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Kinetic study on the preparation of 4,4′-dinitrostilbene-2,2′-disulfonic acid (I)—kinetic study on the oxidation of 4,4′-dinitrobibenzyl-2,2′-disulfonic acid to prepare 4,4′-dinitrostilbene-2,2′-disulfonic acid

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Abstract

The aqueous air oxidation of 4, 4′-dinitrobibenzyl-2,2′-disulfonic acid (DND) to prepare 4,4′-dinitrostilbne-2,2′-disulfonic acid (DNS) is studied. It is shown that the by-product formation results from the destruction of DNS under certain conditions. Grounded on the experimental data, the rate equation of the oxidation of DND is established, which can be expressed as follows: $-d[DND] = dt = k[DND][OH]^{1.4}$. At the same time, the parametric values of macroscopic kinetics are obtained and interaction between temperature, hydroxide concentration, reaction time and conversion is discussed.

Keywords: 4,4′-Dinitrostilbene-2,2′-disulfonic acid; 4,4′-Dinitrobibenzyl-2,2′-disulfonic acid; Oxidation; Kinetics; Mechanism

1. Introduction

4,4′-Dinitrostilbene-2,2′-disulfonic Acid (DSD) is an industrial intermediate that is widely used in producing direct dyes, fluorescent brighteners and mothproof agents. The oxidation of *p*-nitrotoluene-*o*-sulfonic acid (NTS) to 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) is a key role in the synthesis of DSD; it is believed that the oxidative reaction is stepwise. NTS, existing in the form of its salt, (e.g. NaNTS if sodium hydroxide is the base) is firstly converted to a low water soluble intermediate 4,4′-dinitrobibenzyl-2,2′-disulfonic acid (DND) through a coupling reaction, which can be further oxidized to give the desired DNS. The reaction above can be summarized in Scheme 1.

Thus far, many methods have been developed for the reaction in which NTS is oxidized in the presence of an aqueous alkaline [1–5], organic solution [6–9] or an aqueous-organic solution [6,10,11]. Due to the low cost and operation efficiency, the air oxidation of NTS under aqueous alkaline conditions is widely adopted. However, this method only gives DNS in a yield of 86% or

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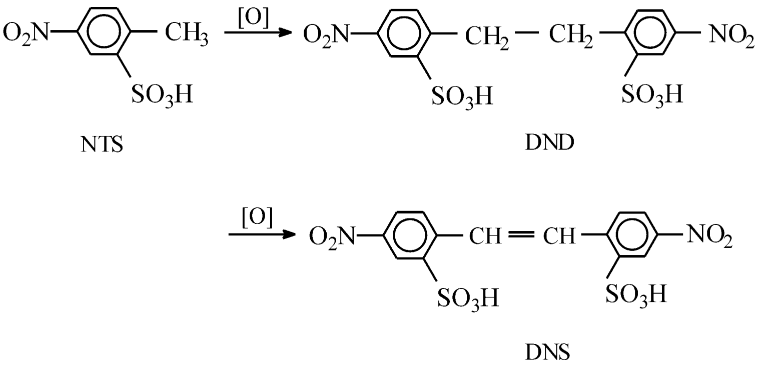
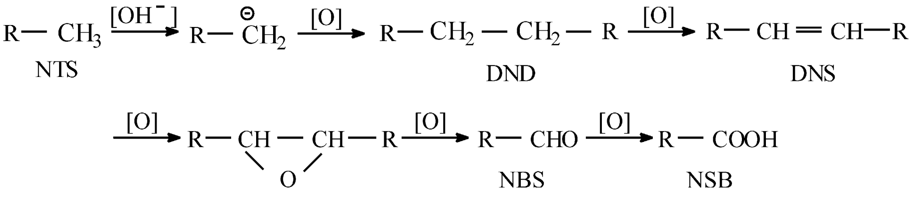
less, resulting from the formation of by-products mainly including 4-nitrobenzaldehyde-2-sulfonic acid (NBS) and 4-nitro-2-sulfobenzonic acid (NSB).

Two mechanisms concerning by-product formation have been elucidated. Lund [8] reported that the formation of NBS and NSB was the result of DNS oxidation, as Scheme 2 describes, whereas Miyata [12] concluded that NBS was the oxidative product of NTS and had nothing to do with DNS, as Scheme 3 indicates. Both authors agreed that the oxidation of DND gave only one product namely DNS.

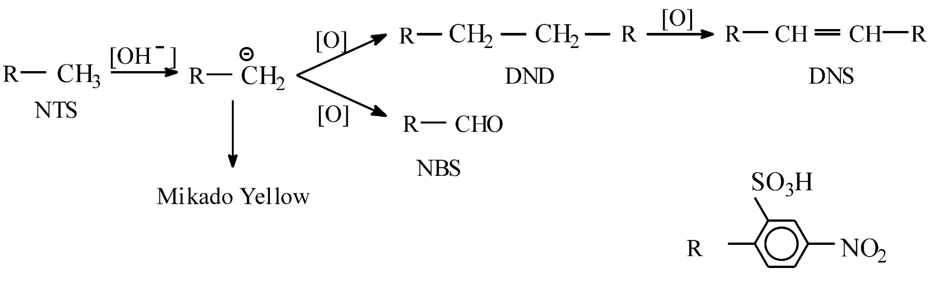
In order to test the two propositions, we conducted experiments on DNS oxidation and temperature and alkali (hydroxide) concentration ranges of 55~80 °C and 0.5~1.5 mol/L respectively. HPLC was employed to analyze the reactions and a potential mechanism has been proposed. At the same time, the appropriate reaction conditions were determined to ensure that the kinetics of the oxidation of DND to form DNS would not be disturbed by by-product formation. As a result, a kinetic model for the reaction was established and values of activation energy and frequency factor were determined. The experimental



Scheme 1.



Scheme 2.



Scheme 3.

results of the oxidation of NTS will be discussed in detail elsewhere.

2. Experimental

2.1. Materials

2.1.1. 4,4′-Dinitrobibenzyl-2,2′-disulfonic acid (DND)

DND was prepared according to [13] and was purified by recrystallization from sodium hydroxide aqueous solution until the purity of DND reached 98.2%.

2.1.2. 4,4′-Dinitrostilbene-2,2′-disulfonic acid (DNS)

DNS (Huayu Chemical Co., practical grade) was recrystallized from pour water for 4∼5 times to give purified product as pale yellow power (99.5%).

The purity of DND/DNS was checked by HPLC methods.

2.2. Oxidation apparatus and procedures

2.2.1. Oxidation of DNS

A five-neck round-bottomed flask equipped with constant speed agitator, thermometer, condenser and gas sparger below the stirrer was charged 0.1% DNS aqueous solution. After the stirred mixture was headed to the reaction temperature in a water bath, a calculated amount of concentrated aqueous sodium hydroxide was poured to it (zero time). Meanwhile, dried compressed air flow was admitted at a steady rate of 0.4 ml/min. A well-defined vortex with frothing was therefore developed. The temperature was kept constant. Samples of the reaction mixture were taken at appropriate intervals, solved in a mixture of water (0 °C) and concentrated HCl and analyzed by HPLC.

2.2.2. Oxidation of DND

All apparatus and procedures were as same as those described in Section 2.2.1 except that the material in the five-neck flask was a 0.1% DND aqueous solution.

2.3. Reaction product analysis

The samples were analyzed with a HPLC system (Hitachi, Japan) at 25±1 °C. The variable-wavelength detector was operated at 254 nm. The mobile phase consisted of methanol and water.

The identification of the reaction products was conducted by comparison of the HPLC peaks retention times (RT) with those corresponding to authentic samples. The RT values (in min) and the concentration (m%) of organic chemicals (shown in parentheses) in a typical run for DND oxidation in aqueous NaOH of 0.8 mol/L at 60 °C (90 min of reaction time) were as follows: DND: 8.438 (6.8074%), DNS: 10.038 (91.6291%), NBS: 2.310 (1.0045%), NSB: 1.878 (0.4859%).

3. Results and discussion

3.1. Mechanism

It was observed that the by-product formation was closely related to the temperature and the hydroxide concentration. The quantitative analysis of the HPLC spectra gave time profiles as shown in Table 1.

As seen, if the temperature and the hydroxide concentration were kept at a low level, the oxidation of DNS didn't yield NBS or NSB. Neither NBS nor NSB was detected by HPLC and the DNS concentration didn't fluctuate substantially. However, DNS reduced while NBS and NSB showed themselves when either the temperature or the hydroxide concentration was increased. The hydroxide concentration that might lead to the by-product formation descended with the raise in the temperature, and vice versa. From the fact that the total concentration of DNS. NBS and NSB maintained equivalent to the initial concentration of DNS on the whole, it was concluded that the NBS and NSB observed resulted from the destruction of DNS.

Thus, Scheme 2 was revised by our experimental results. That is: only under certain conditions, which mean high temperature and high alkaline concentration, do NBS and NSB form. Temperature and hydroxide are two factors determining whether DNS decomposes or not. It can also be concluded that the destruction of DNS displays no disturbance on the kinetic study of the DND oxidation with a temperature ranging from 55 to 75 °C and a hydroxide concentration ranging from 0.5 to 1.0 mol/L.

Data in Table 1 also indicated that the formation of NSB from DNS consisted of a two-step reaction with NBS as the intermediate because NBS always started to decay after reaching a maximum, while NSB continued to increase, if they appeared in the reaction mixture.

3.2. Kinetic studies

The reaction rate fluctuated as a function of the temperature and the hydroxide concentration. With the temperature or hydroxide concentration going up, it increased and vice versa, as reported in Figs. 1 and 2. That could also be concluded directly by observing the color of the reaction mixtures, which turned deeper with time. As the hydroxide concentration remained constant in every kinetic experiment, the rate law can be written:

$$\begin{aligned}\text{Rate} &= -\frac{\mathrm{d}[\text{DND}]}{\mathrm{d}t} = k[\text{DND}]^n[\text{OH}^-]^m \\ &= k'[\text{DND}]^n\end{aligned}$$

where $k' = k[\text{OH}^-]^m$

Linear coefficients of 0.986$\sim$0.99 observed in the plots of $-\ln[\text{DND}]$ vs. reaction time indicated that pseudo first order kinetics applied in each experiment.

The slope of $-\ln[\text{DND}]$ vs. reaction time represented the pseudo first order rate constant k'. So values of k' corresponding to different hydroxide concentrations at several temperatures ranging

Table 1
Product distribution (m%) in the oxidation of DNS

Temp.t' (°C)	Reaction time$t$ (min)	[NaOH] (mol/L)								
		0.5			1.0			1.5		
		DNS	NBS	NSB	DNS	NBS	NSB	DNS	NBS	NSB
55	0	98.22	–	–	98.15	–	–	98.26	–	–
	30	98.13	–	–	98.15	–	–	98.22	–	–
	60	98.16	–	–	98.20	–	–	98.17	–	–
	90	98.40	–	–	98.26	–	–	98.20	–	–
	120	98.21	–	–	98.11	–	–	98.16	–	–
	150	98.18	–	–	98.20	–	–	98.20	–	–
65	0	98.17	–	–	98.20	–	–	98.31	0	0
	30	98.20	–	–	98.20	–	–	98.11	0	0.10
	60	98.23	–	–	98.20	–	–	98.15	0.05	0.12
	90	98.22	–	–	98.23	–	–	97.90	0.08	0.27
	120	98.28	–	–	98.18	–	–	97.86	0.14	0.32
	150	98.18	–	–	98.19	–	–	97.80	0.19	0.35
75	0	98.14	–	–	98.23	0	0	98.18	0	0
	30	98.18	–	–	98.13	0.101	0.02	97.18	0.74	0.20
	60	98.20	–	–	98.00	0.19	0.05	96.33	1.4	0.578
	90	98.21	–	–	97.93	0.26	0.08	95.53	1.85	1.05
	120	98.17	–	–	97.86	0.32	0.125	94.81	1.86	1.65
	150	98.18	–	–	97.82	0.34	0.19	94.10	1.48	2.11
	250	98.17	–	–	97.65	0.11	0.42	93.58	0.05	4.52

from 55 to 75 °C were obtained once the linear expressions were built up by using a least squares program. Applying this procedure to plots of lnk' vs. ln[NaOH] (Fig. 3), we obtained the value of reaction order m and rate constant k from the slope and intercept respectively. The results for m and k are shown in Table 2.

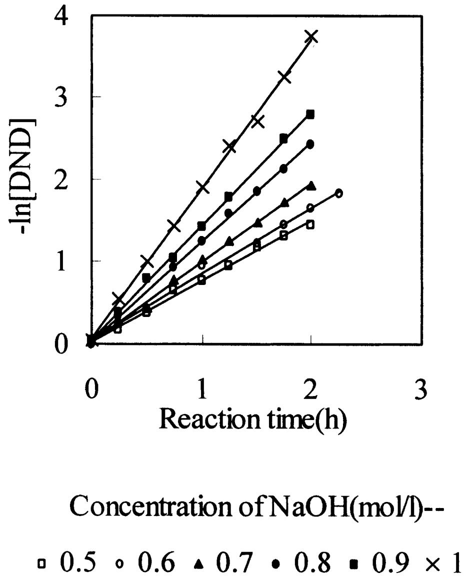


Fig. 1. Plots of –ln[DND] vs. reaction time at 55 °C.

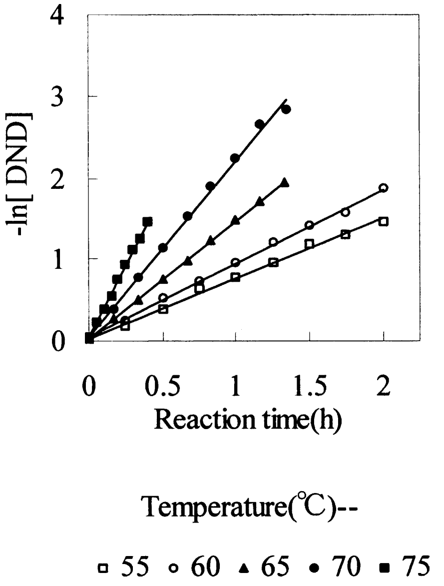


Fig. 2. Plots of –ln[DND] vs. reaction time when [NaOH] = 0.5 mol/l.

Consequently, the rate law was built up as below:

$$\text{Rate} = k[\text{DND}][\text{OH}^-]^{1.4}$$

By applying a least squares program to the plot of lnk vs. $1/T$, a straight line with a linear coefficient of 0.98, values of the activation energy and the frequency factor, under aqueous alkaline conditions were calculated.

$$E_a = 83577.4\text{J/mol},$$

$$k_0 = 8.626 \times 10^9(\text{mol/l})^{-1.4}/\text{s}.$$

3.3. Kinetic characteristics

3.3.1. Reaction time and hydroxide concentration

The reaction time required to convert certain amount of DND to DNS follows the expression:

$$t = -\frac{\ln(1-x)}{k[\text{OH}]^{1.4}}$$

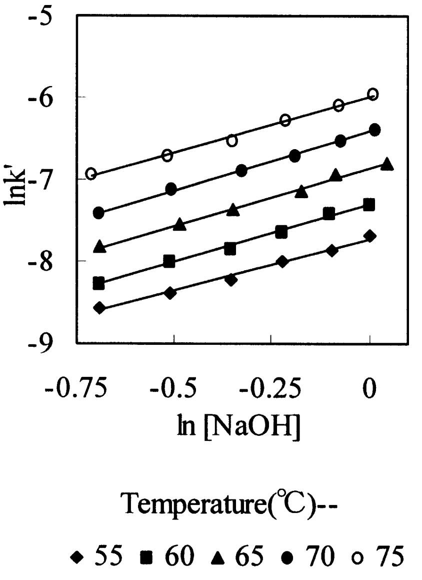


Fig. 3. Plots of lnk' vs. ln[NaOH].

The correlation of reaction time with a variety of base concentrations but constant temperatures is given in Fig. 4. The effect of hydroxide concentration on the necessary reaction time becomes obvious with the temperature decreases. That indicates that raising base concentration can result in a noticeable or a slight reduction in reaction time, depending on whether the reaction mixture is of a relative low temperature or not. However, once the base concentration goes beyond a certain value that varies with the reaction temperature, no marked reduction in reaction time can be achieved.

Table 2
Reaction order m and the reaction constant *k* for a series of temperatures

Temperature*t*' (°C)	*m*	$10^4 \times k$ $[(mol/l)^{-1.4}/s]$
55	1.40−0.04	4.670
60	1.40+0.03	6.731
65	1.40+0.02	10.34
70	1.40+0.02	16.26
75	1.40−0.03	25.81

3.3.2. Conversion and reaction time

The binding of the conversion of DND to the reaction time can be described in the form:

$$x = 1 - e^{-kt[OH]^{1.4}}$$

Fig. 5 shows their correlation with a constant hydroxide concentration of 0.7 mol/l. The conversion of DND increases with reaction time. Especially in the initial stage, a remarkable increment is observed when the reaction time is prolonged. Nevertheless, there is no apparent increase in conversion after a specific reaction time determined by hydroxide concentration and reaction temperature. For example, the conversion of DND at 60 °C increases from 86.1% to 94.8% due to reaction time is extended from 0.2 to 0.3 h and only to 98.8% if another 0.1 h is added. In addition, further oxidation of DNS often occurs at a long reaction time. Therefore, the product yield cannot be improved by increasing reaction time excessively.

3.3.3. Temperature and reaction time

Because of the high value of the activation energy, reaction temperature influences the rate of

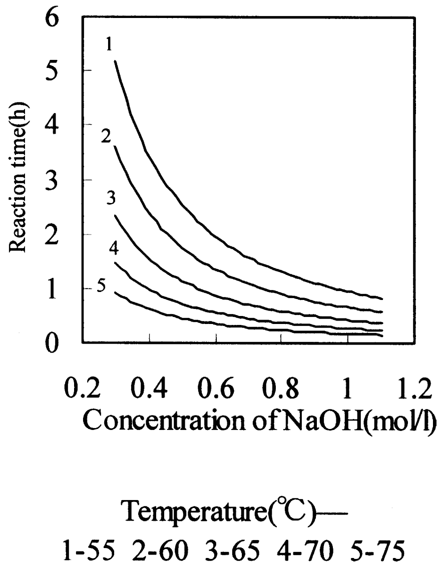


Fig. 4. Plots of reaction time vs. the concentration of NaOH (80% DND converted).

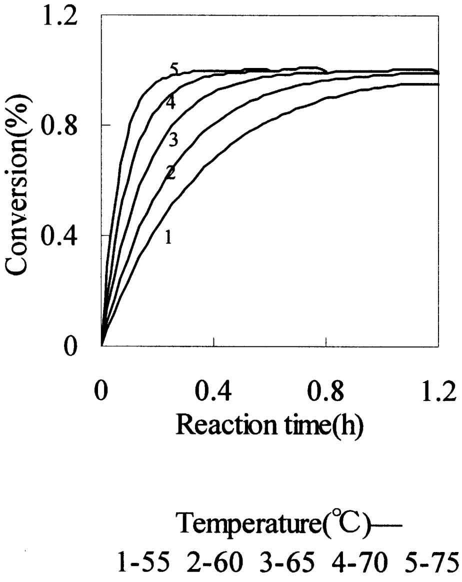


Fig. 5. Plots of conversion of DND vs. reaction time when [NaOH] = 0.7 mol/l.

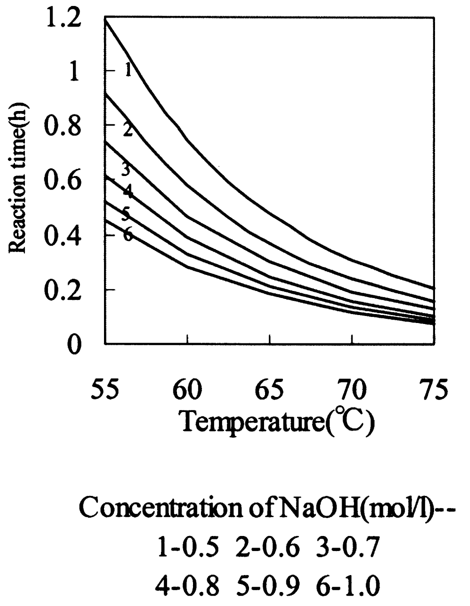


Fig. 6. Plots of reaction time vs. temperature (50% DND converted).

DNS formation significantly, as judged by Fig. 6. Reaction time required decreases considerably with the increase of temperature when the hydroxide concentration keeps at a low level. But by-products may also form rapidly at high temperatures, especially when the hydroxide concentration is also of a high value. As a result, the reaction temperature must be optimized in accordance with the base concentration.

Acknowledgements

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