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Metal phthalocyanine catalyzed oxidation of 4-nitrotoluene-2-sulfonic acid to 4,4′-dinitrostilbene-2, 2′-disulfonic acid

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Abstract

The effects of catalyst, alkali concentration, 4-nitrotoluene-2-sulfonic acid concentration, reaction temperature, and time of preparation of 4,4′-dinitrostilbene-2,2′-disulfonic acid from 4-nitrotoluene-2-sulfonic acid was investigated. The results showed that the liquid-phase oxidation of 4-nitrotoluene-2-sulfonic acid under optimal conditions gives 4,4′-dinitrostilbene-2,2′-disulfonic acid in 81.8% yield and in 96.7% purity.

Keywords: 4-Nitrotoluene-2-sulfonic acid; 4,4′-Dinitrostilbene-2,2′-disulfonic acid; Metal phthalocyanine catalysis; Synthesis; Liquid-phase oxidation

1. Introduction

Macromolecules such as enzymes have captured the eye of chemists for many years. Azotoenzyme in plants is able to turn N_2 into amines [1], and P-450 in blood enables O_2 to oxidize organisms selectively [2]. Both enzymes are metal-organic compounds.

After naturally occurring heme and chlorophyll were shown to be iron porphyrin and magnesium porphyrin compounds, respectively [3], metal phthalocyanines were used as analogs of enzyme catalysts and were shown to effect catalytic oxidations at room temperature [4–6].

4,4′-Diaminostilbene-2,2′-disulfonic acid (DSD acid) is an important precursor for fluorescent whiteners and dyes. It is the compound for a variety of optical brighteners, direct dyes and reactive dyes that are listed in the Color Index. More than 2000 tons of DSD acid are produced in China every year [7]. Normally, DSD acid is synthesized by oxidizing 4-nitrotoluene-2-sulfonic acid (NTS) to 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) and then reducing DNS by catalytic hydrogenation or dissolving metal reduction. The present method for converting NTS to DNS involves air oxidation using alkaline NaOH and $FeSO_4$. Oxidation is followed by acidification and salting, giving a yield of 65–74%. Many approaches to increasing the yield of this reaction have been developed; One involves the use of LiOH instead of NaC [8,9], but the former is expensive and cannot be recycled easily. Another approach involves using an organic solvent such as DMSO or DMF as the reaction medium [10,11], but a large volume of solvent is required and it can not be recycled easily. A third approach uses NaOCl or Cl_2 instead of oxygen for the oxidation process and

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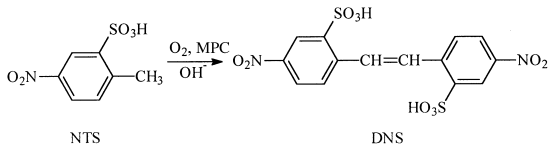
increases the yield to 85% [12–14]. Unfortunately, storing and transporting NaOCl poses potential environmental problems. The present paper pertains to the synthesis of DNS, by oxidizing NTS in the presence of metal phthalocyanines (MPc) (Scheme 1).



Scheme 1. Oxidation of NTS to DNS using MPC catalysis.

2. Experimental

2.1. Synthesis of DNS under optimum conditions

NTS (3.4 g, 0.01 mol) was dissolved in H_2O (20 ml) in a three-necked round bottom flask. Oxygen was bubbled into the solution with stirring, and a solution of NaOH (1.05 g) in H_2O (6.3 ml) was added dropwise. After the reaction mixture was heated to 50°C, MPc (34 mg) was added, the reaction was heated to 60°C at the rate of 1°C/h, and stirred for 8 h. After cooling to room temperature, the pH was adjusted to 3–4 with 50% H_2SO_4 and solid NaCl (4.8 g) was added. The precipitate was collected and dried.

2.2. Selection of catalyst

NTS (3.4g, 0.01 mol) was dissolved in H_2O (20 ml) in a three-necked round bottom flask. Oxygen was bubbled into the solution with stirring and a solution of NaOH (1.65g) in H_2O (12 ml) was added dropwise. After the reaction mixture was heated to 50°C, the catalyst was added, and the reaction mixture was treated as described in Section 2.1 above.

2.3. Selection and optimization of base

The procedure was the same as described in Section 2.1 above, except that a solution of base in H_2O (6.3 ml) and MPc (39 mg) were used.

2.4. Influence of NTS concentration

Different amounts of NTS were dissolved in water (20 ml) in a three-necked round bottom flask. Oxygen was bubbled into the solution with stirring and a solution of NaOH (1.05 g) in H_2O (6.3 ml) was added dropwise. After the reaction mixture was heated to 50°C, MPc (34 mg) was added, then the reaction mixture was treated as described in Section 2.1 above.

2.5. Influence of reaction temperature

The procedure was the same as described in Section 2.4 except that the catalyst was added at 10°C below the final reaction temprature. The temperature was then raised at the rate of 1°C/h and stirred for 8 h.

2.6. Influence of reaction time

NTS (3.4 g, 0.01 mol) was dissolved in H_2O (20 ml) in a three-necked round bottom flask. Oxygen was bubbled into the solution with stirring and a solution of NaOH (1.05 g) in H_2O (6.3 ml) was added dropwise. After the reaction mixture was heated to 50°C, MPc (34 mg) was added, the reaction was heated to 60°C at the rate of 1°C/h, stirred at 60°C, and the reaction mixture was treated as described in Section 2.1 above.

2.7. Analysis of DNS

The structure of DNS was analyzed by ^1H NMR using a JEOL FX-90Q spectrometer. D_2O was used as solvent and TMS as the internal standard. The purity of DNS was also assessed with a UV3100 Ultraviolet–Visible-NIR spectrophotometer using the working curve method [15].

3. Results and discussion

3.1. Structure confirmation

DNS was examined by ^1H NMR, the results of which are shown in Fig. 1 and Table 1. It is clear that the data are consistent with the structure.

3.2. Oxidation of NTS to DNS

3.2.1. Selection and optimization of catalyst

The influence of different catalysts on the yield of DNS was studied and the results are shown in Table 2. It can be seen from Table 2 that the yield of DNS was only 60.8% when no catalyst was involved, and that each catalyst increased the yield. Since MPc gave the best yield and it is economical and readily available, it was used as catalyst for the remainder of this study. To determine the optimum catalyst/NTS ratio, 0, 0.2, 0.4, 0.6, 0.8, 1, 1.2 and 1.4% catalytic amounts of MPc were used. The results are shown in Fig. 2. It can be seen that increasing the amount of catalyst gave an increase in yield but the yield started to approach linearity after 1.0%. It is also clear that the purity of the product decreased incrementally as the amount of MPc catalyst was increased. Based on these results, 1.0% catalyst was selected as optimum.

3.2.2. Selection and optimization of base

The influence of different bases on the reaction yield was studied, the results of which are shown in Table 3. NaOH and LiOH proved to be more suitable for this reaction. When KOH was used an azo compound formed, indicating that the basicity of KOH was too great. On the other hand, $Ca(OH)_2$ was not basic enough to effect oxidation. Consequently, NaOH was selected as the preferred base. The influence of different NaOH concentrations on reaction yield was studied and the results are shown in Fig. 3. It was determined that the yield of DNS increased rapidly, with increased

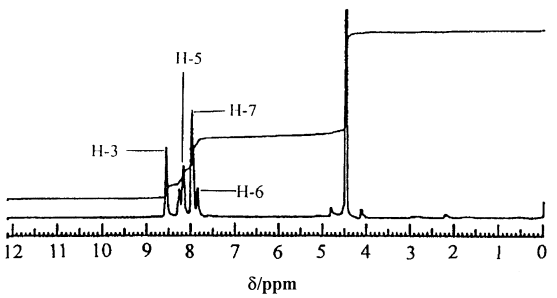


Fig. 1. ^1H NMR spectrum of DNS in D_2O.

Table 2
Effects of catalyst on the yield of DNS

Catalyst		$MnSO_4$	$FeCl_2$	$MnSO_4 + FeCl_2$	FePc	MPc
Yield (%)	60.8	70.1	71.2	75.3	78.0	78.9

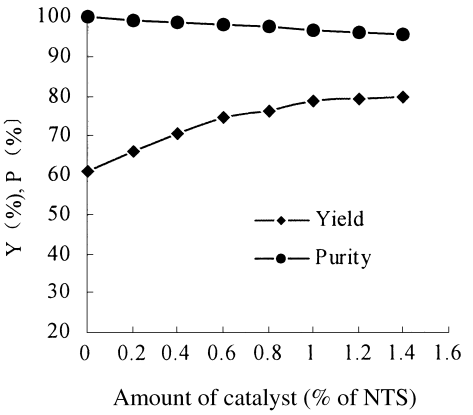
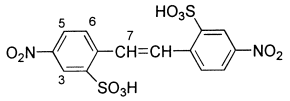


Fig. 2. Effect of MPc on yield and purity of DNS.

Table 3
Effect of different bases on the yield of DNS

Base	NaOH	LiOH	KOH	$Ca(OH)_2$
Yield (%)	78.2	74.6	31.2	0

Table 1
Structure and ^1H NMR data of DNS

Structure	Proton	Chemical shift (δ, ppm)	Coupling constant (*J*, Hz)
	H-3	8.54 (s)	–
	H-5	8.21 (d)	8.50
	H-6	7.84 (d)	8.50
	H-7	8.00 (s)	–

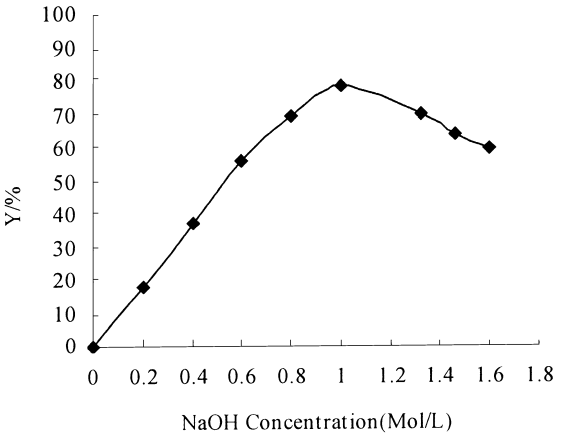


Fig. 3. Effect of NaOH concentration on the yield of DNS.

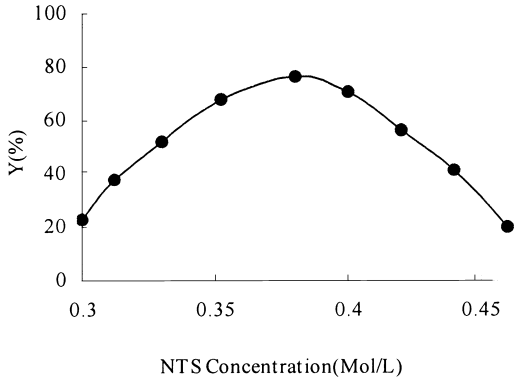


Fig. 4. Effect of NTS concentration on the yield of DNS.

concentration, reaching a maximum at 1 mol/L. Above that concentration, an azo compound formed.

3.2.3. *Influence of NTS concentration*

Fig. 4 shows that the starting NTS concentration had a significant effect on the yield of DNS. The data show that the yield of DNS increased sharply over the 0.30–0.38 mol/L range, and then decreased sharply. At concentrations above 0.38 mol/L, precipitation or foaming occurred and formation of an azo compound began.

3.2.4. *Influence of reaction temperature*

Our search for the optimum temperature led to the data shown in Table 4. Low yields resulted at temperatures below 60°C, owing to incomplete dissolution of NTS. When the reaction temperature was higher than 60°C, the crude product contained an azo compound.

Table 4
Effect of reaction time on the yield of DNS

Temperature (°C)	45	50	55	60	65	70
Yield (%)	11.5	22.3	36.8	78.6	72.4	67.9

Table 5
Effect of reaction time on the yield of DNS

Time (h)	1	4	6	8	10	12	14	16	18	20	22
NTS (%)	65.1	36.7	14.9	11.1	7.5	5.3	4.1	2.0	0.2	0	0
DNS (%)	10.2	41.7	45.2	48.8	58.8	71.9	74.6	79.8	82.1	72.1	66.3

3.2.5. *Influence of reaction time*

The percentages of NTS and DNS in the reaction mixture at different reaction time are shown in Table 5. It can be seen that the longer the reaction time, the higher the conversion of NTS to product. When the reaction time reached 18 h, the conversion of NTS was 99.8%. A further increase in reaction time caused a decrease in DNS concentration.

4. Conclusion

MPc catalyzed oxidation of NTS gives an 81.8% yield of DNS in an aqueous medium. The purity of the NTS produced was >96.7%.

Acknowledgements

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