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The bromination mechanism of 1-aminoanthraquinone-2,4-disulfonic acid in sulfuric acid

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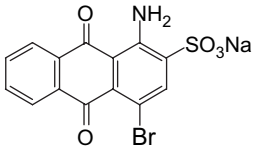
Abstract

1-Amino-4-bromoanthraquinone-2-sulfonic acid (bromoamine acid) is an important intermediate for dyes. 1-Aminoanthraquinone-2,4-disulfonic acid is the major impurity when 1-aminoanthraquinone is sulfonated in oleum to synthesize bromoamine acid. The mechanism of bromination of 1-aminoanthraquinone-2,4-disulfonic acid in sulfuric acid has been studied. It is proved that 1-aminoanthraquinone-2,4-disulfonic acid undergoes de-sulfonation first to form 1-aminoanthraquinone-2-sulfonic acid, and then bromination to form bromoamine acid. Based on this mechanism, a new optimal process for the synthesis of bromoamine acid is developed. In this way, bromoamine acid is afforded in high yield and good quality.

Keywords: Bromoamine acid; De-sulfonation; 1-Aminoanthraquinone-2,4-disulfonic acid

1. Introduction

1-Amino-4-bromoanthraquinone-2-sulfonic acid (bromoamine acid, BAA for short in this paper) is a valuable intermediate for dyes, especially acid and reactive dyes, usually in its sodium salt form.



There are two main conventional methods in sulfonation process of synthesizing bromoamine acid, solvent method and oleum method.

1-Aminoanthraquinone is sulfonated with chlorosulfonic acid in inert solvents (such as chlorobenzene, *o*-dichlorobenzene or nitrobenzene) to form a salt, then transformed intramolecularly to give 1-aminoanthraquinone-2-sulfonic acid, which is further brominated to bromoamine acid [1,2]. This is the so-called ''solvent method''.

1-Aminoanthraquinone is sulfonated with oleum to give 1-aminoanthraquinone-2-sulfonic acid (ASA-2) which is brominated by adding bromine in the same pot to give the target product [2–7]. The sodium salt is crystallized from the reaction mixture, and is refined to the required purity [8]. This is the so-called ''one-pot method'' or ''oleum method'', in which sulfonation and bromination are performed continuously. This process is simple and cost effective. However, compared with the ''solvent method'', the yield is relatively low and the quality is poor because of side reactions. About 40% of 1-aminoanthraquinone-2,4-disulfonic acid (ADS), the major by-product of sulfonation, is formed in conventional sulfonation condition.

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In this work, we found that the by-product ADS can be converted to the product BAA during bromination at conventional condition. This leads to a great improvement in the quality and the yield of BAA. The mechanism of this process is discussed.

2. Experimental

1-Aminoanthraquinone (98%) (AAQ), bromoamine acid (BAA) (98%) which were used as standard samples for High Pressure Liquid Chromatography (HPLC) were provided by Zhongxing Chemicals Ltd. Others were prepared as below. Other chemicals were purchased commercially. ^{1}H NMR spectra were measured on Varian-400 MHz spectrometers.

2.1. Standard sample for HPLC analysis

2.1.1. 1-Aminoanthraquinone-2-sulfonic acid (ASA-2)

To a suspension of AAQ (22.3 g, 0.1 mol) and of *o*-dichlorobenzene (1200 g), chlorosulfonic acid (12.3 g, 0.105 mol) was added at 80 °C for 1.5 h. The reacting mixture was heated to 120 °C for 5 h before it was poured into 1500 g of water. The water layer was neutralized with NaOH, the water-insoluble solid was filtered off at 95 °C, and then cooled to room temperature. The precipitate was re-crystallized twice from water to give the desired ASA-2 (sodium salt).

^{1}H NMR (400 MHz, DMSO): δ 7.84 (d, 1H, H_3), 9.40 (d, 1H, H_4), 8.23 (d, 1H, H_5), 8.14 (d, 1H, H_8), 7.91 (m, 2H, H_6 and H_7).

2.1.2. 1-Aminoanthraquinone-2,4-disulfonic acid (ADS)

BAA (20.2 g, 0.05 mol), Na_2SO_3 (10.3 g, 0.1 mol) and water (500 g) were heated to reflux for 16 h, cooled to room temperature, filtered, then re-crystallized three times from water to give the desired ADS (disodium salt).

^{1}H NMR (400 MHz, DMSO): δ 8.60 (s, 1H, H_3), 8.09 (t, 2H, H_5H_8), 7.81 (m, 2H, H_6H_7).

2.1.3. 1-Amino-2-bromoanthraquinone (BAQ)

AAQ (22.3 g, 0.1 mol) was agitated in 80% sulfuric acid (200 g) at 70 °C. Bromine (16.8 g 0.105 mol) was added to this mixture during 3 h. The reacting mixture was agitated for another 2 h, and then diluted with water, filtered, and washed with water. Crude BAQ was re-crystallized three times from DMF to give the refined BAQ with a purity of 98.5%.

^{1}H NMR (400 MHz, DMSO): δ 7.36 (m, 1H, H_3), 7.94 (m, 1H, H_4), 8.13 (d, 1H, H_5), 8.22 (d, 1H, H8), 7.84 (m, 1H, H_6), 7.89 (m, 1H, H_7).

2.2. Analysis with HPLC

Equipment: HP1050 HPLC.

Analysis condition: Column: Spherisorb, C18, 5 μm, φ4.6 × 200 mm; fluent: 80% methanol and 20% water containing 1 g/l hexadecyltrimethylammonium bromide; fluent speed: 1 ml/min; detected wavelength: 254 nm.

Contents are given by area.

Analyzed results and compound codes are shown in Table 1.

2.3. Bromination of ADS in concentrated sulfuric acid

A mixture of ADS (disodium salt) (8.54 g, 0.02 mol) and 100% sulfuric acid (50 g) was heated to 80 °C. Then bromine (3.2 g, 0.02 mol) was added dropwise into the mixture at 80 °C for 8 h, and the reaction mixture was agitated at 80 °C for another 7 h. During the whole reaction time, the extra unreacted bromine was kept in reflux with a cold salt-water cooled condenser. A sample was taken from the reaction mixture for HPLC analysis at every 3 h.

2.4. Hydrolysis of ADS

2.4.1. Hydrolyzing in 100% sulfuric acid

A mixture of ADS (disodium salt) (8.54 g, 0.02 mol) and 100% sulfuric acid (50 g) was heated to 80 °C for 24 h. A sample was taken from the reaction mixture for HPLC analysis at every 8 h.

2.4.2. Hydrolyzing in 99% sulfuric acid

A mixture of ADS (disodium salt) (8.54 g, 0.02 mol) and 99% of sulfuric acid (50 g) was heated to 120 °C for 3 h. A sample was taken from the reaction mixture for HPLC analysis at every 1 h.

Table 1
The retention time of the main components on HPLC during sulfonation and bromination of BAA

Code	Components	Retention time (min)
AAQ	1-Aminoanthraquinone	7.52
ASA-2	1-Aminoanthraquinone-2-sulfonic acid	13.32
BAA	Bromoamine acid	18.24
ASA-4	1-Aminoanthraquinone-4-sulfonic acid	8.14[a]
BAQ	1-Amino-2-bromoanthraquinone	21.37
BAA-i	1-Amino-2-bromoanthraquinone-4-sulfonic acid	10.20[b]
ADS	1-Aminoanthraquinone-2,4-disulfonic acid	62.22

[a] Confirmed by detecting the transition components in the process of de-sulfonating of ADS.
[b] Confirmed by bromination of ASA-4.

Table 2
The contents of the products of sulfonating 1-amino-anthraquinone by convention oleum method

Code	Components	Content (HPLC area %)
AAQ	1-Aminoanthraquinone	1
ASA-2	1-Aminoanthraquinone-2-sulfonic acid	48
ADS	1-Aminoanthraquinone-2,4-disulfonic acid	37
	Others	14

2.5. The improved process for BAA manufacture

A mixture of AAQ (22.3 g, 0.1 mol) and oleum (100 g, containing 15% SO_3) was heated to 130 °C for 6 h until the sum of the content ASA-2 and ADS reached the maximum (91%). The sulfonating solution was cooled to 110 °C, and water (2.1 g) was added into it. The solution was kept at 120 °C for 3 h until almost all of the ADS were hydrolyzed. The hydrolyzed solution was brominated at 80 °C for 8 h by adding bromine (12 g, 0.075 mol), and 86.5% of AAQ was converted to BAA [9].

3. Results and discussion

3.1. The contents of brominating products by conventional method

In the process of synthesizing bromoamine acid by conventional "oleum method", several impurities were formed, nearly 40% of ADS was formed among the other impurities (Table 2). These impurities were carried to next step, bromination.

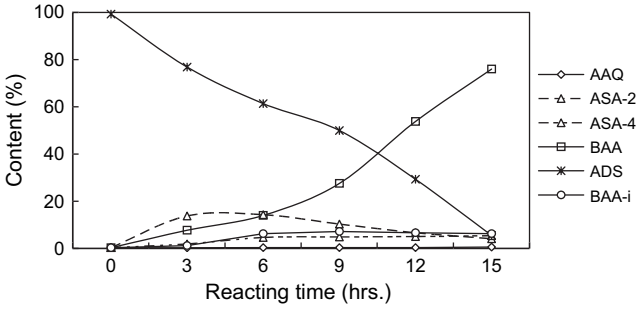


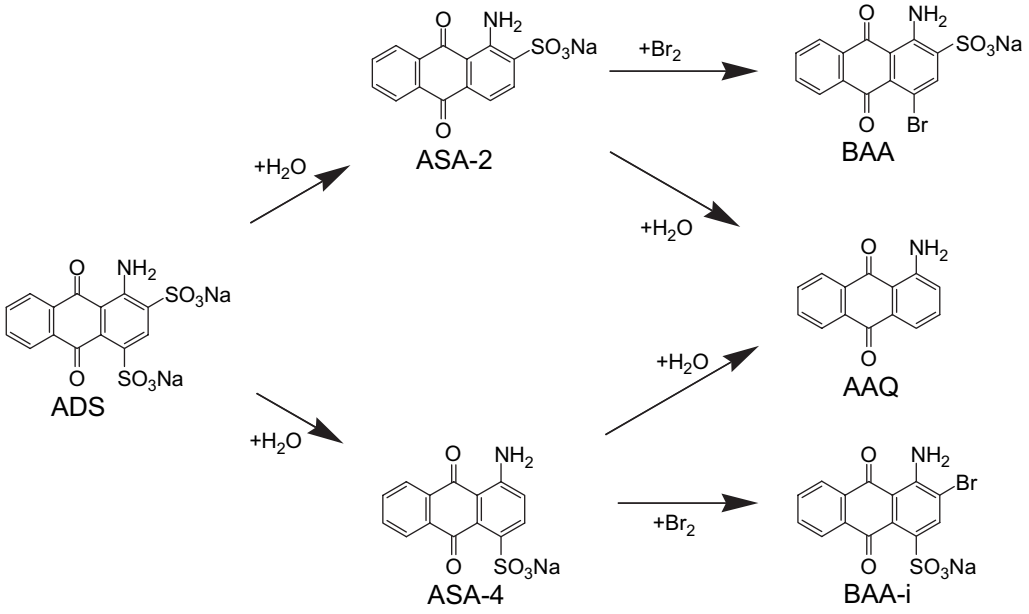
Fig. 1. The results of HPLC tracing for the bromination of ADS.

In conventional manufacture of BAA, bromination time is about 8 h in 100% sulfuric acid at 80 °C until ASA-2 disappeared, but a lot of ADS still existed. We found that ADS was converted to BAA if the reaction time was prolonged. This leads us to a further study of the mechanism of this process.

3.2. The conversion from ADS to BAA and its mechanism

To test our idea, pure ADS was brominated under the conditions of preparing BAA (in 100% sulfonic acid at 80 °C). The reaction was monitored with HPLC. 1-Aminoanthraquinone-2-sulfonic acid (ASA-2) and 1-aminoanthraquinone-4-sulfonic acid (ASA-4) were found as the intermediates and finally 95% ADS reacted and 75% of it was converted to BAA (Fig. 1).

The following mechanism is proposed: 1-aminoanthraquinone-2,4-disulfonic acid undergoes de-sulfonation first, and then bromination of 1-aminoanthraquinone



Scheme 1.

Table 3
The hydrolysis behavior of 1-aminoanthraquinone-2,4-disulfonic acid in 100% sulfuric acid

Hydrolysis time (h)	Content (HPLC area %)			
	ADS	ASA-2	ASA-4	AAQ
0	99.05	0.95	0	0
8	72.64	22.04	3.45	0
16	0.63	83.06	12.04	1.60
24	0	83.67	11.70	2.60

mono-sulfonic acid to form BAA and its isomer, as it is shown in Scheme 1.

The question is: could ADS be de-sulfonated in 100% sulfuric acid. In order to prove the above mechanism, ADS was reacted with 100% sulfuric acid under the same conditions but without adding bromine. The result shows that most of ADS were hydrolyzed to ASA-2 and ASA-4, and little amount of AAQ was also found (Table 3).

If the reaction is carried out at 120 °C in 99% sulfuric acid, all ADS were hydrolyzed after 3 h, and 83% of ADS was converted to ASA-2 and 12% of which was converted to ASA-4. Little amount of water present is very favorable to hydrolyzation of ADS (Fig. 2).

Due to higher electron density, the sulfo group located on position 4 of ADS is more easily hydrolyzed than that of position 2. When one of the sulfo groups of ADS is hydrolyzed, the remaining sulfo groups become more inactive, and therefore only 3–5% of AAQ could be detected at end of the reaction. Then ASA-2 is converted to BAA on bromination and, at the same time, ASA-4 is converted to 1-amino-2-bromoanthraquinone-4-sulfonic acid (BAA-i), the isomer of BAA, which can be detected by HPLC. This means that the mechanism of bromination of ADS assumed above is plausible.

3.3. The improved process for manufacturing BAA based on this mechanism

Based on the fact that most of the by-product ADS can be converted to product BAA and addition of a little water increases hydrolyzation rate, a new optimized process of preparation of BAA by "oleum method" is developed. Both ASA-2 and ADS are considered as valuable intermediates for the preparation of BAA. This concept is used for sulfonation of AAQ, optimized condition is given by sulfonation of AAQ with 4 times of 15% oleum (w/w) for 5 h at 140 °C, 65% of ASA-2 and 26% of ADS with 9% other impurities (AAQ 3% and ASA-4 acid 3%) were achieved.

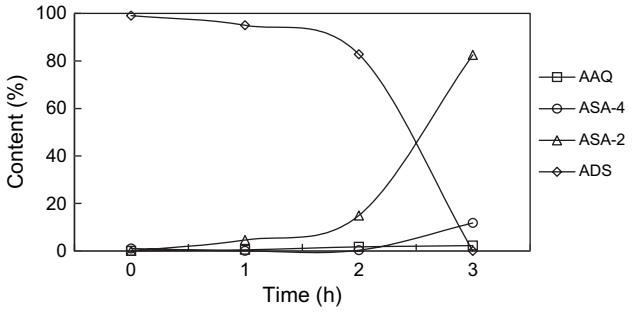


Fig. 2. De-sulfonation of 1-aminoanthraquinone-2,4-disulfonic acid in 99% sulfuric acid 120 °C.

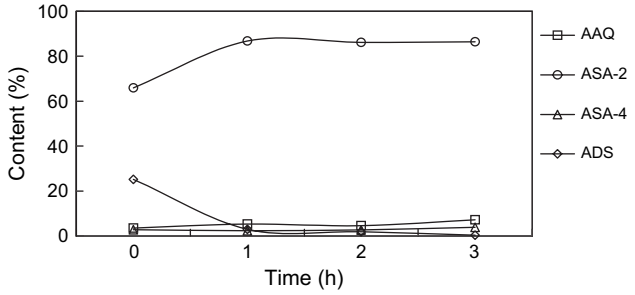


Fig. 3. The reactant consists of de-sulfonation for the sulfonating products of 1-aminoanthraquinone.

The sulfonation solution was adjusted that the concentration of sulfuric acid is 99% by adding a little amount of water. Then de-sulfonation was performed at 120 °C for 3 h (Fig. 3). Eighty-seven percent of starting material (AAQ) had been converted to ASA-2.

Then the hydrolyzed solution was used for bromination directly at 80 °C for 7 h by dropping bromine. Almost all of the 1-aminoanthraquinone-2-sulfonic acid was converted to bromoamine acid. The overall yield of 86.5% from AAQ to BAA was achieved [9]. This yield is much higher than that by conventional technology (maximum of 83% was ever reported, less than 78% in actual mass production).

4. Conclusions

1-Amino-anthraquinone-2,4-disulfonic acid (ADS) has been converted to bromoamine acid (BAA) by bromination in concentrated sulfuric acid during the preparation of bromoamine acid. Mechanistic study shows that it is via the hydrolysis of the 4-position sulfo group the bromination occurs. Based on these results, a new process is proposed. By regulating the effective sulfonating contents of 1-aminoanthraquinone (AAQ), adjusting the concentration of sulfuric acid (99%) to hydrolyze ADS acid to 1-aminoanthraquinone-2-sulfonic acid (ASA-2), and brominating the hydrolyzed product in same pot, 86.5% yield of bromoamine acid was achieved.

Acknowledgements

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