Polyaniline: Aniline oxidation with strong and weak oxidants under various acidity

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HIGHLIGHTS

- Comparison of aniline oxidation with oxidants of different redox potential.
- UV—vis, FTIR and Raman spectroscopies combined with size-exclusion chromatography.
- The contents of polymer and oligomers were analyzed and discussed.
- General model of aniline oxidation with strong and weak oxidants was formulated.

GRAPHICAL ABSTRACT
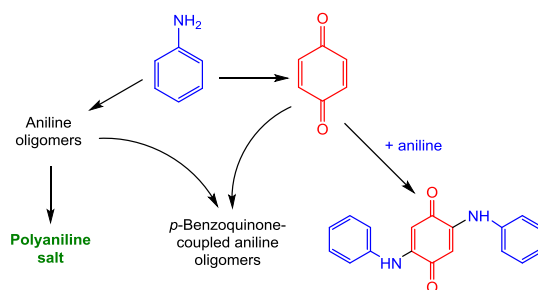
ABSTRACT

Aniline was oxidized with three strong inorganic oxidants (ammonium peroxydisulfate, cerium(IV) sulfate, potassium dichromate), two weak inorganic oxidants (iron(III) chloride, silver nitrate), and one organic oxidant (*p*-benzoquinone) in aqueous solutions of methanesulfonic acid (MSA) of various concentration. Whereas oxidation of aniline with ammonium peroxydisulfate yielded high-molecular-weight conducting polyaniline (PANI) in the whole acidity range, the oxidation with cerium(IV) sulfate led also to a single product close to PANI with considerably lower molecular weight and lower conductivity. Potassium dichromate gave PANI only at high concentration of MSA. The use of iron(III) chloride yielded composite mixtures of PANI and low-molecular-weight aniline oligomers. The oxidation of aniline with silver nitrate led to composites of silver and an organic part, which was constituted either by aniline oligomers or conducting polyaniline or both. *p*-Benzoquinone as oxidant produced mainly aniline oligomers with poor conductivity and 2,5-dianilino-*p*-benzoquinone-like structure detected in FTIR and Raman spectra when oxidation proceeded with weak oxidants. A general model of oxidation with strong and weak oxidants was formulated.

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1. Introduction

Polyaniline (PANI), one of the most intensively studied conducting polymers [1], is usually prepared by the oxidation of aniline with ammonium peroxydisulfate (APS) in acidic aqueous medium [2—7]. In order to improve the properties, *viz.* conductivity, other

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oxidants have also been tested, such as iron(III) chloride [8—12], cerium(IV) sulfate [11,13,14], potassium dichromate [15—18], potassium iodate [15,19,20], periodic acid [21], sodium chlorite [22], manganese(IV) oxide [23], vanadic acid [24], silver nitrate [25—29] and other noble-metal compounds [30,31], benzoyl peroxide [32,33], and *p*-benzoquinone [34,35]. Occasionally, oxidant mixtures have been used for specific purposes [36—38]. Several catalytic systems using iron(III) ions as catalyst and hydrogen peroxide [32,39—43] or its complexes with organic compounds [44] as stoichiometric part of the catalyst system have also been studied.

The oxidation of aniline with APS has to be carried out in strongly acidic media [45,46], pH < 2.5, in order to produce the conducting form of PANI; non-conducting aniline oligomers are produced under alkaline conditions [47]. On the other hand, oxidation of aniline in highly acidic medium can also lead to *p*-benzoquinone [35,48,49]. Moreover, it has been previously shown that reaction of *p*-benzoquinone with aniline results in formation of 2,5-dianiline-*p*-benzoquinone-like oligomers [35]. The role of quinones has been recently widely discussed when analyzing the structure of aniline oligomers responsible for formation of PANI nanostructures prepared by APS in the environment of high initial acidity [47,50,51]. The oxidation of aniline with potassium dichromate in acidic environment leads to PANI [15—17] or *p*-benzoquinone [48] according to the conditions applied. Cerium(IV) sulfate was reported as an oxidant yielding PANI [11,13,14], but its ability to decompose aniline has been also tested [48]. Next oxidant often used for PANI synthesis, iron(III) chloride [8—12], is weaker oxidant compared to APS, potassium dichromate and cerium(IV) sulfate. The use of iron ions in combination with hydrogen peroxide in highly acidic environment results in the formation of PANI [39—44]. On the contrary, aniline degradation with active role of iron ions and hydrogen peroxide proceeds in an environment of lower acidity [52,53]. Finally, silver nitrate has recently become of interest as oxidant because the oxidation of aniline yields PANI—silver composites [26,28,54,55]. The oxidation potential of silver ions is comparable to the oxidation potential of iron(III) ions and of *p*-benzoquinone. Since most acids precipitate silver ions, the oxidation with silver nitrate has to be carried out in nitric or sulfonic acids [27]. Based on occurrence of additional bands in the FTIR spectra, the presence of oligomers was reported also for PANI—silver composites prepared with silver nitrate [27].

On the bases of authors' knowledge of the literature, the role of *p*-benzoquinone formed as product or by-product of aniline oxidation in the further oxidation of aniline towards PANI or to 2,5-dianilino-*p*-benzoquinone-like oligomers has not yet been elucidated. The present study reports the use of three strong and two weaker inorganic oxidants (all discussed in the previous paragraph) and *p*-benzoquinone for the oxidation of aniline with respect to their standard redox potentials and the concentrations of acid used. Since silver nitrate was selected as one of the oxidants, aqueous solutions of methanesulfonic acid (MSA; this acid does not precipitate silver(I) ions) were used as reaction medium and acid concentration was the variable parameter in all experiments. Even though some comparison of the oxidation with various oxidants has been also provided [15,56—59], general survey presenting the relation between molar-mass distribution, molecular structure deduced from vibrational spectra and UV—visible spectra, and conductivity of aniline oxidation products is missing in the literature. The aim of this communication is thus to provide relation between the conductivity and molecular structure of the aniline oxidation products obtained with various oxidants under comparable reaction conditions, and to propose general mechanism of aniline oxidation in acidic aqueous medium.

2. Experimental

2.1. Chemicals

Aniline (p.a.; Penta, Czech Republic), ammonium peroxydisulfate (APS; 98%; Lach-Ner, Czech Republic), cerium(IV) sulfate, iron(III) chloride hexahydrate, p.a., ≥98% (both Sigma-Aldrich), silver nitrate (p.a.; Lach-Ner, Czech Republic), *p*-benzoquinone (≥98%; Sigma-Aldrich), potassium dichromate (Lachema, Czech Republic), methanesulfonic acid (MSA; ≥99.5%; Sigma-Aldrich), triethanolamine (p.a.; Lach-Ner, Czech Republic), 1-methyl-2-pyrrolidone (NMP; ≥99%), lithium bromide (both Sigma-Aldrich, USA) and ammonium hydroxide (p.a.; Lach-Ner, Czech Republic) were used as supplied.

2.2. Oxidation of aniline

Aniline (0.2 M) was oxidized with APS (0.25 M), cerium(IV) sulfate (0.5 M), potassium dichromate (0.0833 M), silver nitrate (0.5 M), iron(III) chloride (0.5 M), and *p*-benzoquinone (0.5 M) in aqueous solutions of MSA (for the reasoning of oxidant-to-aniline mole ratios see part 3.1). The oxidation with silver nitrate was accelerated by 0.002 M *p*-phenylenediamine [26]. After mixing the solutions of aniline and oxidant, the mixture was left at room temperature for 24 h. The solids were isolated by filtration, rinsed with 0.2 M MSA solution, then with acetone, dried in air and then over silica gel. Part of each sample was deprotonated to convert PANI salt to base form (Scheme 1) by immersion in a large excess of 1 M ammonium hydroxide, subsequently washed with water and acetone and dried as described above.

2.3. Characterization

Room-temperature conductivity of the samples was determined on pellets ($d = 13$ mm; compressed at 540 MPa) by the four-point van der Pauw method using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter as a voltmeter and a Keithley 705 Scanner equipped with a Keithley 7052 Matrix Card. When pellets could not be prepared, the resistivity of the powder sample was estimated by compressing the powder in a glass tube between two gold-coated copper pistons at pressure of 40 g cm^{-2}). Two-point method using a Keithley 6517 Electrometer/High Resistance System was applied for samples with conductivity lower than 10^{-5} S cm^{-1}. Before such measurements, circular gold electrodes were deposited on both sides of the pellets. The density of pellets was determined from their weights (Sartorius R160P balance) measured in air and when immersed in decane at 20 °C. Size-exclusion chromatography (SEC) was performed on a Calc 100 chromatograph (Labio, Czech Republic) equipped with a PLgel mixed-C column (Polymer Laboratories, UK) using NMP containing 0.005 g cm^{-3} of lithium bromide (to prevent aggregation) as the eluent at the flow rate of 0.70 mL min^{-1}. Samples (base forms) were dissolved in mobile phase containing 0.005 g cm^{-3} of triethanolamine (to remove possible residual protons). Samples were detected spectrophotometrically at 340 nm. UV—visible spectra of base forms dissolved in NMP were recorded with a Lambda 20 spectrometer (Perkin Elmer, UK). Infrared spectra in region 4000—400 cm^{-1} were recorded using a Thermo Nicolet NEXUS 870 FTIR Spectrometer (DTGS TEC detector; 64 scans; resolution 2 cm^{-1}) in transmission mode in potassium bromide pellets. The spectra were corrected for the carbon dioxide and humidity in the optical path. Raman spectra were collected on a Renishaw inVia Reflex Raman spectrometer (HeNe 633 nm laser; Leica DM LM microscope; objective magnification ×50; holographic grating 1800 lines mm^{-1}).