



# Mechanism of oxidation of 3-hydroxy-2,7-naphthalenedisulfonic acid disodium salt with oxygen in subcritical water



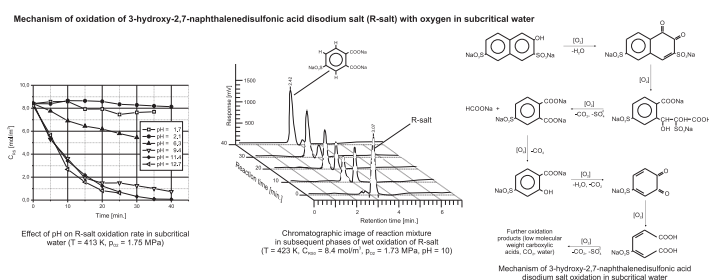
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## HIGHLIGHTS

- Process of wet oxidation of R-salt with oxygen at pH = 10 was studied.
- Stable salts of 4-sulfophthalic acid are formed during that process.
- At temperature 569 K only 60% reduction of TOC was obtained.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The article presents the results of studies on the oxidation mechanism of 3-hydroxy-2,7-naphthalenedisulfonic acid disodium salt (R-salt) with oxygen in subcritical water. To this aim, a series of experiments were carried out which showed that at a temperature of 413 K and  $pH > 9$  the oxidation reaction of a substrate with oxygen was relatively quick and after approximately 40 min the R-salt oxidation yield exceeded 95%. In an acidic medium ( $pH < 7$ ), the rate of R-salt oxidation is small.

In order to identify the mechanism of R-salt oxidation, experiments were carried out at 413–569 K in solutions with  $pH = 10.0$  and at partial oxygen pressure  $p_{O_2} = 1.73\text{ MPa}$ . As a result of these experiments, a stable oxidation product was isolated from the reaction mixture and subjected to spectroscopic analysis. The analysis of  $^1H$ NMR of this product proved that a stable intermediate product of R-salt oxidation was 4-sulfophthalic acid sodium salt.

The results of the experiments have shown that destructive oxidation of R-salt can easily be obtained at a temperature of 413 K, but satisfactory reduction of TOC in wastewater containing this substrate requires the use of very high temperature: at 569 K only 60% reduction of TOC was achieved.

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## 1. Introduction

3-Hydroxy-2,7-naphthalenedisulfonic acid disodium salt (R-Salt,  $C_{10}H_6Na_2O_7S_2$ , CAS No 135-51-3) is an organic intermediate widely used in industry to prepare dyes, surfactants and wetting agents. Wastewater from the production of such organic

intermediates and dyes contains a large amount of inorganic salts and harmful organic compounds. Chemical oxygen demand (COD) of this wastewater ranges from 30 to 40  $g\ O_2\ dm^{-3}$  and the concentration of inorganic salts reaches 100–150  $g\ dm^{-3}$ . Purification of such wastewater through a conventional activated sludge process is very difficult.

An alternative to the classical treatment methods for wastewater containing large amounts of organic compounds and inorganic salts is the oxidation of pollutants in subcritical water (wet

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oxidation). This method is effective in removing most of the toxic substances contained in the treated wastewater and does not cause secondary pollution. Wastewater from the dye industry, purified by the wet oxidation method, can be sent to a biological treatment plant where it is subjected to final purification [Mishra et al., 1995; Bhargava et al., 2006]. The use of wet oxidation in the pretreatment of wastewater from dye production allows for a significant COD reduction. This technology improves the safety and reliability of operations of biological treatment plants because it decreases the risk of failure of these systems.

Studies on the wet oxidation of wastewater generated during the synthesis of organic dyes have been conducted since the 1990s. Many works from this period refer to the decolorisation of textile wastewater using hydrogen peroxide [Chen et al., 1999, Dhale and Mahajani, 2000; Lei et al., 2000]. These publications, however, include very little information on the mechanism of oxidation of organic intermediates contained in the dyeing mixtures and treated wastewater. Wanpeng et al. (1996) published data concerning the mechanism and reaction kinetics of the oxidation of 1-amino-8-naphthol-3,6-disulfonic acid (a so-called H-acid) with a  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  system. For this purpose, the IR spectra of the reaction mixture were analysed. It has been concluded that the oxidation of this compound proceeded according to the free radical mechanism and consisted, in the first place, of the substitution of functional groups in the naphthalene ring such as  $-\text{NH}_2$  and  $-\text{SO}_3\text{H}$  by  $-\text{OH}$  groups, which activated the ring. Next, the naphthalene ring was cleaved to form unsaturated fatty acids, which were easily oxidised to  $\text{CO}_2$  and water. Dongalić and Levec (1997, 1998, 1999) described the mechanism of decomposition of hydroxynaphthalene acid derivatives included in Orange II dye. In the process of wet oxidation, the oxidative fragmentation of this dye proceeded via the formation of  $\alpha$ - or  $\beta$ -naphthol and isophthalic acid anhydride (1,3-isobenzofurandione). The oxidation of Orange II dye in subcritical water was studied also by Raffainer and von Rhor (2001), but in their article they did not discuss the mechanism of this dye's decomposition. They described the kinetics of dye decomposition and oxidation of TOC contained in the reaction mixture.

The aim of the research presented in this paper was to identify the mechanism of the reaction of oxidation of sodium salt of 2-hydroxy-3,6-naphthalenedisulfonic acid (R-salt) with oxygen in alkaline subcritical water. Understanding the destructive oxidation of pollutants in the process of wet oxidation, in particular the determination of the reaction scheme, and the identification of intermediate products obtained during the process is helpful for designing wastewater treatment.

## 2. Experimental

In the experiments, a Parr high-pressure reactor made of titanium with capacity  $V = 0.6 \text{ dm}^3$  equipped with a propeller stirrer, reflux cooler and heating jacket controlled by a regulator to maintain isothermal conditions of the process was used. Variation of temperature from the predetermined value did not exceed  $\pm 1 \text{ }^\circ\text{C}$ . Gases were pumped to the reactor from a cylinder, maintaining the predetermined pressure of oxygen in the reactor with a controller and a Brooks back-pressure valve. The impeller of the reactor was driven by an air turbine, which enabled changes in its revolutions and produced velocities ranging from 400 to  $1000 \text{ rpm}^{-1}$ . Data from measuring the systems of the experimental setup were transmitted using an A/C converter to a computer system, which collected information from individual experiments.

3-Hydroxy-2,7-naphthalenedisulfonic acid disodium salt with purity >95%, supplied by Sigma-Aldrich, and oxygen of purity 99.5% supplied by AirLiquid were used in the experiments. Correction of the pH of R-salt solutions was made using 5 M NaOH or  $\text{H}_2\text{SO}_4$  (1:4)

of analytical grade. Concentrations of substrate and intermediates in the reaction mixture were determined by high performance liquid chromatography (HPLC). A liquid chromatograph (Perkin Elmer, USA) equipped with a 20  $\mu\text{l}$  metering loop and Diode Array UV/VIS Spectrophotometer to obtain spectrophotometric spectra of the tested substances with wavelengths ranging from 195 to 360 nm was used for determinations. In the experiments, a chromatographic column 250 mm long with an inner diameter of 4.6 mm and  $\text{C}_{18}$  packing (octadecyl phase) of 5  $\mu\text{m}$  particle diameter was used. The mobile phase was a methanol:water mixture (40:60 v/v) supplemented with tetrabutylammonium phosphate. The presence of R-salt and intermediate oxidation products was confirmed by the identification of spectrophotometric spectra of these compounds and their retention times, while the concentration was determined from the calibration curve drawn on the basis of standard solutions of analytes. Surface areas of chromatographic peaks were calculated automatically using software supplied by Perkin-Elmer. Total organic carbon (TOC) in the solutions was determined by the coulometric method using a Strohleim 702Li/C Coulomat. All TOC and HPLC determinations were repeated three times and the final value was calculated as an average of these determinations. The stable intermediate product of R-salt oxidation, isolated from the reaction mixture, was identified by performing a series of spectroscopic measurements.

Studies on the oxidation of 3-hydroxy-2,7-naphthalenedisulfonic acid disodium salt in subcritical water were carried out at different temperatures (413–569 K) and different pH (1.7–12.7), using gaseous oxygen as an oxidant with partial pressure  $p_{\text{O}_2} = 1.73 \text{ MPa}$ . Total pressures in the reactor were established as a sum of water vapor partial pressure and oxygen partial pressure used at given experiments. Water partial pressure was derived from Haar and Gallagher (1984), and oxygen pressure in each of the experiments was  $p_{\text{O}_2} = 1.73 \text{ MPa}$ . When the oxygen was consumed during the oxidation processes, an appropriate amount of fresh oxygen was pumped into the mixture and total pressure in the reactor was kept constant. Carbon dioxide ( $\text{CO}_2$ ) obtained during the oxidation processes did not affect the total pressure inside the reactor. The amount of this product was insignificant, because the mass of R-salt used in the experiments was small and at alkaline conditions all of  $\text{CO}_2$  was converted into  $\text{CO}_3^{2-}$  ions.

The experiments were conducted according to the following procedure: the aqueous solution of R-salt at the predetermined initial concentration was pre-purged with nitrogen at room temperature. Then, 400  $\text{cm}^3$  of this solution were charged to the reactor and after closing the cover the reaction mixture was heated to the desired temperature. Upon reaching this temperature, oxygen was fed to the reactor. The reaction was carried out for about 1 h maintaining a constant total pressure in the reactor by means of a back-pressure controller. To minimise diffusion resistance, the speed of the impeller was established at about  $800 \text{ rpm}^{-1}$ . During the process, 5 to 6 samples of the reaction mixture (15 ml each) were taken and after cooling and expansion these were subjected to HPLC analysis and TOC determination.

The individual experiments were carried out according to the above-described procedure, i.e. in a semi-batch regime maintaining constant partial pressure of oxygen and taking samples of the reaction mixture during the process.

## 3. Results and discussion

### 3.1. Identification of intermediate product of R-salt oxidation

#### a) Hydrolysis of R-salt in alkaline solution

In the initial phase of the research, an experiment was

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