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Detailed parameter study on the mechanisms in electrochemical oxidation of p-nitrosodimethylaniline in chloride electrolyte

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Abstract

This paper studies the use of p-nitrosodimethylaniline (RNO) as a selective probe compound for hydroxyl radical detection in electrochemical oxidation studies. In the applied recirculation experimental setup with a Ti/Pt₉₀-Ir₁₀ anode, oxidation of RNO was found in both inert sulphate, phosphate, and nitrate electrolytes and electroactive chloride electrolytes, where the rate of oxidation was dramatically enhanced due to the indirect hypochlorous acid/hypochlorite oxidation. No influence on the rates of oxidation was found by addition of excess amounts of t-BuOH as hydroxyl radical scavenger, and hence the oxidation of RNO can be entirely contributed to the oxidative abilities of the lattice active oxygen of the Ti/Pt₉₀-Ir₁₀ anode and the chlorine species. The reaction kinetics changed from standard first order kinetics in the inert electrolytes to second order kinetics in the chloride electrolyte. Comparison of the oxidative performance of the electrochemical oxidation in a chloride electrolyte and the chemical oxidation by sodium hypochlorite under similar conditions showed a superior oxidation power of the in-situ electrochemical oxidation of RNO.

Key Words : Electrochemical oxidation; hydroxyl radical scavenger; p-nitrosodimethylaniline, RNO, NDMA, pNDA, chlorine oxidation

1 Introduction

The present study concerns the use of p-nitrosodimethylaniline (RNO) as a probe compound and spin trap for detection of hydroxyl radicals in aqueous electrochemical oxidation studies. Determination and quantification of hydroxyl radicals is a challenging task due to its extremely reactive nature, existing only in the order of nanoseconds. When they are produced in relative high concentrations, direct detection by electron spin resonance is possible, but for detection of low concentrations of hydroxyl radicals, indirect techniques apply involving trapping of the hydroxyl radical by an addition reaction (spin trap) to produce a more stable radical (spin adduct) [1]. RNO, also abbreviated pNDA or NDMA in the literature, is a widely applied spin trap compound in several fields of chemistry and is reported to be very selective to hydroxyl radicals as it neither reacts with singlet oxygen (¹O₂), superoxide anions (O₂⁻) or other peroxy compounds [1-4].

During the last 15 years, electrochemical oxidation has been developed into a strong physico-chemical oxidation technique for degradation of organics in polluted water utilizing hydroxyl radicals and lattice active oxygen depending on the electrode material used [5]. In electrochemical oxidation studies, the method of bleaching of the organic dye molecule RNO has been adapted from medicinal and medical chemistry [6-8], cell biology [3] and photobiology fields [2] as a tool for evaluation of the oxidation performance [1,4,9-13]. RNO is claimed to act as a selective probe compound towards hydroxyl radicals through a one electron oxidation of the chromophore nitroso group (fig. 1).

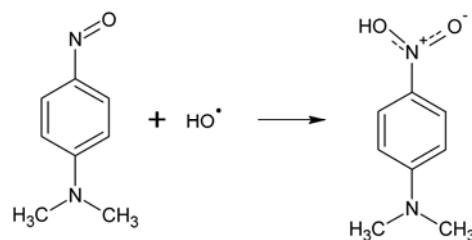


Figure 1: The one electron oxidation of the nitroso group in p-nitrosodimethylaniline (RNO) by the hydroxyl radical.

Discrepancies are found in the literature; even though RNO was showed to be electrochemically inactive at Pt, IrO₂, SnO₂ and PbO₂ anodes by cyclic voltammetry [1,9], bleaching and hence oxidation was observed in Ti/Pt and Ti/RuO₂ anode systems [13], types of anodes, which according to the general accepted models [1,5,14], utilize chemisorbed lattice active oxygen, MO_{x+1}, due to a higher adsorption enthalpy towards the adsorbed hydroxyl radical [5]. In addition, several studies report bleaching of RNO by other strong oxidants as ozone [9] and chlorine [13,15]. The bleaching by these oxidants was explained by oxidation mechanisms through radical chain reactions generating hydroxyl radicals as the main intermediate oxidative agent [16-18].

In the present study, the role of RNO as a fully selective hydroxyl radical probe compound was questioned. The kinetics of the RNO bleaching reaction has been studied in different electrolyte systems, with special attention on chloride electrolytes where indirect oxidation of RNO by electrolytic generated hypochlorous acid/hypochlorite has been showed in former research [13,15]. In addition, the bleaching power of the in situ generated chlorine has been compared to bleaching by alkaline sodium hypochlorite solution, and scavenging and reducing agents has been used to investigate the proposed role of hydroxyl radical in chlorine oxidation.

2 Materials and methods

The investigation has been performed in a batch recirculation experimental setup, where the RNO solution was pump from a reservoir through the electrochemical cell at a flow rate of 430 L h⁻¹. The temperature was kept at 20±1 °C in all experiments and the cell was a commercial one compartment cell of tubular design with Ti/Pt₉₀-Ir₁₀ rod like anode and SS 316 cathode with a specific volume of 43 ml, an anode surface of 60.3 cm², an electrode gap of 3 mm and a mass transfer coefficient of 2.25·10⁻⁵ m s⁻¹, determined by the diffusion limiting current technique with the ferro/ferri cyanide couple [19]. During all electrochemical oxidation experiments, the cell was operated at galvanostatic conditions with a current density of 32 mA cm⁻². The initial concentration of RNO was 10 mg L⁻¹ (6.66·10⁻⁵ M) with a total solution volume of 3 L. The investigated electrolytes were Na₂SO₄, NaNO₃, Na₂HPO₄, NaH₂PO₄, Na₃PO₄, and NaCl, in concentrations from 0.001 M to 0.154 M. All chemicals were of analytical grade and obtained from Merck and Sigma Aldrich. In the chemical bleaching experiment, an alkaline concentrated sodium hypochlorite solution was pumped to the reservoir in a concentration of 0.272 M at a flow rate of 1.18 mL min⁻¹ corresponding to the electrolytic formation of 1.69·10⁻⁴ mole A⁻¹ min⁻¹ available chlorine at an equal chloride electrolyte concentration of 0.154 M, determined in prior research [15].

Excess amounts of tertiary butyl alcohol (t-BuOH) was applied as hydroxyl radical scavenger due to its fast reaction rate ($k = 6.0 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [20], for qualitative determination of the role of hydroxyl radicals in the studied electrolyte systems. Na₂S₂O₃ was used as reducing agent in order to neutralize all oxidative species produced. The bleaching of RNO was followed by spectrophotometric absorbance measurements at 440 nm, and bulk oxidation and reduction potential (ORP) and pH were monitored with sensors in the reservoir.

3 Results and discussion

In the first experiment, the aim was to study if the one electron oxidation of the chromophore nitroso group to a nitro group, with no absorption in the visible range, was possible with the applied Ti/Pt₉₀-Ir₁₀ anode. Additionally, to clarify the observed reaction kinetics of the RNO oxidation in different electrolyte systems utilizing both direct anodic and indirect mediated oxidation.

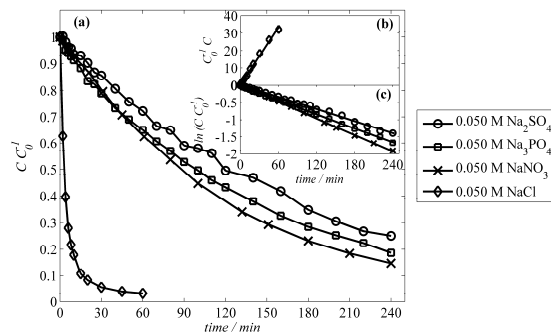


Figure 2: The evolution in the relative RNO concentration with time in different electrolyte systems at constant current density of 32 mA cm^{-2} (a). In the subplots, the reaction kinetics is illustrated by second order (b) and first order (c) plots.

The decrease in bulk RNO concentration during the runs in inert sulphate, phosphate, and nitrate electrolytes showed that direct anodic oxidation of the nitroso group occurred during the electrolysis (fig. 2a). The experiments also showed a clear difference in the RNO oxidation kinetics between the inert and the electrolytic active chloride electrolyte. The bleaching in the inert electrolytes showed a clear first order dependence on the RNO concentration with comparable apparent rate constants ($k = 9.67 \cdot 10^{-5} - 1.35 \cdot 10^{-4} \text{ s}^{-1}$) as in agreement with literature reportings (fig. 2c) [11,12]. The rate of oxidation was significantly enhanced in a similar concentrated chloride electrolyte, due to the contribution from the indirect hypochlorous acid / hypochlorite oxidation. In addition, the electrolysis in a chloride electrolyte shifted the oxidation kinetics to follow a second order dependence on the concentration of RNO (fig. 2b). This observation agrees with prior findings [13], where a similar evolution of the absorption curve in chloride electrolyte was seen, however, the reaction kinetics being second order has not formerly been clarified.

Throughout the study, the different electrolyte solutions applied resulted in changes of the solution pH, which was monitored, but not kept constant during the runs. For this reason, the absorbance of the RNO solution was studied versus changes in pH. In the pH range from 6 to 12, no influence was found on the absorbance at 440 nm, whereas below pH 6 a sharp reversible decrease in absorbance was seen, probably due to proton interactions with the nitrogen lone pair of the chromophore nitroso group in the acidic environment. In all experiments, bulk pH was kept above 6 in order to avoid loss of absorbance at the 440 nm due to pH.

Bleaching experiments in mixed electrolyte solutions showed that addition of 0.001 and 0.005 M sodium chloride to a 0.050 M sodium sulphate supporting electrolyte significantly enhanced the rate of oxidation, still following first order kinetics (fig. 3a). When 0.010 M sodium chloride was added to the sodium sulphate electrolyte, the rate showed a cross over between first and second order kinetics, which was turned fully into second order kinetics in pure 0.010 M sodium chloride electrolyte. It was hypothesised that the high cell voltage applied in the pure 0.010 M chloride electrolyte (17.8 V), in order to run at the galvanostatic 32 mA cm^{-2} current density, could cause a decrease in the RNO oxidation efficiency towards the oxygen evolution side reaction. However, compared with the oxidation rate observed in the 0.010 M sodium chloride and 0.050 M sodium sulphate mixed electrolyte operated at similar current density at a cell voltage of 4.9 V, the oxidation rate was lower and hence less efficient (fig. 3a). This might be due to formation of small amounts of ozone at the high cell voltage, contributing to the indirect RNO oxidation [9]. Increased

concentrations of chloride from 0.010 M to 0.154 M in the pure sodium chloride electrolytes enhanced the oxidation rate, with the second order apparent rate constant being linearly correlated with the sodium chloride concentration (fig. 3b), providing evidence that the bleaching was due to indirect chloride mediated oxidation.

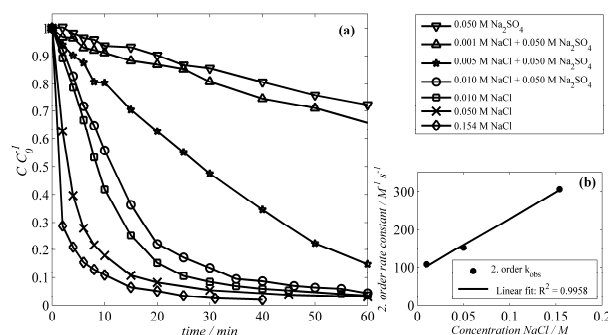


Figure 3: The oxidation of RNO in pure and mixed sulphate and chloride electrolytes (a). (b) Linear correlation of the second order rate constants and the chloride concentration.

The electrolytic formation of available free chlorine species in a 0.154 M sodium chloride electrolyte was simulated with addition of alkaline sodium hypochlorite solution in similar amount and rate at no applied voltage and hence zero current density, in order to compare the oxidation rate of the in-situ generated and the physically added chlorine. The rate of the chemical oxidation obeyed none of the standard kinetic expressions, but comparison of the evolution in the relative RNO concentration revealed a superior oxidation efficiency of the in-situ generated hypochlorous / hypochlorite species (fig. 4).

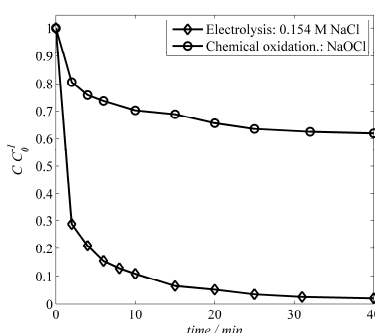


Figure 4: Evolution in the RNO concentration upon electrolysis at a current density of 32 mA cm^{-2} and chemical oxidation by alkaline sodium hypochlorite solution.

This major difference observed was believed to be due to the chloride/chlorine being adsorbed to the anode surface during the electrolytic formation as proposed by Bonfatti et al. [14]. In this way RNO is both directly oxidized by chlorine upon contact with the anode surface and indirectly through mediated bulk oxidation resulting in higher oxidation efficiency. The direct oxidation is controlled by the hydrodynamic conditions in the cell, providing good contact between the reactants, whereas the bulk oxidation is controlled by diffusive mechanisms in the solution guided by the concentrations. In the chemical oxidation experiment, only bulk oxidation occurred, and the very low initial chlorine concentrations going up from zero provided a slow chemical bleaching kinetics.

It has been proposed that the oxidative mechanism of chlorine is a radical chain reaction with hydroxyl radicals as the main oxidative specie [16-18]. In order to study the role of hydroxyl radicals in the oxidation reactions observed, tertiary butyl alcohol (t-BuOH) was added in excess to remove all hydroxyl radicals if present. In 0.050 M sodium sulphate electrolyte an almost similar evolution in the RNO concentration was found with or without the presence of 0.05 M t-BuOH

stating that no hydroxyl radicals was formed by the Ti/Pt₉₀-Ir₁₀ anode material and that the oxidation was due entirely to lattice active oxygen MO_{x+1} (fig. 5). In a similar fashion, neither 0.05 M nor 0.10 M t-BuOH slowed down or even affected the rate of RNO oxidation in the 0.050 M sodium chloride electrolyte (fig. 5). This observation rejects the hydroxyl radical chain reaction proposal and states that indirect RNO oxidation by chlorine entirely is due to the oxidative abilities of the hypochlorous acid/hypochlorite pair. The oxidative performance of the conjugated hypochlorous acid and hypochlorite acid base pair ($pK_a = 7.4$) was studied by bleaching experiments in phosphate buffer solutions at pH 6, where hypochlorous acid was the primary specie, and pH 10.3 where hypochlorite was present (results not showed). The experiments showed very similar first order reaction rates, a little faster at pH 6, attributed to the higher standard reduction potential of hypochlorous acid ($E^0 = 1.48$ V) compared to hypochlorite ($E^0 = 0.81$ V).

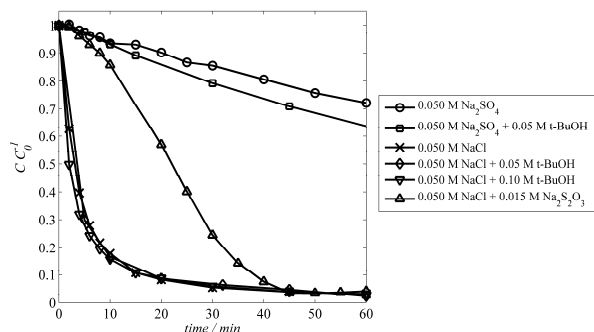


Figure 5: Evolution in the RNO oxidation with addition of hydroxyl radical scavenger and reducing agent.

Addition of 0.015 M of the reducing agent sodium thiosulphate to the 0.050 M sodium chloride electrolyte hindered the initial RNO oxidation due to neutralization of the electrolytic generated chlorine. The concentration of sodium thiosulphate was calculated to be sufficient to neutralize the amount of chlorine produced in 60 min at the 32 mA cm⁻² current density, however since sodium thiosulphate was oxidized by anodic oxidation as well, an s-shaped curve was observed with oxidation of RNO occurring as the concentration of sodium thiosulphate was decreased and finally depleted.

4 Conclusions

In the present study, the electrochemical oxidation of p-nitrosodimethylaniline (RNO) has been studied in different electrolyte systems, and the role of RNO as a selective hydroxyl radical probe, as very often used and applied in literature, has been studied. RNO was found to be directly anodic oxidized in inert electrolytes at the applied Ti/Pt₉₀-Ir₁₀ anode due to lattice active oxygen with no influence by hydroxyl radicals. In sodium chloride, the rate of oxidation was greatly enhanced, again without the presence of hydroxyl radicals in the oxidation mechanisms. In this fashion, RNO is both oxidized by lattice active oxygen and chlorine species, and can not be regarded as a fully selective hydroxyl radical probe compound in electrochemical studies. However, it is a very applicable and easy to use compound for evaluation of the electrochemical oxidation potential, taking account of all oxidative species generated in the process.

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