Surfactant-Assisted Selective Oxidation of Aromatic Amines to Nitro Compounds by in Situ-Formed Performic Acid

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Supporting Information

ABSTRACT: Development of novel and greener methods for the selective oxidation of various organic compounds is a challenging task. Herein, a novel protocol for the selective oxidation of aromatic amines to nitroaromatics at room temperature is developed. The oxidation reaction was carried out using a mixture of formic acid and aqueous hydrogen peroxide, which resulted in the in situ formation of performic acid. Further, improvement of selectivity was studied using different surfactants, of which cetyltrimethylammonium bromide (CTAB) gave the highest selectivity (85%) toward nitrobenzene. The role of CTAB in achieving higher selectivity is discussed. Under optimized reaction conditions, various substituted amines were successfully oxidized to corresponding nitro compounds. It is worth mentioning that this is the first report on oxidation of amines to nitro compounds in an aqueous medium with high selectivity.

INTRODUCTION

The selective oxidation of amines to the desired product is a challenging task.1 It leads to the formation of hydroxylamine, nitroso, nitro, oxime, azone, azo compounds, etc., and most of them are very reactive, which lead to the formation of self-condensed products. However, all of them are very attractive synthons and could be used in the synthesis of a variety of products in pharmaceutical, perfumery, explosive, and dye industries.2 There are numerous pathways reported for the synthesis of nitro compounds via the electrophilic substitution reaction using a hazardous nitrating mixture, diazotization of amines, and oxidation of aniline (Scheme 1).2 However, these reported methods require harsh reaction conditions and handling of spent acid is the primary environmental concern. Apart from this, many nitro-substituted compounds are difficult to synthesize via the aforementioned methods.3 Many research groups have focused on the development of novel ecofriendly methods using different catalysts and oxidants. The first report on the oxidation of aromatic amines to nitroaromatics was studied in depth by Emmons et al. using anhydrous peracetic acid as an oxidant to achieve selective nitroaromatics.4 However, the use of anhydrous conditions is industrially not feasible. Hence, the development of an alternate method is desired. For this purpose, many homogeneous and heterogeneous catalysts were reported. However, there are only a few reports available on the use of a homogeneous catalyst for oxidation of amines. For instance, Doyle et al. reported the use of the dirhodium caprolactamate/T-HYDRO homogeneous catalyst for oxidation of substituted aniline to nitro compounds.5 In another report, Defoin et al. reported the use of molybdenum complex for selective oxidation of aniline to nitrosobenzene at room temperature with 53–80% yield.6 Furthermore, several heterogeneous catalysts like MnO2, Pb(OAc)2, Hg(OAc)2, W, Zr, Re, Ti, Au, Cu, Ag, Co, etc. were also used to achieve mediocre to good selectivity.7–17 Also, Ti/
Cr silicates,

18 various heteropolyacids,19 and Nb2O5 20 have also been reported to achieve maximum selectivity. Ranga Rao et al. used methyl imidazolium phosphotungstate as a catalyst for selective oxidation of aniline to nitrobenzene using m-MCPBA as an oxidant.21 These catalysts have a drawback in terms of either poor selectivity or the cost of the catalysts used. The use of a greener and safer oxidant like H2O2 or oxygen is an advantage.

Thus, from the environmental point of view, many research groups have been interested in using greener oxidants and solvent or solvent-free conditions. Additionally, there are a very few literature reports available for selective formation of nitro compounds from arylamines, wherein the selectivity toward nitroarenes is controlled by a surfactant/ionic liquid, by varying the concentration of oxidant or pH.22 The use of cetyltrimethylammonium bromide (CTAB) with tungstophosphoric acid (H2O2 as and when required to oxidize arylamines to could in situ generate performic acid when mixed with 50% aq acid, which is cheaply available and an ideal solvent as well as solvents or solvent-free conditions. Additionally, there are a very few research papers available for selective formation of nitro compounds from arylamines, wherein the selectivity toward nitroarenes is controlled by a surfactant/ionic liquid, by varying the concentration of oxidant or pH.22

RESULTS AND DISCUSSION

Oxidation of aniline leads to the formation of various products like hydroxylamine, nitroso, nitro, oxime, azoxy, and azo compounds as shown in Scheme 2. As stated earlier, the selective oxidation of arylamines is a difficult task. Herein, we have developed a novel method for selective formation of nitro compounds.

Initially, oxidation of aniline was tested in the presence of only hydrogen peroxide, which gave no reaction (Table 1, entry 1). This indicates that hydrogen peroxide is not efficient to oxidize aniline to any product. Further, the reaction conducted using formic acid and hydrogen peroxide to nitrobenzene compounds. Further, crude nitrobenzene was purified by a column chromatography method using silica gel (100–200 mesh) as the stationary phase and eluted by hexane/ethylacetate (95:5) as an eluent. Yields were calculated based on isolated products. Products were characterized by gas chromatography–mass spectrometry (GC–MS) and NMR spectroscopy (Supporting Information (SI), S1). The GC–MS spectra of the products are shown in SI, Figures S1–S8. The 1H and 13C NMR spectra are shown in SI, Figures S9–S26, and data is given below.

1H NMR and 13C NMR.

1. Nitrobenzene: Yellow liquid: 1H NMR (600 MHz, CDCl3) δ 8.24 (d, J = 8.3 Hz, 2H), 7.73 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.9 Hz, 2H); 13C (1H) NMR (150 MHz, CDCl3) δ 148.24 (s), 134.69 (s), 129.39 (s), 123.53 (s).

2. 4-Nitrotoluene: Reddish yellow solid: 1H NMR (600 MHz, CDCl3) δ 8.11 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H); 13C (1H) NMR (150 MHz, CDCl3) δ 146.13 (d, J = 22.9 Hz), 129.88 (s), 123.57 (s), 21.67 (s).

3. 1-Ethyl-4-nitrobenzene: Yellow liquid: 1H NMR (600 MHz, CDCl3) δ 8.15 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 2.72 (m, 2H), 1.18 (t, 3H); 13C (1H) NMR (150 MHz, CDCl3) δ 152.08 (s), 146.34 (s), 128.71 (s), 123.72 (s), 29.19 (s), 15.02 (s).

4. 1-Butyl-nitrobenzene: Yellow liquid: 1H NMR (600 MHz, CDCl3) δ 8.12 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 2.78–2.68 (m, 2H), 1.62 (dd, J = 15.1, 7.9 Hz, 2H), 1.36 (dd, J = 14.8, 7.7 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H); 13C (1H) NMR (150 MHz, CDCl3) δ 150.92 (s), 146.28 (s), 129.22 (s), 123.60 (s), 35.62 (s), 33.16 (s), 22.32 (s), 13.89 (s).

5. 2,4-Dimethyl-nitrobenzene: Yellow liquid: 1H NMR (600 MHz, CDCl3) δ 7.90 (d, J = 8.1 Hz, 1H), 7.12 (d, J = 8.7 Hz, 2H), 2.58 (s, 3H), 2.39 (s, 3H); 13C (1H) NMR (150 MHz, CDCl3) δ 146.98 (s), 144.25 (s), 133.87 (s), 133.42 (s), 127.53 (s), 124.97 (s), 21.37 (s), 20.77 (s).

6. 1-Fluoro-4-nitrobenzene: Yellow liquid: 1H NMR (600 MHz, CDCl3) δ 8.14 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H); 13C (1H) NMR (150 MHz, CDCl3) δ 167.19 (s), 144.45 (s), 126.35 (s), 116.55 (s).

7. 1-Bromo-4-nitrobenzene: Pale yellow solid: 1H NMR (600 MHz, CDCl3) δ 7.98–7.89 (m, 4H); 13C (1H) NMR (150 MHz, CDCl3) δ 138.74 (s), 124.93 (s).

8. 1-Iodo-4-nitrobenzene: Pale yellow solid: 1H NMR (600 MHz, CDCl3) δ 7.95 (d, J = 8.8 Hz, 2H), 7.92 (d, 2H); 13C (1H) NMR (150 MHz, CDCl3) δ 138.75 (s), 124.93 (s), 102.76 (s).

9. 1,4-Dinitrobenzene: Yellow solid: 1H NMR (600 MHz, CDCl3) δ 8.43; 13C (1H) NMR δ 151.15 (s), 124.88 (s).
comprised in water by the hydrophobic core of micelles can solubilize hydrophobic reactants. Strukul et al. reported the asymmetric Baeyer–Villiger oxidation with Co(Salen) and H$_2$O$_2$ in water, and the yield and selectivity of the desired product both increased compared to those without the surfactant. The polar or nonpolar nature of an organocatalyst dictates its affinity for the micellar environment or the aqueous phase, and this influences the outcome of the reaction. Novač and co-workers have proposed the oxidation of benzyl alcohol, and the reaction rate was increased by using an anionic surfactant, sodium dodecyl sulfate, for the dissolution of the substrate. The amphiphilic nature of the surfactants controls the selectivity of the product by altering the reaction rate and chemoselectivity. Thus, we also used various surfactants like trimethyl(tetra-decyl ammonium bromide), CTAB, poly(vinyl pyrrolidone), and potassium bromide as additives in this reaction. It was observed that the cationic surfactants increase the selectivity of the product by altering the reaction rate and chemoselectivity. Among these, CTAB showed better selectivity toward nitrobenzene. The selectivity for nitrobenzene increased from 42\% (Table 1, entry 6) to 81\% (Table 2, entry 6). As stated earlier, CTAB might stabilize the nitroso intermediate and avoid the further addition to aniline to form the azoxy compounds and thus results in the selective formation of nitrobenzene.

The effect of the concentration of hydrogen peroxide was studied by varying the molar ratio of aniline to H$_2$O$_2$. With the increase in the concentration of H$_2$O$_2$, the conversion of aniline and selectivity to nitrobenzene both increased. This shows that the formation of peroxymethyl acid is directly dependent on H$_2$O$_2$ concentration (Table 3).

The longer reaction time for the oxidation of aniline to corresponding nitrobenzenes is well reported in the literature. However, in our case, the reaction time was much less, precisely 15 min (Table 4, entry 2). No substantial change in the selectivity was observed with a further increase in the reaction time (Table 4, entry 3). Also, our results were compared with those reported in the literature, and comparative data is given in SI, Table S1.

To demonstrate the versatility of our developed protocol, we have further extended our protocol for oxidation of differently substituted amines to nitro compounds. When p-toluidine was used as the substrate, a complete conversion of p-toluidine was observed with 90\% selectivity and 75\% yield of p-nitrotoluene in 15 min. Similarly, the electron-donating alkyl substituents gave better selectivity toward corresponding nitro products (Table 5, entries 5 and 9). However, the aniline with electron-withdrawing substituents gave moderate selectivity (Table 5, entry 6). In the case of halogen substituents, the selectivity decreased due to the self-aromatic nucleophilic substitution (Table 5, entries 8 and 9). This did not happen in the case of fluorine due to the poor leaving nature of fluorine (Table 5, entry 7). In the case of benzylamine and benzylhydroxylamine, no conversion was observed, which indicates that the aromatic ring is activating the oxidation reaction.

The proposed mechanism for oxidation of aniline to nitrobenzene is depicted in Scheme 3. The addition of H$_2$O$_2$ to formic acid results in the in situ formation of performic acid. With 20 mg of CTAB, conv.: conversion of aniline.

### Table 1. Results of Solvent Variation on Oxidation of Aniline$^a$

| entry | solvent  | oxidant (mL) | conv. (%) | selectivity (%) |
|-------|----------|--------------|-----------|-----------------|
| 1     | -        | 0.8          | 0         | 0 0 0 0         |
| 2     | -        | 0.8          | 0         | 0 0 0 0         |
| 3     | formic acid$^b$ | 0           | 98        | 0 4 0 0         |
| 4     | CH$_3$CN | 0.8          | 86        | 4 12 84         |
| 5     | toluene  | 0.8          | 61        | 0 48 52         |
| 6     | formic acid | 0.8        | 97        | 42 8 50         |
| 7     | acetic acid | 0.8        | 18        | 0 100 0         |

$^a$Reaction conditions: aniline (2.68 mmol), formic acid (26.5 mmol), 50\% H$_2$O$_2$ (13.5 mmol), 35 °C, 15 min.

### Table 2. Results of Surfactant on the Selectivity of Nitrobenzene$^a$

| entry | additives                  | conv. (%) | selectivity (%) |
|-------|----------------------------|-----------|-----------------|
| 1     | poly(vinyl pyrrolidone)    | 100       | 34 2 64         |
| 2     | potassium bromide          | 100       | 37 7 56         |
| 3     | sodium bromide             | 100       | 25 37 38        |
| 4     | tetra-n-butyl ammonium bromide | 100       | 44 4 52         |
| 5     | trimethyl(tetra-decyl ammonium bromide) | 100       | 50 2 48         |
| 6     | cetyltrimethylammonium bromide | 100       | 81 9 10         |

$^a$Reaction conditions: aniline (2.68 mmol), formic acid (26.5 mmol), 50\% H$_2$O$_2$ (13.5 mmol), 35 °C, 15 min, conv.: conversion of aniline.

### Table 3. Results of Molar Ratio Variation Studies$^a$

| entry | aniline/H$_2$O$_2$ molar ratio | conv. (%) | selectivity (%) |
|-------|-------------------------------|-----------|-----------------|
| 1     | 1:1                           | 16        | 16 11 73        |
| 2     | 1:2                           | 87        | 22 38 40        |
| 3     | 1:3                           | 96        | 40 22 38        |
| 4     | 1:4                           | 100       | 64 10 26        |
| 5     | 1:5                           | 100       | 81 9 10         |
| 6     | 1:6                           | 100       | 81 9 10         |

$^a$Reaction conditions: aniline (2.68 mmol), formic acid (26.5 mmol), 50\% H$_2$O$_2$ (13.5 mmol), CTAB (20 mg), 35 °C, 15 min, conv.: conversion of aniline.

### Table 4. Results of Time Variation$^a$

| entry | time (min) | aniline/H$_2$O$_2$ molar ratio | conv. (%) | selectivity (%) |
|-------|------------|-------------------------------|-----------|-----------------|
| 1     | 10         | 1:5                           | 100       | 78 8 16         |
| 2     | 15         | 1:5                           | 100       | 81 9 10         |
| 3     | 20         | 1:5                           | 100       | 81 7 12         |

$^a$Reaction conditions: aniline (2.68 mmol), formic acid (26.5 mmol), 50\% H$_2$O$_2$ (13.5 mmol), CTAB (20 mg), 35 °C, conv.: conversion of aniline.
the solubility of the organic substrates as well as oxidizing agents in the liquid phase and at the same time catalytic activity in free radical reactions. It is a well-established fact that the oxygen atoms of peracids are not in the same electronic environment; the oxygen atom of the carbonyl group is nucleophilic and the other one is electrophilic. It is expected that the positively charged CTAB will interact with the negatively charged oxygen atom of peracids to favor the formation of radicals. The formed radicals interact with aniline to give the \( \text{N-phenylhydroxylamine} \) radical and subsequently \( \text{N-hydroxy-N-phenylhydroxylamine} \). Then, formic acid transfers the proton to \( \text{N-hydroxy-N-phenylhydroxylamine} \) to give the corresponding nitroso product, which again interacts with performic acid and abstracts the electron-deicient oxygen, forming a final nitro product.

### CONCLUSIONS

In conclusion, we have developed a method for oxidation of various aromatic amines to selectively produce nitro compounds (39–92%) using aqueous hydrogen peroxide under mild reaction conditions by following a metal-free, ecofriendly, and economically viable protocol. The high selectivity of nitro compounds using a greener oxidant like aq H\(_2\)O\(_2\) is reported within a short period of 15 min. The optimized protocol was also applied for selective oxidation of various substituted aromatic amines, where the electron-donating substituents gave good selectivity above 92%, while the electron-withdrawing substituents gave moderate (48%) selectivity. This protocol would be beneficial for many organic transformations.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00543.

Spectroscopic and analytical data as well as the original copy of GC−MS and \(^1\)H and \(^{13}\)C NMR spectra of all new compounds (PDF)

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The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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