



A metal-free aerobic oxidation of nitrotoluenes catalyzed by N,N',N''-trihydroxyisocyanuric acid (THICA) and a novel approach to the catalyst

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ABSTRACT

A metal-free catalytic system with N,N',N''-trihydroxyisocyanuric acid (THICA) as the catalyst for the oxidation of nitrotoluenes is introduced, and a novel Pd-free approach for the synthesis of THICA was developed. In a solution of acetic acid, THICA and concentrated nitric acid, nitrotoluenes especially polynitrotoluenes such as 2,4,6-trinitrotoluene (TNT), were converted into the desired carboxylic acids under 0.2 MPa of O₂ at 100 °C with yields up to 99%. THICA was synthesized from N-hydroxyphthalimide through a four-step synthesis in a total yield of 46%. A possible mechanism of this catalytic process was proposed where NO₂ and nitric acid first induced a radical of THICA, which then abstracts a hydrogen atom from the methyl on the aromatic ring to form a benzyl radical. This radical then initiates subsequent reactions. The production of the benzyl radical was supported by ESR measurements.

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1. Introduction

Nitrobenzoic acids are important intermediates for organic synthesis and are widely used in the synthesis of pharmaceuticals, pesticide, dyes, photographic materials and perfumes. Generally, they are prepared through oxidation of the corresponding nitrotoluenes. Because of the strong electron-withdrawing effect of the nitro group, the methyl on the aromatic ring is rather difficult to oxidize except by strong oxidants.

The oxidation can be achieved by using stoichiometric oxidants, such as potassium dichromate, but these reagents cause serious pollution problems, such as the generation of chromium-containing wastewater [1,2]. Sudadai and co-workers [3] used NaIO₄ and LiBr in dilute sulfuric acid to oxidize p- and m-nitrotoluene into the corresponding carboxylic acids with yields 76% and 69%, respectively. The presence of bromine, however, may cause serious corrosion of reactor vessels, limiting its application in industry, and side reactions, such as bromination and decarboxylation, were inevitable [4]. Oxygen oxidation is environmentally friendly and economical, but a matched catalyst is required to activate the oxygen molecule. With these challenges in mind, different catalysts were synthesized for the aerobic oxidation of nitro-

toluenes. Unwillingly these catalysts generally consisted of heavy metals, such as Co and Mn salts and their derivatives. For example, She [5,6] reported the catalyzed oxidation of p-nitrotoluene to its carboxylic acid with a maximum yield of 90% using metalloporphyrins (metals include Fe, Co and Mn) as biomimetic catalysts. With iron phthalocyanine as the catalyst in ionic liquids [7], o-nitrotoluene and p-nitrotoluene, as well as dinitrotoluene (DNT), which is much more difficult to oxidize, were turned into their corresponding carboxylic acids in good yields. Nevertheless, m-nitrotoluene and toluene could not be oxidized in this system, which was explained by a mechanism of ionization where toluene and m-nitrotoluene were not able to participate [5,7].

Ishii et al. used N-hydroxyphthalimide (NHPI) as the catalyst for the oxidation of substituted toluenes, achieving high yields of the carboxylic acids. They also developed a more effective catalyst, N,N',N''-trihydroxyisocyanuric acid (THICA), whose structure is similar to that of NHPI, and applied it to the oxidation of nitrotoluenes [8–14]. To complete the catalytic oxidation, THICA needed to be combined with Co acetate and Mn acetate. These heavy metal ions, however, may cause environmental damage due to increased discharge, their non-biodegradable properties and their toxicity [15]. Additionally, their use may harm the health of laboratory personnel. For instance, accidentally inhalation of Co acetate can cause pharyngitis, vomiting, abdominal cramps and leg weakness, and skin contact with the salt can cause dermatitis [16]. In addition, if Mn acetate dust enters the respiratory tract, it will be absorbed into the blood stream. Manganese is then deposited in major organs, particularly the liver, spleen and certain nerve cells of the brain

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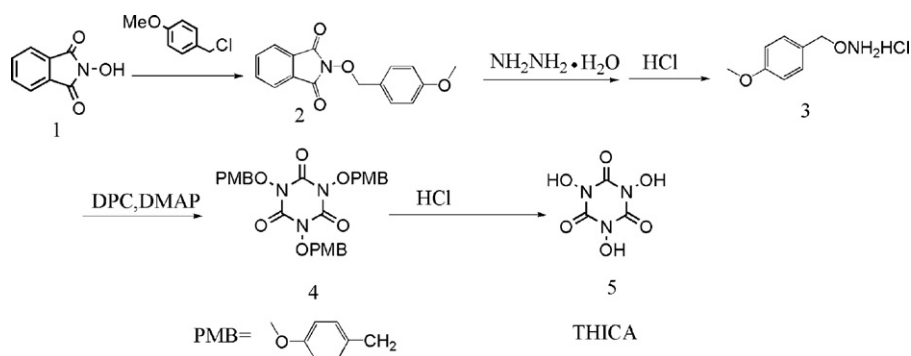


Fig. 1. Preparation of the THICA catalyst.

and spinal cord [15]. On the other hand, up to now in the literature, Pd was essential for catalyzed hydrogenolysis in the preparation of THICA [13,14,17], and Pd is on the list of hazardous chemicals [18].

Herein, we report a metal-free and efficient catalytic system with THICA as the catalyst under the action of nitric acid. We also report a novel approach for the synthesis of THICA without using Pd. A series of nitrotoluenes, particularly polynitrotoluene compounds, such as 2,4,6-trinitrotoluene (TNT), were selectively transformed into the corresponding carboxylic acids with high conversion rates. To the best of our knowledge, no literature report has been published on the efficient oxidation of nitrotoluenes by such a system.

2. Experimental

2.1. Materials and methods

Starting materials were purchased from commercial sources and used without further treatment. The products and the substrates were analyzed by HPLC (Knauer HPLC System, Germany, including the Knauer K2501 liquid chromatography pump, Knauer K22501 adjustable UV detector and EUROCHROM 2000 chromatography workstation). A C-18 RP-HPLC column was used for the HPLC analysis with a mobile phase consisting of water (pH = 2–3) and acetonitrile (2:3, v/v). ESR measurements were performed on a Bruker ESP 300 (Bruker Corporation, Germany).

2.2. General procedure for the oxidation

The experiment was carried out in a 25-ml sealed glass tube to which was added a certain amount of substrate, nitric acid, acetic acid and catalyst. The tube was then filled with O₂ (0.2 MPa), and the mixture was stirred at 100 °C for a certain time. After the reaction was complete, the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate, washed with water and the ethyl acetate was removed by rotary evaporation. The recovered residue was analyzed by HPLC.

2.3. Synthesis of THICA

2.3.1. N-Hydroxyphthalimide p-methoxybenzylether (2) [19]

N-Hydroxyphthalimide **1** (2.87 g) and K₂CO₃ (1.92 g) were combined in DMSO (25 ml). p-Methoxybenzyl chloride (5 ml) was then added drop wise to the suspension. The reaction mixture was stirred for 24 h, poured into 60 ml of cold water, and kept on ice. The precipitate was filtered, washed twice with cold water, and dried under vacuum. Product **2** (4.71 g, 94%) was used in the next step without further purification and characterization.

2.3.2. O-(4-Methoxybenzyl) hydroxylamine hydrochloride (3) [19–21]

Methanol (120 ml) was added to compound **2** (1.70 g) and then hydrazine (80%, 1.20 g) was introduced into the solution. The mixture was stirred for 3 h, then the solvent was removed, 30 ml ethyl acetate was added to the residue, and the solution was stirred for 0.5 h. Then, the mixture was filtered, and the filtrate was washed twice with water. The solvent was evaporated under reduced pressure to give a yellow liquid. The recovered liquid was diluted with ether (25 ml), and the resulting solution was reacted with concentrated hydrochloric acid (0.55 ml) for 0.5 h in an ice bath. The mixture was filtered to give a white solid, which was washed with ether and dried to give **3** (0.95 g, 84%). mp 172–174 °C; ¹H NMR [DMSO-*d*₆, 400 MHz]: δ 3.77 (m, 3H), 4.95 (m, 2H), 6.97–6.99 (d, 2H), 7.35–7.36 (d, 2H), 10.93 (m, 3H).

2.3.3.

1,3,5-Tri(p-methoxybenzyloxy)-1,3,5-triazinane-2,4,6-trione (4) [12]

A mixture of **3** (0.66 g), diphenyl carbonate (DPC, 1.07 g), and 4-dimethylaminopyridine (DMAP, 1.22 g) was heated at 120 °C for 0.5 h under N₂. After cooling to room temperature, methanol (15 ml) was added to the reaction mixture and stirred for 0.5 h. The resulting precipitate was filtered and washed with additional methanol (10 ml). The precipitate was dried to give **4** (0.39 g, 65%). ¹H NMR [DMSO-*d*₆, 400 MHz]: δ 3.78 (m, 3H), 5.01 (m, 2H), 6.99–7.00 (d, 2H), 7.45–7.47 (d, 2H).

2.3.4. THICA (5) [22]

Ethanol (10 ml) and concentrated hydrochloric acid (37%, 4 ml) was added to reactant **4** (0.20 g). The mixture was stirred at 100 °C for 3 h. Ethanol and hydrochloric acid were then removed under reduced pressure, and dichloromethane (8 ml) was added to the residue. The mixture was filtered, and washed with ethyl acetate (5 ml) to give **5** (60 mg, 91%). mp 253–256 °C; ¹H NMR [DMSO-*d*₆, 400 MHz]: δ 3.77 (m, 3H), 4.95 (m, 2H), 6.97–6.99 (d, 2H), 7.35–7.36 (d, 2H), 10.93 (m, 3H); ¹³C NMR (DMSO-*d*₆): 147.

3. Results and discussion

3.1. Preparation of the catalyst THICA

The reported preparative methods for THICA involved using Pd/C at the last step of hydrogenolysis [13,14,17]. To avoid using heavy metals, we developed a new route to THICA as shown in Fig. 1. The total yield of THICA by this novel approach was found to be 46%.

The reaction of NHPI (**1**) to **2** proceeded according to the literature process [19]. Then, hydrochloride **3** was prepared through a modified procedure [19–21] that first employed hydrazinolysis

Table 1
Oxidation of 2,4-DNT with THICA under different pressures of O₂ and in different solvents.^a

Run	Solvent	Pressure of O ₂ (MPa)	Conv. (%)	Selectivity of acid (%)
1	AcOH	0.2	>99	>99
2	AcOH	0.1	92	>99
3	AcOH	0.1 ^b	54	>99
4	Perfluoronaphthalene	0.2	>99	>99
5	Benzotrifluoride	0.2	47	>99
6	[Bmim] ⁺ BF ₄ ⁻	0.2	8	>99
7	[Bmim] ⁺ PF ₆ ⁻	0.2	0	0
8	Methanesulfonic acid	0.2	70	85%

^a 1 mmol 2,4-DNT was reacted under O₂ in the presence of THICA (10 mol%) in a certain solvent (2 ml) and with conc. HNO₃ (0.2 ml) at 100 °C for 20 h. The conversion and selectivity were based on HPLC.

^b 0.1 MPa air.

with hydrazine in methanol to give **2**, 3-dihydrophthalazine-1,4-dione (**6**) and O-(4-methoxybenzyl) hydroxyl amine (**7**). Because of the different solubilities of **6** and **7** in ethyl acetate, compound **7** could be easily separated from **6** by extraction with ethyl acetate. Hydrochloric acid was added to an ether solution of **7** to give **3** in a yield of 84%, which is much higher than the reported literature yield of 50% [21].

The reaction of **3**–**4** was conducted under anhydrous conditions, and DMAP was chosen as the best base for this type of reaction [12]. Intermediate **4** was produced in a yield of 65%. p-Methoxybenzyl as a protective group on the hydroxyl was found to be much easier to remove than benzyl because this could be achieved by heating in ethanol and hydrochloric acid [22] instead of using Pd. Upon this method, compound **4** was converted to product **5** in a yield of 91%.

3.2. Influence of the pressure of O₂, solvent choice and HNO₃ loading on the oxidation

2,4-Dinitrotoluene (2,4-DNT) was selected as a typical substrate for the study of the influence of the pressure of O₂ and solvent choice (Table 1) on the oxidation.

Oxidation with air is more economical than with oxygen, but in our system, the conversion rate with air (run 3, 54%) was much lower than that with oxygen (runs 1 and 2, up to 99%). When the initial oxygen pressure was 0.2 MPa, a maximum pressure of 0.45 MPa was observed during the reaction. Literature reports [12–14] acetic acid as the solvent due to the excellent solubility of the catalyst in this acid [23]. Perfluoronaphthalene was also a good medium for the oxidation reaction [24], which worked well for our system with yields up to 99% (run 4). This solvent, however, was so expensive that it was not suitable for large-scale applications. Benzotrifluoride and other ionic liquids have been successfully applied to nitrations with NHPI [25,26], but runs 5–7 did not adapt well to our oxidation system. When using methanesulfonic acid as the solvent, it was observed that the final products contained unknown side products (run 8). Based on the above results, the optimum conditions for the

Table 2
Oxidation of TNT under various conditions.^a

Run	Temp. (°C)	Catalyst (mol%)	O ₂ (MPa)	Conv. (%)	Selectivity of acid (%)
1	120	20	0.2	86	70
2	100	20	0.2	82	>99
3	80	20	0.2	25	>99
4	30	20	0.2	0	0
5	100	0	0.2	0	0
6	100	20	0.2	71 ^b	>99 ^b
7	100	10	2	88 (90) ^c	89 (87) ^c
8	100	5	2	84 ^d	97 ^d

^a 1 mmol TNT was reacted under O₂ in the presence of THICA in AcOH (2 ml) with conc. HNO₃ (0.2 ml) for 20 h. The conversion and selectivity were based on HPLC.

^b Co(AcO)₂ (1 mol%) and Mn(AcO)₂ (0.5 mol%) were added.

^c Isolated data.

^d The solvent was perfluoronaphthalene.

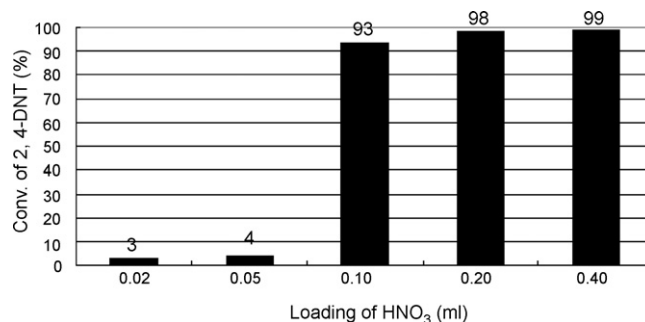


Fig. 2. Influence of loading of HNO₃ on oxidation of 2,4-DNT. 1 mmol 2,4-DNT was reacted under O₂ in the presence of THICA (10 mol%) in AcOH (2 ml) at 100 °C for 20 h.

catalyzed oxidation were ascertained to be 0.2 MPa O₂ with acetic acid as the solvent.

The influence of HNO₃ loading was studied (Fig. 2) through trials of different mole ratios between substrate and HNO₃. Although the maximum conversion was obtained by adding 0.4 ml of HNO₃ (the mole ratio was about 1:8), a fewer HNO₃ loading of 0.2 ml (the ratio was 1:4) showed almost the same performance with only a little decrease in conversion rate 98%. It is noted that when ratios were lower than 1:1, only little (4%) substrate was oxidized into carboxylic acid.

3.3. Oxidation of TNT

2,4,6-Trinitrotoluene (TNT) is a conventional monomer explosive that can make wastewater difficult to process and is being replaced by other high-energy explosives. Chemical conversion of this explosive to insensitive materials, such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [2,27,28], is therefore of great significance to wastewater processing. The oxidation of the methyl to a carboxyl on the benzene ring of TNT is essential for these conversions. To our knowledge, TNT can only

Table 3
Oxidation of substituted toluenes with THICA as the catalyst.^a

Run	Substrate	Catalyst (mol%)	Time (h)	Conv. (%)	Selectivity of acid (%)
1	Toluene	1	10	>99	>99
2	2-Chlorotoluene	5	14	>99	>99
3	o-Nitrotoluene	5	14	>99	>99
4	m-Nitrotoluene	5	14	97	>99
5	p-Nitrotoluene	5	14	>99	>99
6	2,4-Dinitrotoluene	10	20	>99	>99
7	2,6-Dinitrotoluene	10	20	71(95 ^b)	>99
8	3,4-Dinitrotoluene	10	20	>99	>99
9	3-Chloro-4-nitrotoluene	10	20	>99	>99
10	2-Chloro-4-nitrotoluene	10	20	>99	>99
11	4-Methyl-3-nitropyridine	10	20	30	>99
12	4-Methoxytoluene	3	10	>99	93

^a 1 mmol substrate was reacted under O₂ (0.2 MPa) in the presence of THICA in AcOH (2 ml) with conc. HNO₃ (0.2 ml) at 100 °C; the conversion and selectivity were based on HPLC.

^b 20 mol% catalyst was added to the reaction.

be oxidized through the method using potassium dichromate [1,2].

To improve such chromium-containing wastewater processing, the oxidation of TNT was extensively studied under various conditions in our new catalytic system (Table 2).

At 120 °C, the conversion rate of TNT was the highest, but simultaneously the accompanying decarboxylation also occurred, leading to the lowest selectivity of acid (run 1). At 80 °C the conversion rate was the lowest (run 3, 25%) which could be ascribed to the slow decomposition of nitric acid at the lower temperature of 80 °C [29,30]. There was no reaction at room temperature (run 4). At 100 °C, TNT was converted into carboxylic acid in a yield of 82% (run 2). It was ascertained that no reaction took place without THICA (run 5) in the reaction mixture. We also compared the effect of Co acetate and Mn acetate as co-catalysts (run 6), indicating that our new, metal-free system was more efficient than a system containing either Co or Mn salts. To reduce the load of THICA from 20 mol% of substrate to 10 mol%, the pressure of O₂ should be increased from 0.2 to 2 MPa (run 7, experiment conducted in a 100 ml stainless steel reactor, and the maximum pressure was 5.2 MPa during reaction) and the conversion rate raised from 82% to 88% but decarboxylation took place during the process. When we tried to further decrease the catalyst load to 5 mol% under the same conditions, the conversion rate dropped substantially to 57% (not listed). By using perfluoronaphthalene instead of acetic acid, however, the load of catalyst could be decreased to 5 mol% with little decrease in the conversion rate (run 8, 84%), while the decarboxylation side reaction was also suppressed. Furthermore, the isolated yield was close to the HPLC yield (run 6), suggesting that there was no decomposition of either TNT or product during the oxidation.

3.4. Oxidation of other substituted toluenes with strong electron-withdrawing groups

To extend the scope of this oxidation method, we chose a series of other substituted toluenes with different strong electron-withdrawing groups as substrates and applied the new catalytic system to their oxidation. Table 3 shows the catalytic efficiency and selectivity of our catalytic system. As can be seen from the table, most of the substrates tested were converted into the desired carboxylic acids in high yields.

As an example, benzoic acid is a very important intermediate in organic synthesis and is manufactured exclusively by a cobalt-catalyzed liquid-phase air oxidation of toluene [31] that suffers from a low reaction rate [32]. In our metal-free system, however, it was obtained in an almost quantitative yield using a very low load of catalyst (1 mol%) in a short time (10 h, run 1).

As the number of electron-withdrawing groups, such as nitro groups or halogens, increases, the methyl on the benzene ring becomes more difficult to oxidize. For example, the C–H bond energy of methyl group on the benzene ring increases about 5 kJ/mol when toluene was substituted by a nitro group at its meta position [33,34]. Additionally, we have computed the average C–H bond length of methyl group of TNT, 2,4-DNT and 4-nitrotoluene using the B3LYP/6-31G method, showing that TNT owned the shortest bond length (1.091 Å), 2,4-DNT the moderate length (1.093 Å) and 4-nitrotoluene the longest length (1.096 Å). Generally a longer bond length represents a weaker bond. In other words the order of the difficulty of oxidation is supposed to be: 4-nitrotoluene < 2,4-DNT < TNT. This was proved by our experiments that larger amounts of catalyst were loaded (from 5 to 10 mol%) or the reaction time was prolonged (from 14 to 20 h) to achieve complete oxidation (runs 2–11).

Oxidation of chloro-substituted toluene was also examined (run 2). 2-Chlorobenzoic acid is of great commercial interest as an intermediate in the production of saccharin, agricultural chemicals and dyes. For oxidation in our system, the acid yield reached nearly 100%, showing the potential industrial application value of our catalytic system. Additionally, when compared to the literature [5–7,13], nitrotoluenes were oxidized successfully into carboxylic acids in this system with yields of almost 100%, which were not affected by the position of the nitro group (runs 3–5). According to the literatures [34,35], the bond energy of m-nitrotoluene is about 2 kJ/mol larger than the p-nitrotoluene. It seems reasonable to observe in our case that the conversion of m-nitrotoluene is 3% lower than that of p-nitrotoluene under the same reaction condition.

Dinitrobenzoic acids were usually produced through nitration of nitrobenzoic acids because DNTs were resistant to oxidation. In our system, however, DNTs were oxidized into acids in excellent yields of approximately 99% (runs 6 and 8). The conversion of 2,6-DNT was slightly lower than the other DNT isomers because of the steric effect of two ortho nitro groups [36], whereas the selectivity of the carboxylic acid was as remarkable as that for other DNTs. When the catalyst loading raised to 20 mol%, 2,6-DNT was converted to the acid product in a good conversion rate of 95% (run 7b).

Generally, the nitrogen atom on the ring of 4-methyl-3-nitropyridine was believed to be easier to oxidize than the methyl group. In our system, only the methyl group was selectively oxidized (run 11). There are two reasons that may account for the low conversion. One is that the nitrogen atom likely has a large inactivating effect towards the ring and methyl group. To prove this, we calculated the structure of TNT and 4-methyl-3-nitropyridine by the B3LYP/6-31G method. For the C–H bond of methyl group, the average population value of 4-methyl-3-nitropyridine (0.3597)

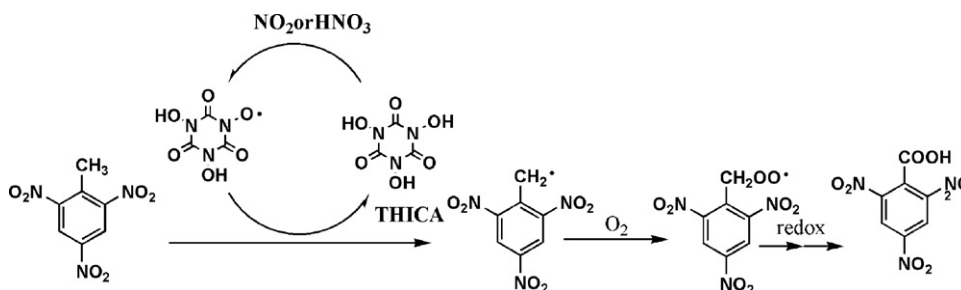


Fig. 3. A possible mechanism of the catalytic oxidation of TNT.

is larger than that of TNT (0.3561) using the SCF density, which indicates 4-methyl-3-nitropyridine owned a stronger C–H bond of methyl group than TNT. The other reason may be that part of 4-methyl-3-nitropyridine could combine nitric acid to a nitrate salt, just like pyridine did [37].

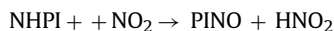
When the substrate was substituted in toluene containing electron-donating group, such as 4-methoxy group (run 12), the desired acid product was obtained in a yield of 93% while 4-methoxy-nitrotoluene was a by-product detected by GC–MS.

3.5. The mechanism of the oxidation

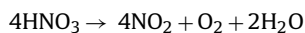
Ishii et al. have done in-depth research on the catalytic mechanism of NHPI [38,39]. According to their proposed mechanism, Co (III) would first abstract the hydrogen atom from NHPI to form the phthalimide N-oxyl (PINO) radical. The resulting PINO abstracts the hydrogen atom of a methyl group, forming the benzyl radical that leads to subsequent reactions. When using THICA, an analogue of NHPI, they suggested a similar catalytic process also occurs.

Our catalytic system was free of heavy metals, but the oxidation was still applied successfully to the oxidation of nitrotoluenes. We believe that nitric acid can be an alternative to heavy metals in the initiation of the reaction.

In fact, the literatures [40–43] have reported oxidation using nitric acid at high temperature. For instance, TNT can be oxidized into trinitrobenzene or trinitrobenzoic acid by nitric acid at high temperature over 190 °C. The oxidation of nitric acid is closely linked with the catalysis of NO₂ produced by decomposition of nitric acid when heating or lighting [29,44]. The literatures [25,45,46] reported both nitric acid and NO₂ can induce the production of catalyst NHPI radical:



Similarly, in our THICA catalysis system, both nitric acid and NO₂ could directly abstract hydrogen from THICA to form its radical. Herein nitric acid plays another role that is to produce NO₂ through its decomposition under heating condition [30]:



Notably when we added NaNO₂ (50 mol%) to the AcOH solution without addition of HNO₃, we observed the reddish brown gas (NO₂) during the reaction under conditions described in Fig. 2, and in the end 25% substrate was converted. This testified the catalysis of NO₂ in the process of oxidation.

Taking the oxidation of TNT for example, we proposed a possible mechanism of catalytic oxidation. First, HNO₃ and NO₂ convert the THICA into its radical by abstracting a hydrogen atom from THICA. The THICA radical then abstracts the hydrogen atom from the methyl of TNT to form the corresponding benzyl radical (shown in Fig. 3). This benzyl radical is then readily captured by O₂ to give

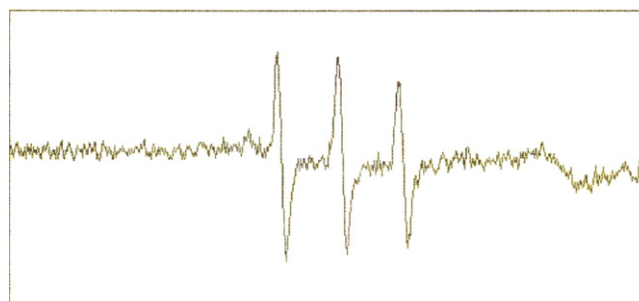


Fig. 4. ESR spectrum of the THICA radical.

a benzylperoxy radical, followed by a complicated redox process to finally produce the carboxyl acid.

The production of the THICA radical in nitric acid was observed through ESR measurements. By heating the nitric acid solution of THICA, we observed the radical signal of THICA ($g = 2.00075$, $A_N = 4.86\text{G}$) as shown in Fig. 4. This signal then disappeared upon addition of 2,4-DNT to the solution. This proved that our system was based on a radical process rather than a mechanism based on a carbon anion under basic conditions [5,7]. Thus, our oxidation system can be applied to a much wider range of substrates, as compared with the literature [5,7].

4. Conclusion

We have developed a new, metal-free aerobic oxidation system catalyzed by THICA, avoiding the use of heavy metals in either of the processes of preparation or utilization of the catalyst. By using this catalytic approach, nitrotoluenes, especially polynitrotoluenes such as TNT, were efficiently converted into the desired carboxylic acids in yields up to 99%. We also suggested a possible mechanism of this catalytic method, which undergoes a radical process observed by ESR measurements.

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