NMST and forms intermediate **4**. This inference is verified by the experimental result that trace NMSBA was detected without NaOH in the oxidation system (Table 4, entry 9). In contrast, the yield of NMSBA was rapidly increased with increasing NaOH concentration (Table 4, entries 1–6).

The second step of the catalytic procedure is adsorption of oxygen to the FePc to fully form the iron-oxygen complex. Fe(II) phthalocyanine (FePc) would be converted into the starting Fe(III) species with generation of radical (Fe(III)PcOO ·),[29] and then the radical reacts with **4** to give benzylic radical **5**. Then, oxygen is trapped by benzylic radical to afford benzylperoxy radical **6.** This radical could abstract a hydrogen from NMST to obtain an intermediate **5** and give benzylic hydroperoxide **7**. The homolysis of hydroperoxide can promote the generation of key intermediate alcohol. Finally, alcohol **9** is further oxidized to give the product NMSBA. Thus, the pathway of NMST to NMSBA can be assigned to a deprotonation and radical mechanism.



Scheme 2. Plausible mechanism for the oxidation of NMST to NMSBA.

4. Conclusions

In conclusion, we have developed a practical method for the preparation of NMSBA by aerobic oxidation. The reaction is catalyzed by metal phthalocyanine, which is inexpensive and non-toxic. Furthermore, the oxidation system was economical, environmentally friendly compared with the conventional oxidation methods. The catalytic performance was greatly affected by the metal ions of phthalocyanine, reaction time, reaction temperature, oxygen pressure and the concentration of phthalocyanines and NaOH. It is found that the iron(II) phthalocyanine exhibits better catalytic activity, which efficiently converted NMST into NMSBA in yields up to 53%. The results of the present study will be readily applicable to large-scale oxidation of NMST in the chemical industry in the future.

Acknowledgements

We greatly acknowledge the financial support in part by the National Key Research and Development Program of China (2016YFB0301703), National Natural Science Foundation of China (21602106), Natural Science Foundation of Jiangsu Province-Outstanding Youth Foundation (BK20170104) and Industry-Academy-Research Prospective Joint Project of Jiangsu Province (BY2016005-06).

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