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Kinetic study on the preparation of 4,4′-dinitrostilbene-2,2′-disulfonic acid (II)—kinetic study on the oxidation of *p*-nitrotoluene-*o*-sulfonic acid to prepare 4,4′-dinitrobibenzyl-2,2′-disulfonic acid

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Abstract

The aqueous air oxidation of *p*-nitrotoluene-*o*-sulfonic acid (NTS) to prepare 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) is studied. It is shown that the by-product formation results from either the direct oxidation of NTS or DNS destruction or both under certain conditions. Based on the experimental data, the rate equation of the oxidation of NTS is established, which can be expressed as follows: $-\mathrm{d}[\mathrm{NTS}]/\mathrm{d}t = k[\mathrm{NTS}][\mathrm{OH}]^{2.8}$. The kinetic parameters are obtained and interaction between temperature, hydroxide concentration, reaction time and conversion is discussed.

Keywords: *p*-Nitrotoluene-*o*-sulfonic acid; 4,4′-Dinitrostilbene-2,2′-disulfonic acid; 4,4′-Dinitrobibenzyl-2,2′-disulfonic acid; Oxidation; Kinetics; Mechanism

1. Introduction

During the oxidation of *p*-nitrotoluene-*o*-sulfonic acid (NTS) to prepare 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) [1–11], by-products such as 4-nitrobenzaldehyde-2-sulfonic acid (NBS) and 4-nitro-2-sulfobenzonic acid (NSB) can be formed, as summarized in Scheme 1 [8] and Scheme 2 [12]. In our previous work [13], studies are concentrated on the connection between DNS and NBS as well as NSB. Furthermore, the oxidative kinetics of DND under aqueous alkaline conditions was investigated.

In the present work, we conducted the experiments on NTS oxidation at temperature and hydroxide concentration ranges of 55–75 °C and 0.4–1.6 mol/L, respectively. HPLC was employed to analyze the reaction systems and a potential mechanism was put forward based on data obtained. At the same time, the appropriate reaction conditions were defined that ensure kinetic studies on the oxidation of NTS to form DND unaffected by by-product formation. A kinetic model for the reaction was established and values of the activation energy and the frequency factor were determined.

2. Experimental

2.1. p-Nitrotoluene-o-sulfonic acid (NTS)

NTS, purchased from Huyu Chemical Co., was recrystallized from sodium hydroxide aqueous solution until the purity of NTS reached 98.8%. The purity was measured by HPLC.

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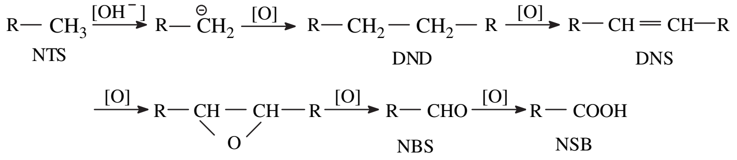


Scheme 1.

2.2. Oxidation of NTS

A five-neck round-bottomed flask equipped with constant speed agitator, thermometer, condenser and gas sparger below the stirrer was charged with 0.1% NTS aqueous solution. The mixture was stirred and heated in a water bath. When the reaction temperature was approached, a calculated amount of concentrated aqueous sodium hydroxide was added to it (zero time). At the same time, a 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.

2.3. Reaction product analysis

The samples were analyzed with an HPLC system (HITACHI, Japan) at 25 ± 1 °C. The variable-wavelength detector was operated at 254 nm. The mobile phase consisted of methanol and pure 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 NTS oxidation in aqueous NaOH of 1.6 mol/L at 65 °C (60 min of reaction time) were as follows: NTS: 6.158 (60.596%), DND: 8.438 (2.849%), DNS: 10.038 (32.923%), NBS: 2.310 (0.565%), NSB: 1.878 (1.392%).

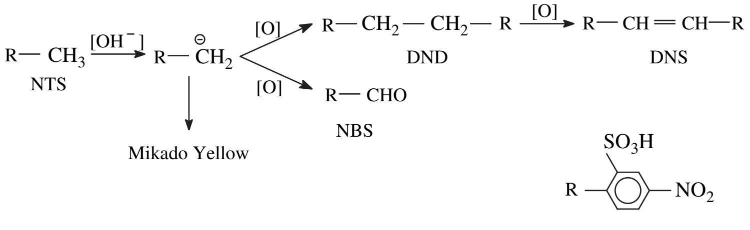
3. Results and discussion

3.1. Mechanism

It was observed that 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 NTS did not yield NBS or NSB. Neither NBS nor NSB was detected by HPLC and the total concentration of NTS, DND and DNS, which is denoted by *S* in Table 1 maintained equivalent to the initial concentration of NTS on the whole. With an increase in either the temperature or the hydroxide concentration, *S* reduced while NBS and NSB were formed. However, the total concentration of NTS, DND, DNS, NBS and NSB did not change substantially. Comparing the product distribution with that in the oxidation of DNS [13], we found that only in the oxidation of NTS with a base concentration of 0.5 mol/L at 75 °C did NBS and NSB appear and under certain conditions, e.g. 75 °C, [NaOH] = 1.0 mol/L, much more NBS and NSB existed in the oxidation of NTS. Those phenomena signified that NBS and NSB could result from the direct oxidation of NTS or the simultaneous oxidation of NTS and DNS, depending on the reaction temperature and the base concentration. Data in Table 1 also indicated that the hydroxide concentration that enables by-product formation reduces with the raise in the temperature, and vice versa.

Meanwhile, it was noted that 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, when they appeared in the reaction mixture. Particularly, two maximums of NBS concentration were observed when the oxidation of NTS was carried out in aqueous NaOH of 1.6 mol/L at 75 °C. Taking our early study results [13] into account, their appearance, we believe, demonstrate a change in by-product formation mechanism. In the initial reaction stage, NBS and NSB were obtained from NTS oxidation and the first maximum resulted. With NTS reducing and DNS increasing,



Scheme 2.

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

Temperature t' (°C)	Reaction time T (min)	[NaOH] (mol/L)								
		0.5			1.0			1.6		
		NBS	NSB	S	NBS	NSB	S	NBS	NSB	S
55	0	–	–	98.23	–	–	98.20	–	–	98.18
	30	–	–	98.17	–	–	98.19	–	–	98.23
	60	–	–	98.20	–	–	98.19	–	–	98.28
	90	–	–	98.14	–	–	98.16	–	–	98.15
	120	–	–	98.16	–	–	98.21	–	–	98.20
	150	–	–	98.18	–	–	98.22	–	–	98.21
65	0	–	–	98.17	–	–	98.19	0	0	98.18
	27	–	–	98.16	–	–	98.16	0.55	0.45	97.06
	38	–	–	98.19	–	–	98.22	0.71	0.70	96.74
	70	–	–	98.21	–	–	98.15	0.65	1.61	95.88
	106	–	–	98.23	–	–	98.18	0.32	2.53	95.21
	126	–	–	98.18	–	–	98.18	0.14	3.08	94.81
75	0	0	0	98.23	0.01	0	98.21	0.01	0.01	98.16
		0.10								
	30	1	0.02	98.10	0.92	0.34	97.18	0.44	1.30	96.53
	60	0.19	0.05	97.96	1.48	0.80	96.12	0.08	3.75	94.41
	90	0.26	0.09	97.87	1.15	1.80	95.45	0.23	4.97	92.95
	120	0.32	0.13	97.80	0.61	2.71	94.83	0.72	6.1	91.43
	150	0.35	0.19	97.72	0.33	3.55	94.31	0.62	7.07	90.52
	180	0.33	0.28	97.65	0.14	4.08	94.11	0.47	7.88	89.54

DNS destruction became prominent and enabled the second maximum to manifest.

Therefore, the mechanisms concerning by-product formation were revised by our experimental results. That is, only with a high temperature or a high alkaline concentration, does the oxidation of NTS give NBS and NSB. Temperature and alkaline concentration are two factors determining whether NTS converts to those by-products or not. In addition, the mechanism of by-product formation can be represented by Scheme 1 or Scheme 2, or both, depending on the reaction temperature, the hydroxide concentration and the ratio of NTS to DNS.

In order to eliminate any interference from by-product formation on the kinetic study of the NTS oxidation to prepare DND, kinetic experiments were conducted within a temperature of 50–60 °C and a hydroxide concentration of 0.8–1.6 mol/L (adjusted with the temperature). Under such conditions, any significant by-product formation was eliminated.

3.2. Kinetic studies

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

$$\mathrm{Rate} = -\frac{\mathrm{d(NTS)}}{\mathrm{d}t} = k[\mathrm{NTS}]^n\left[\mathrm{OH^-}\right]^m = k'[\mathrm{NTS}]^n$$

where $k' = k\left[\mathrm{OH^-}\right]^m$.

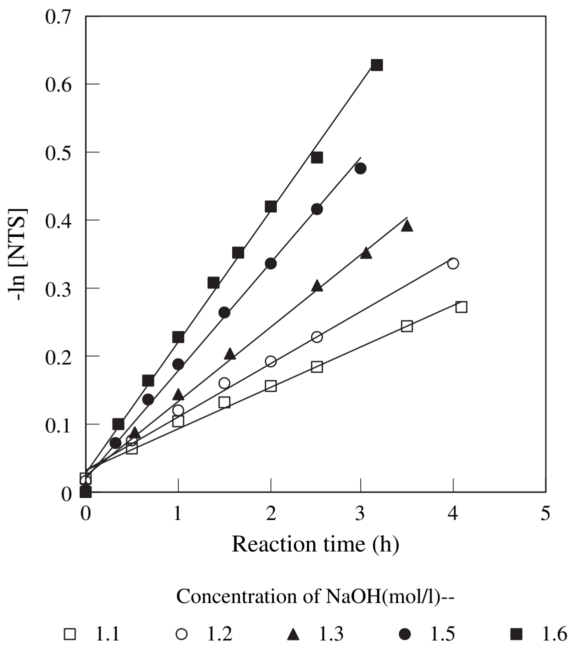


Fig. 1. Plots of −ln[NTS] vs. reaction time at 50 °C.

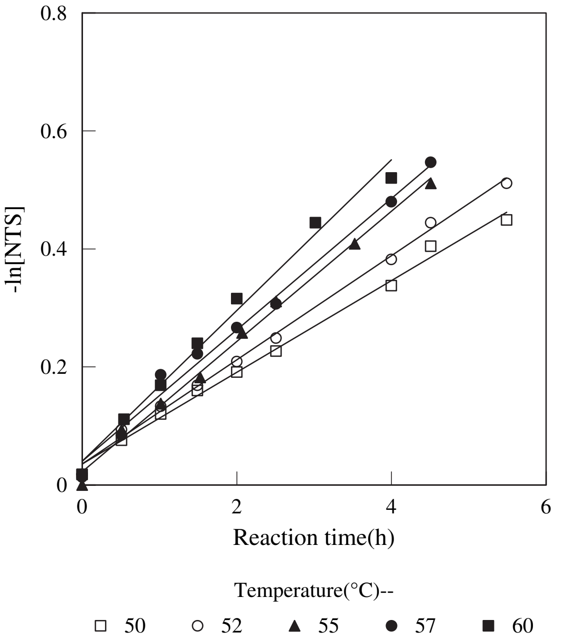


Fig. 2. Plots of $-\ln[\mathrm{NTS}]$ vs. reaction time when [NaOH] = 1.2 mol/L.

Linear coefficients of 0.91–0.99 observed in the plots of $-\ln$ NTS vs. reaction time indicated that pseudo first order kinetics applied in each experiment.

The slope of $-\ln$ NTS vs. time represented the pseudo first order rate constant k'. So values of k' corresponding to different hydroxide concentrations at temperatures ranging from 50 to 60 °C were obtained once the linear expressions were built up by using a least squares program. Applying this procedure to plots of $\ln k'$ vs. ln[NaOH] (Fig. 3), we obtained the values of reaction order, m, and rate constant, k, from the slope and intercept, respectively. The values of m and k are given in Table 2.

Consequently, the rate law was built up as below:

$$\mathrm{Rate}=k[\mathrm{NTS}]\left[\mathrm{OH}^-\right]^{2.8}$$

By applying a least squares program to the plot of $\ln k$ vs. $1/T$, a straight line with a linear coefficient of 0.994, values of the activation energy and the frequency factor, under aqueous alkaline conditions were calculated.

$$E_a=43\,119\ \mathrm{J/mol}$$

$$k_0=125.2\ (\mathrm{mol/L})^{-2.8}/s$$

3.3. Kinetic characteristics

3.3.1. Reaction time and hydroxide concentration

The reaction time required to convert an amount of NTS to DND follows the expression:

$$t=-\frac{\ln(1-x)}{k[\mathrm{OH}]^{2.8}}$$

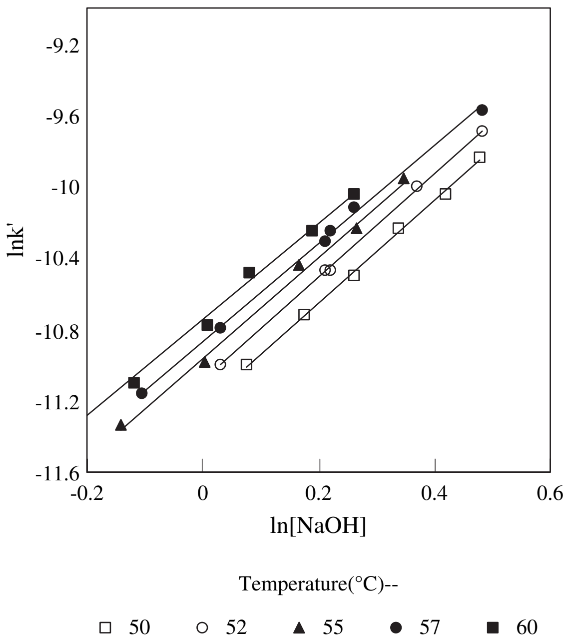


Fig. 3. Plots of $\ln k'$ vs. ln[NaOH].

The correlation of reaction time with a variety of base concentrations at constant temperatures is given in Fig. 4. The effect of hydroxide concentration on the required reaction time becomes obvious as the temperature decreases. This indicates that raising base concentration can result in a noticeable, or a slight reduction, in reaction time, depending on the temperature of the reaction mixture. However, once the base concentration goes beyond a certain value, dependent upon the reaction temperature, no marked reduction in reaction time can be achieved.

3.3.2. Conversion and reaction time

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

$$x=1-\mathrm{e}^{-kt[\mathrm{OH}]^{2.8}}$$

Fig. 5 shows their correlation with a constant hydroxide concentration of 1.5 mol/L. The conversion of NTS increases with reaction time, especially in the

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

Temperature t' (°C)	m	$10^5 \times k$ ((mol/L)$^{-2.8}$/s)
50	2.81 + 0.07	1.33
52	2.81 − 0.09	1.48
55	2.81 + 0.07	1.72
57	2.81 − 0.04	1.90
60	2.81 − 0.01	2.12

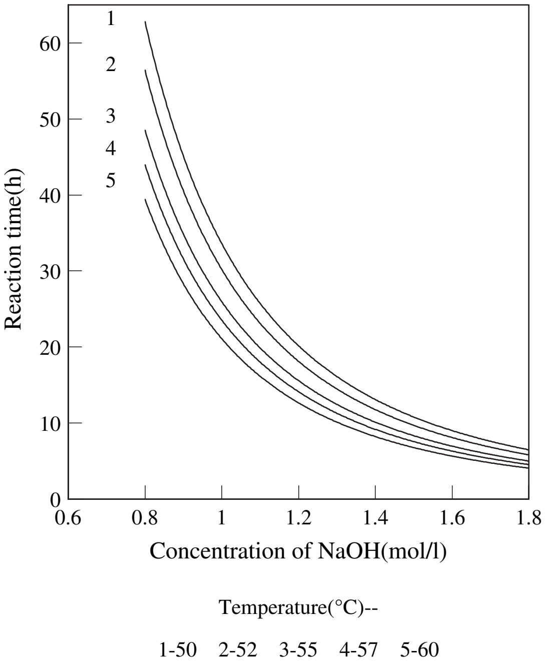


Fig. 4. Plots of reaction time vs. the concentration of NaOH (80% NTS converted).

initial stage, where a noticeable increment is observed when the reaction time is prolonged. Depending on the reaction time and hydroxide concentration, the conversion reaches a maximum at a specific time, after which no further conversion is observed. For example, the conversion of NTS at 60 °C increases from 61.3 to 81.0% when reaction time is extended from 4 to 7 h but only to 90.7% after a further 3 h. In addition, DNS destruction often occurs at a long reaction time. Therefore, the product yield cannot be improved by increasing reaction time excessively.

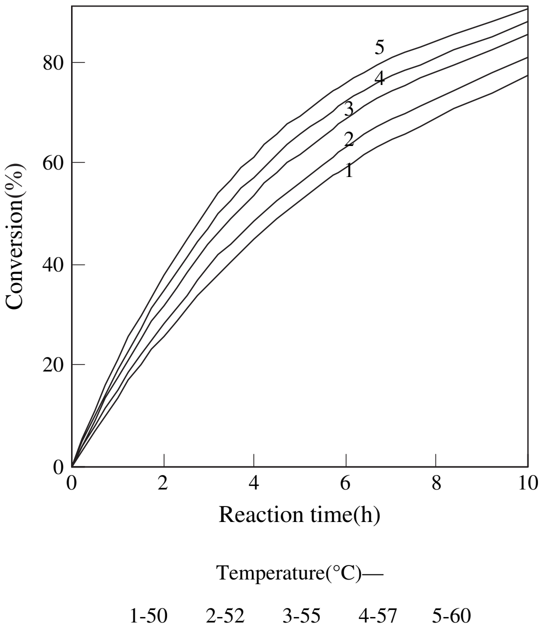


Fig. 5. Plots of conversion of NTS vs. reaction time when [NaOH] = 1.5 mol/L.

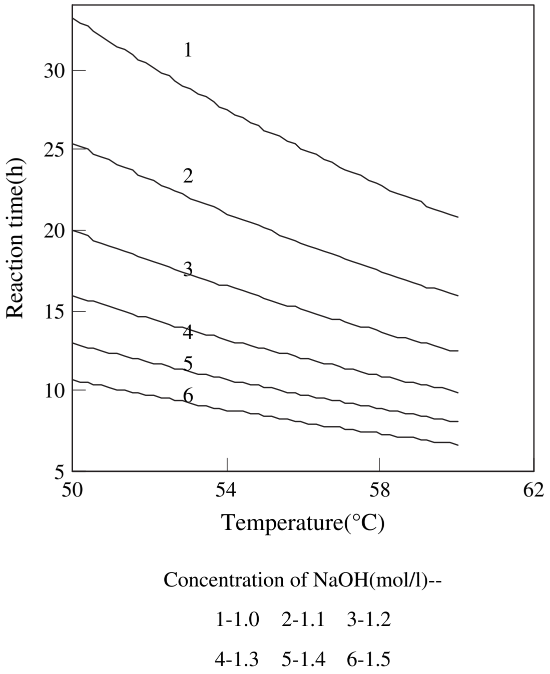


Fig. 6. Plots of reaction time vs. temperature (80% NTS converted).

3.3.3. Temperature and reaction time

Because of the high value of the activation energy, reaction temperature influences the rate of DND formation significantly, as judged by Fig. 6. The reaction time required decreases considerably with the increase of temperature when the hydroxide concentration is kept at a low level. 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 base concentration.

Acknowledgements

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