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Mechanism of 5-amino-2-formylbenzene sulfonic acid formation during reduction of 4,4′-dinitrostilbene-2,2′-disulfonic acid by Zero-Valent Iron

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Abstract

5-Amino-2-formylbenzene sulfonic acid (ABAS) as a by-product during reduction of 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) by Zero-Valent Iron has been detected. Experiments show that the pH and temperature are the most important factors controlling the formation of ABAS. In addition, diluted solution of DNS (<0.001 mol/L) favors the formation of ABAS other than 4,4′-diaminostilbene-2,2′-disulfonic acid (DSD). Competitive oxidative reactions in dark with the cleavage of C═C double bond by $Fe(OH)^{2+}$ between DNS and DSD may occur during the reduction process. In addition, we provide mechanistic explanations for the pH, temperature and initial concentration dependences of ABAS formation. Optimized conditions with pH being 5.5 and rapid cooling following incubation have been applied to yield DSD with purity of more than 99.0%.

Keywords: 5-Amino-2-formylbenzene sulfonic acid; Mechanism; Zero-Valent Iron; 4,4′-Dinitrostilbene-2,2′-disulfonic acid; 4,4′-Diaminostilbene-2,2′-disulfonic acid; $Fe(OH)^{2+}$

1. Introduction

(*trans*)-4,4′-Diaminostilbene-2,2′-disulfonic acid (DSD) is an important industrial intermediate widely used in producing direct dyes, fluorescent brighteners and mothproof agents [1]. Over the last decades, a great deal of interest has developed in the synthesis of DSD by reduction of 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) [2–6]. As a consequence, the mechanism leading to by-products has been widely investigated.

cis-DSD, as the dominant by-product, is due to a rapid photoisomerisation of *trans*-DSD in aqueous solution exposure to light or heat [7]. 4-Amino-4′-nitrostilbene-2,2′-disulfonic acid comes from incomplete reduction of DNS [8]. Selective reduction of the C═C double bond in DNS results in 4,4′-diamino-2,2′-bibenzyldisulfonic acid [9]. Azoxy and azo compounds are also frequently observed in significant yields from nitro reduction [10]. Other impurities contained, such as *p*-aminotoluene-2-sulfonic acid and *p*-nitrotoluene-2-sulfonic acid, evidently come from DND and its impurities [11].

However, scarce study has reached 5-amino-2-formylbenzene sulfonic acid (ABAS) during the past decades perhaps due to negligence or lack of authentic standard. Since by-products significantly reduce the yield and quality of desired product, and are difficult to be separated, study on the formation of ABAS as a by-product is of great importance.

Therefore, one of the objectives of this work was to get a comprehensive knowledge of DNS reduction to develop strategies for manufacture. The other was to provide a model to further develop the mechanistic understanding of the nitro aromatic compounds (with C═C double bond)/Fe^0 aqueous systems, which is the most commonly used synthetic method for aniline manufacturing. The effects of pH, initial concentration of DNS and temperature on the formation of ABAS were studied, and the mechanism of formation of 5-amino-2-formylbenzene sulfonic acid was proposed.

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2. Materials and methods

2.1. Chemicals

4,4′-Dinitrostilbene-2,2′-disulfonic acid (DNS) was supplied by Huayu Chemicals Co. and recrystallized from water to get a purity of 99.5%. 5-Amino-2-formylbenzene sulfonic acid (ABAS) was supplied by Bayer Chemicals Ltd with a purity of 90.4%. The powdered iron used in this study had a coarser grain size (mostly >40 mesh) and is commercially available. Other chemical reagents and solvents were either analytic or chromatography grade and used without further purification.

2.2. Reduction of DNS

Water (500 mL) was added at room temperature to powdered iron (100%; 150 g) in a 1000 mL four-neck round-bottom flask. H_2SO_4 (98%, 0.3 mL) and acetic acid (99%, 0.6 mL), as the catalyst, were added to the stirring mixture, followed by continuous heating for 1 h at 100 °C. Reduction began by the addition of DNS with desired concentration by needle injection. The mixture solution was maintained at certain pH by adding either H_2SO_4 or sodium carbonate anhydrous solution with great care. When charging of the DNS was completed, the mixture was incubated at 100 °C for desired time. Then Fe_3O_4 was filtrated from the mixture solution following which 50% (v/v) NaOH was slowly charged to get a solution with a pH of 9.5. DSD was crystallized out from the filtrate by adjusting the pH to 1 with 30% H_2SO_4 and filtrated.

2.3. HPLC analysis

The DSD and by-products were analyzed by reverse-phase high performance liquid chromatography (Hitachi L-2000) equipped with a quaternary gradient pump and a variable wavelength absorbance detector. The sample was separated at room temperature on a 250 mm × 4.6 mm Spherisorb ODS-2 (5 μm pore size) C18-column. A mixture of water, methanol, and 1.7 g/L tetrabutylammonium hydrogen sulfate buffered with 0.05 M phosphate at pH 7 was used as eluent. For analytical separations, the sample of the final product was dissolved in the same eluent or was periodically taken from the reactor followed by dilution with eluent after cooling with ice-water, and then analyzed by HPLC and 20-μL portions were injected. Reduction products were identified by comparing the retention times with available pure standards.

3. Results and discussion

3.1. By-product identification

HPLC chromatograms of 5-amino-2-formylbenzene sulfonic acid (ABAS) authentic sample and DSD with its by-products are shown in Fig. 1. Reduction products were identified by comparing the retention times with available pure standards. ABAS was identified as a by-product of DSD (Fig. 1(a)) by comparison with the authentic sample (Fig. 1(b)). It should be noted that by-product of 1 in both (a) and (b) is supposed to be 4-amino-2-sulfo-benzoic acid but there was lack of authentic standard.

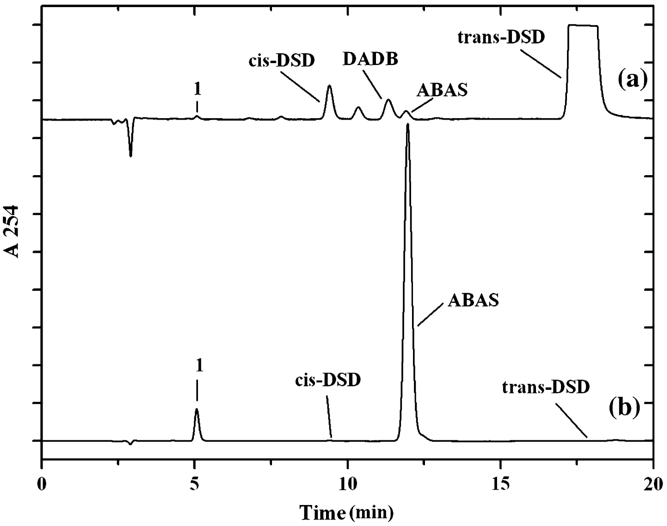


Fig. 1. HPLC chromatograms of ABAS (a) and DSD with its by-products (b).

3.2. The effect of pH

Quick decrease of pH was observed with the charging of DNS during the reduction. It is proposed to be due to the zero salt effect [12]. Under the point of zero salt effect (PZSE), which is the pH where the total surface charge is unaffected by increasing the salt concentration, addition of DNS sodium salt resulted in the immediate decrease in pH. Resume of pH seems to be caused by the combination effect of the aqueous corrosion of the Fe^0 [10] and the protonation of the amino ($-NH_2$) groups in DSD. Since varying pH (3–7) was involved in this process, it was anticipated that pH would influence the formation of 5-amino-2-formylbenzene sulfonic acid (ABAS).

In order to find out the relationship between pH and the formation of ABAS, the reduction of DNS by the procedure described above in various pH was investigated (Fig. 2). It is clear from Fig. 2 that the percentage of ABAS contained in the final product decreases quickly with increasing pH from 3 to 4, and level off gradually in the pH range 4–7. It indicates that the formation of ABAS would be favored under a low pH. Since the pH range of 5–7 showed only a small difference in the amount of the ABAS, the pH of 5.5 was used for the later experiments in order to minimize the error from pH.

3.3. The effect of concentrations of DNS

The influence of initial DNS concentrations on the formation of 5-amino-2-formylbenzene sulfonic acid (ABAS) is shown in Fig. 3. Fig. 3 shows similar trend at different concentrations of DNS with that at different pH. It is observed that

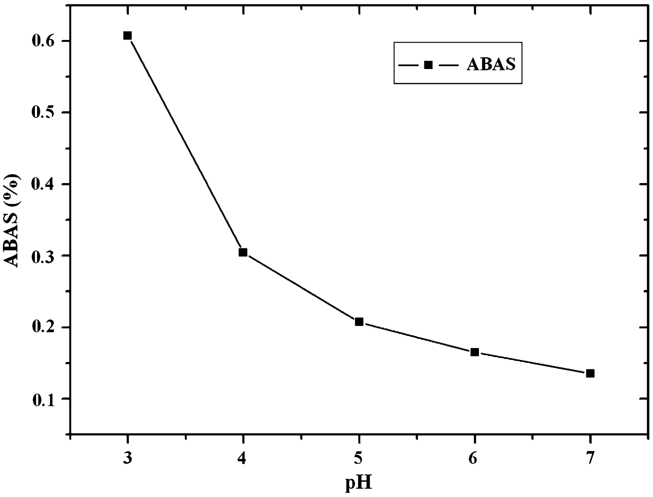


Fig. 2. The effect of pH on the percentage of ABAS. The experiments were carried out under the conditions of constant initial DNS concentration (100 g/L) and incubation of 5 min at 100 °C.

the percentage of ABAS drops rapidly before a concentration of 0.001 mol/L and then decreases gradually. It is proposed that highly diluted solution of DNS tends to favor the by-product formation.

3.4. The effect of incubation and temperature

Instead of discussing the effect of temperature on the formation of 5-amino-2-formylbenzene sulfonic acid (ABAS) during the charging of DNS, we focused on the incubation process in order to minimize the error from pH. Experiment was skillfully arranged by separating the mixture into two parts to investigate the influence of incubation. After incubation (either 0 or 60 min), each part was filtrated to remove the Fe^0 and Fe_3O_4, and then divided into three portions to place at different temperatures (0,10, 90 °C) with desired time. The experimental results are shown in Fig. 4.

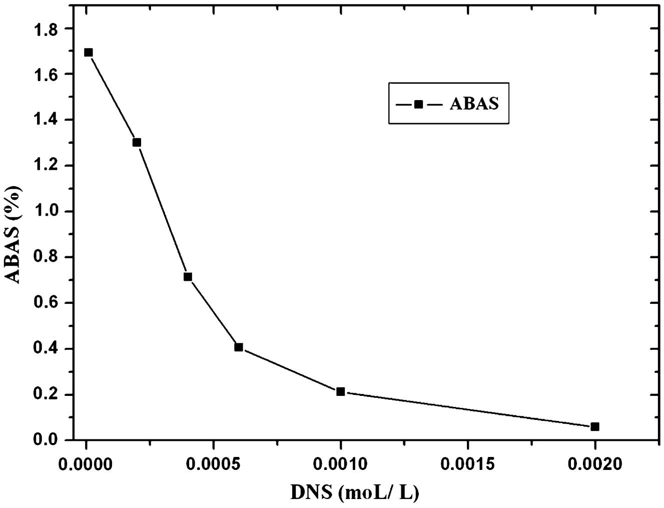


Fig. 3. The effect of DNS concentrations on the percentage of ABAS. The experiments were carried out under the conditions of pH 5.5 with constant incubation of 5 min at 100 °C.

It is observed from Fig. 4 that incubation for 60 min has only a small difference with 0 min in the percentage of ABAS at the same temperatures. It could be explained by the simultaneous increase of ABAS and DAS since formation of ABAS is competitive with the reduction of DNS. It is anticipated that the removal of Fe^0 does not influence the formation of ABAS but would terminate the reduction of DNS. The assumption is confirmed by the increase of ABAS after 120 min with the temperature increasing from 0 to 90 °C (Fig. 4). It is observed that higher the temperature, faster the increase of ABAS. This indicates that temperature is a dominant factor influencing the formation of ABAS, at least in incubation conditions.

3.5. Mechanisms

Perhaps due to relatively small yield and unavailable standard, ABAS and its derivatives have received little attention in the past decades. A similar result came from Studer [3] who showed that more than 1% ABAS was founded during the hydrogenation. Unfortunately, the authors gave neither further details nor the mechanism involved. The reduction in this work was performed in dark and pure DNS without 4-nitro-2-sulfobenzaldehyde (NBS) (checked by HPLC) was used, thus ruling out the possibilities that ABAS may come from the degradation of DSD under solar light [13] and the reduction of NBS, contained as impurity in the starting material, [1] by Fe^0, respectively.

The result indicates that the DNS/Fe^0 aqueous system is initiating an oxidation with the cleavage of C=C double bond besides the reduction process. Since preliminary studies have demonstrated that hydroxyl radicals and ferryl species were involved in the reduction by Fe^0 in aqueous system [14], two possible pathways in the formation of ABAS are proposed by sharing the similar mechanism of DSD degradation

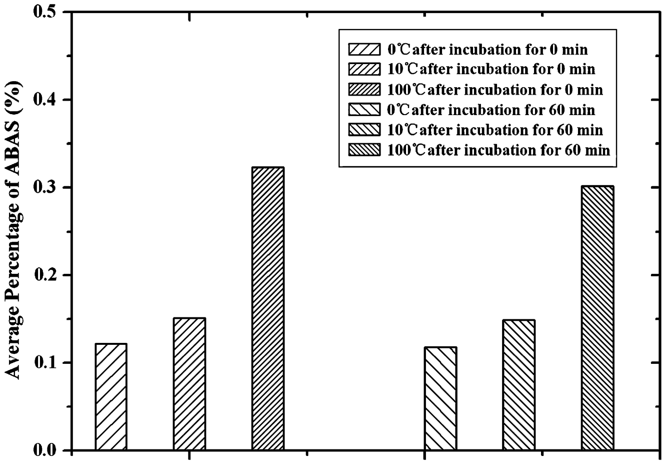


Fig. 4. The effects of incubation time and temperature on the percentage of ABAS. Reduction was performed with 40 mesh granular iron at pH = 5.5 and 100 °C with 200 mL DNS (initial concentration = 100 g/L), followed by incubation for either 0 or 60 min. Then, mixtures after incubation were filtrated to remove the Fe and Fe_3O_4 and divided into three portions to place at different temperatures (0,10, 90 °C) for 120 min.

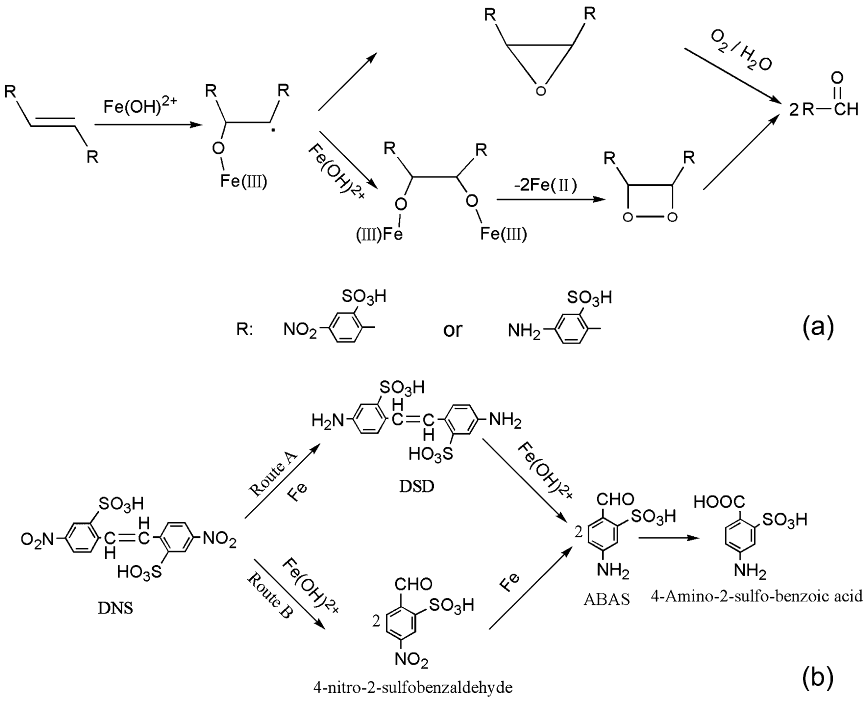
by $Fe(OH)^{2+}$ [15]. A complex between the DNS or DSD and Fe(III) is formed and gives rise to an intermediate radical with Fe(III) linked to the ethylenic carbon through the oxygen atom. In this case, intramolecular photoredoxes lead to the formation of benzaldehyde through dioxo bridge or epoxide derivative (Scheme 1(a)). It should be noted that two mechanisms are provided to explain the formation of ABAS. The first way (route A in Scheme 1(b)) is due to the oxidative cleavage of the double bond in DSD by $Fe(OH)^{2+}$ following the DNS reduction by Fe^0. An alternate pathway to ABAS (route B in Scheme 1(b)) could occur if the NBS which is resulted from the double bond cleavage of DNS by $Fe(OH)^{2+}$ is further reduced by Fe^0 to form aniline. Ultimate products of the two mechanisms are Fe^{2+}, ABAS and its derivative (4-amino-2-sulfo-benzoic acid).

Possible processes concerning the formation of ferrous iron and hydrogen peroxide are shown in Table 1. Fe^{3+} may come from the dissolution of hydroxides ($Fe(OH)_3$) (Eq. (7) in Table 1), which are partly soluble in acid solution. But a more possible resource may be the oxidation of Fe^{2+} which is largely existing in this Fe^0/aqueous system. Reduction of DNS is achieved by a series of two-electron additions with the intermediates of nitroso and hydroxylamino. At the same time, Fe^{2+}, finally leads to Fe_3O_4, is formed with Fe^0 as the ultimate electron donor [10]. Although direct electron transfer from Fe^0 to the nitro group mainly result in the production of Fe^{2+}, further oxidation of Fe^{2+} by O_2, H_2O_2 and DNS may also produce Fe^{3+} or $Fe(OH)^{2+}$(Eqs. (4)–(6) in Table 1). In this way, the $Fe(OH)^{2+}$ is reactivated thereby becoming ready for a new degradation process.

With the pH range below 4, one expects trivalent iron to be present largely in ionic form in solution [16] and more ABAS to be formed. This is in line with our result above. Increasing percentage of ABAS was observed with the increase of temperature and decrease of DNS concentration. This can also be explained by the presence of relatively excessive $Fe(OH)^{2+}$ and higher reaction rate accelerated by higher temperature. Concerning the formation of ABAS in the study by Studer, it is proposed to be due to the similar degradation by the transition metal (e.g. Pt, used as catalyst in hydrogenation) complexes in aqueous solution. It should be noted that competitive oxidations by $Fe(OH)^{2+}$may occur during the reduction process due to the similarities of DNS and DSD. Further kinetic study should be carried out in order to elucidate the formation of ABAS and its derivatives.

4. Conclusion

5-Amino-2-formylbenzene sulfonic acid (ABAS) and its derivatives are obtained as by-products formed during the reduction of DNS by Zero-Valent Iron. The effects of pH, temperature and initial concentrations of DNS on the formation of ABAS were investigated in this study. The experiment shows that pH is the most important factor controlling the formation of ABAS during the reduction at constant temperature (100 °C). Temperature, replacing pH after incubation, becomes the dominant factor. We can also conclude that highly diluted solution of DNS favors the formation of ABAS. Two kind of mechanisms are proposed based on the oxidative cleavage of C=C double bond in either DNS or DSD by $Fe(OH)^{2+}$. The mechanisms concerning the formation of ABAS and its derivatives are shown in Scheme 1. Competitive oxidative reactions with the cleavage of C=C double bond between DNS and DSD may occur during the reduction process. In addition, we provide the mechanistic explanations for the pH, temperature and initial concentration dependences of ABAS formation. The most important point is, under the optimized conditions with a pH being about 5.5 and rapid



Scheme 1. Formation of ABAS and its derivative.

Table 1
Possible reactions involved in the formation of ferrous iron and hydrogen peroxide

$$2Fe^0 + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O \tag{1}$$

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{2}$$

$$ArNO_2 + 3Fe^0 + 6H^+ \rightarrow ArNH_2 + 3Fe^{2+} + 2H_2O \tag{3}$$

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \tag{4}$$

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + Fe(OH)^{2+} \tag{5}$$

$$6Fe^{2+} + ArNO_2 + 6H^+ \rightarrow ArNH_2 + 6Fe^{3+} \tag{6}$$

$$Fe(OH)_3 \rightarrow Fe^{3+} + 3OH^- \tag{7}$$

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \tag{8}$$

$$Fe(OH)^{2+} \rightarrow Fe^{2+} + OH^{\bullet} \tag{9}$$

cooling after incubation, the percentages of ABAS and its derivatives drop quickly, and 3% increase of DSD is achieved.

Acknowledgement

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