

IRON OXIDE AND PYROCATECHOL: A SPECTROSCOPY STUDY OF THE REACTION PRODUCTS

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Recebido em 3/1/06; aceito em 24/3/06; publicado na web em 1/8/06

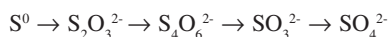
The reaction of 1,2-dihydroxy-benzene (pyrocatechol) ($C_6H_6O_2$) with iron oxide (Fe_2O_3) and sodium thiosulfate ($Na_2S_2O_3$) in aqueous medium (pH 7) was investigated. Pyrocatechol suffers autoxidation and coordinates with Fe^{3+} in solution. The presence of $S_2O_3^{2-}$ in solution was fundamental to generate and stabilize the pyrocatechol oxidation products as *o*-semiquinones. This compound was isolated and its structure characterized using FT-IR, EPR and UV-Vis Spectroscopy as $[CTA][Fe(SQ)_2(Cat)]$. A thermal mass loss mechanism was proposed based on Thermogravimetric Analysis (TG) to support the structural characterization.

Keywords: pyrocatechol; iron oxide; sodium thiosulfate.

INTRODUCTION

Phenolic acids are important components of a variety of processes taking place in soil, including humus formation and accessibility of micronutrients for plants^{1,2}. Wang *et al.*³ demonstrated that several phenolic acids in concentrations from 25 to 100 mg L⁻¹, in culture solution, inhibit the growth of several plant cultures. The phenolic substances are important species to maintain the reduction capacity strength in the aquatic medium⁴ and can be generated by microbial processes, lignin degradation or produced by fungi in wood⁵.

The $S_2O_3^{2-}$ is found in fertilizers as a source of sulfur and its chemical reactions in soil are not still completely understood⁶. Most of the studies on $S_2O_3^{2-}$ in soils concern its inhibitor effects on nitrification, urea hydrolysis and also as an effective activator of nitrogen fixation in the environment. $S_2O_3^{2-}$ also can be produced in soil by cysteine degradation or microbial oxidation of elemental sulfur (S^0). The latter process can be generalized through the mechanism:



There is evidence also for the abiotic oxidation of S^0 and $S_2O_3^{2-}$ in soils, although the importance of this process in relation to the global oxidation is not clear⁷. The interaction of iron with phenolic substances in aqueous medium has hardly been studied^{1,8}. Although there are several studies on phenolic compounds and manganese reactions in solution⁹⁻¹¹, it is possible to consider that the phenolic substances can react with iron and manganese through similar mechanisms in soil. Lehmann¹ has shown, using normal and pre-treated soils with Fe and Mn as substrate, that the phenolic acids were oxidized simultaneously with the reduction of iron and manganese oxides.

Studies carried out by Barreto *et al.*¹², showed that catecholamine, mainly dopamine and adrenaline, were oxidized quickly in aqueous medium in the presence of MnO_2 and sodium thiosulfate without producing melanin as the end product. In that mechanism it was proposed and pointed out that the outstanding presence of thiosulfate in the stabilization of surface compounds occurred in the first reaction steps. Barreto *et al.*¹³ showed that MnO_2 oxidized dopamine or L-dopa, in aqueous solution in the presence of sodium

thiosulphate. Highly stable Mn(II) complexes were generated in this process that could be precipitated with cetyltrimethylammonium bromide. The complexes obtained were characterized as $[CTA]([Mn](SQ)_3)$ and presented an octahedral-type structure, where the SQ ligands were dopamine-*o*-semiquinone or L-dopa-*o*-semiquinone anionic radicals; products of dopamine or L-dopa oxidation. These complexes present the property of maintaining the SQ radical ligands in a stable condition when in contact with air, unlike other complexes of the same type.

The iron complex formation has been studied with various catecholate and semiquinonate ligands¹⁴⁻¹⁹.

Pyrocatechol is the simplest molecule of the *o*-phenols and is useful as a model molecule to verify which are its reaction products in a reducing medium: polymeric compounds, such as humic acids in soil, or stabilizers such as monomeric compounds.

The objectives of this study were to characterize and propose the thermal decomposition mechanism for the compound obtained by the reaction of 1,2-dihydroxy-benzene (pyrocatechol) ($C_6H_6O_2$) with iron oxide (Fe_2O_3) and sodium thiosulfate ($Na_2S_2O_3$) in aqueous medium at pH 7.0.

EXPERIMENTAL PART

Solutions

All solutions were prepared with ultra pure water.

The reaction mixture containing pyrocatechol, iron oxide and sodium thiosulfate was prepared by adding 0.300 g sodium thiosulfate (6.32×10^{-3} mol L⁻¹), 0.100 g pyrocatechol (3.03×10^{-3} mol L⁻¹) and 0.020 g iron oxide (4.17×10^{-4} mol L⁻¹) to 300 mL water. The flasks containing the reaction mixture were covered with PVC film to avoid evaporation loss or dust contamination, and maintained under constant stirring at 25 °C. Before each UV-Vis and pH measurements, stirring was interrupted for 15 min for the iron oxide to sediment.

UV-Vis and pH measurements

After the addition of sodium thiosulfate and pyrocatechol to the water, the solution was stirred for 20 min and the pH measured.

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200 μL of the solution was diluted to 3 mL in a quartz cuvette of 1.0 cm optical path. The UV-Vis absorption spectrum was obtained from 200 to 900 nm with 1 nm resolution for each acquisition point. Iron oxide was added to the initial solution, stirred and the pH and UV-Vis spectra obtained at specific times.

Preparation of the solid compound from the solution

After disappearance of the 275 nm band, indicating the total pyrocatechol oxidation, the mixture was centrifuged for 40 min at 6,000 rpm to remove the iron oxide residue. To the solution was slowly added 10 mL of cetyltrimethylammonium bromide solution (0.027 mol L^{-1}) and stirred to complete precipitation. The solution was then transferred to a 500 mL separation funnel and 50 mL of chloroform was added. The suspension was stirred and the organic phase separated and washed with ultra pure water for complete elimination of cetyltrimethylammonium bromide. The organic phase was separated and evaporated at room temperature. A dark violet solid was obtained and kept in a desiccator for analysis. The analysis of $[\text{CTA}][\text{Fe}(\text{SQ})_2(\text{Cat})] \cdot 5\text{H}_2\text{O}$ where iron is Fe^{3+} , SQ = *o*-semi-quinone radical anion, Cat = catecholate, [CTA] = cetyl-trimethylammonium cation, was found (calculated): C = 58.4 (57.6%); H = 9.2 (8.7%); N = 3.2 (3.6%); Fe = 7.4 (7.3%). All experiments to crystallize the complex failed and instead produced an amorphous solid probably due to the long aliphatic chain present in CTA cation that prevent a regular crystal arrangement.

Physical measurements

The IR spectra of the solid compounds were obtained from 400 to $4,000 \text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} and 80 spectra accumulated (Shimadzu Spectrophotometer) using KBr tablets (Carlo Erba, 99 %) with 1:100 sample:KBr proportion.

EPR experiments were performed near the X-band (9.5 GHz) microwave frequency and with a magnetic field modulation of 100 kHz using Spectrometer Varian E-109 at room temperature. The microwave frequency was accurately read with a Hewlett Packard frequency counter, model HP 5352B. The data were acquired with a PC microcomputer using software for data acquisition developed at the Institute of Physics, University of São Paulo, São Carlos-SP, Brazil.

An iron hollow cathode lamp at 248.33 nm was used for iron analysis by AAS (Shimadzu AA-6601F Spectrometer). The calibration curve was constructed with an iron standard solution (Merck-1,000 ppm) from 0.1 to $1.0 \mu\text{g L}^{-1}$ in 1% (v/v) nitric acid. Samples (4 mg) were digested with 0.2 mL of HNO_3 (Merck 65%) and diluted with HNO_3 1% to 50 mL in a volumetric flask.

Mass losses (Thermogravimetric Analysis) were obtained on a T. A. Instruments TG 2950, High Resolution device under a N_2 atmosphere and a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Study of the reaction in solution

Figure 1A shows the UV-Vis spectra of reagent mixture during the reaction. A band at 275 nm characteristic of pyrocatechol was observed at $t = 0$ (spectrum a) and after 432 h this band disappeared, and a band at 287 nm and a shoulder at 301 nm (spectrum e) appeared. The pH during this period changed from 6.50 to 8.20, Figure 1B.

The accentuated pH increase indicated that an oxidation reaction of pyrocatechol occurred with release of OH^- and had the same pattern as observed by Barreto *et al.*¹² for catecholamine (dopamine, adrenaline, noradrenaline and L-dopa) oxidation reactions with

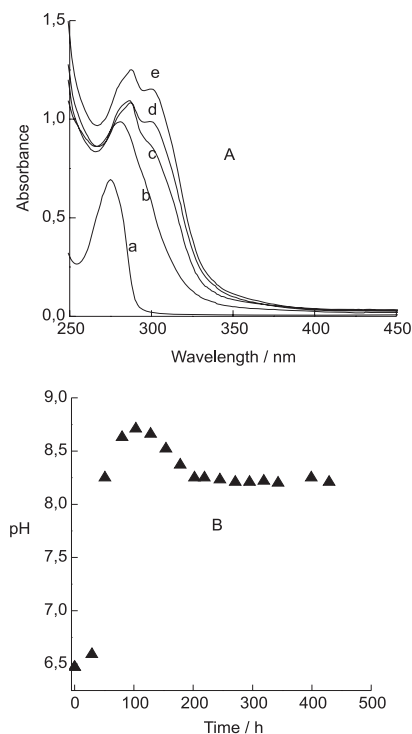


Figure 1. (A) UV-Vis spectra and (B) pH changes of the reagent solution containing pyrocatechol, sodium thiosulfate and iron oxide in the reaction times; 0 h (a), 76 h (b), 186 h (c), 263 h (d) 432 h (e)

MnO_2 . However, it was observed that the reaction time for Fe_2O_3 was considerably higher compared to MnO_2 in the ratio of 1:14. In the presence of sodium thiosulfate the intermediate *o*-semi-quinone was stabilized preventing further oxidation steps. In the absence of thiosulfate the oxidation of the pyrocatechol produces the melanin polymer and the solution presents an UV-Vis spectrum with continuum absorption and without band structures.

Pyrocatechol oxidation in the presence of thiosulfate indicated a complex mechanism probably due to intermediary compounds generated during the long reaction time. The results suggested a minor role for Fe_2O_3 as an oxidizing agent in the pyrocatechol oxidation reaction compared to that of MnO_2 in catecholamine oxidation.

Study of reaction products isolated in the solid state

The EPR technique applied to the reaction products isolated in solid state from the solution, revealed the presence of Fe^{3+} . Figure 2 shows two spin transitions, the first with $g = 4.3$ characteristic of

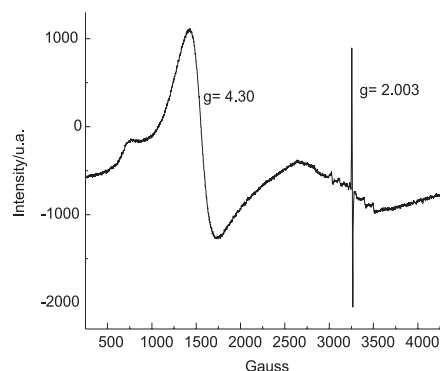


Figure 2. EPR spectrum of the solid complex obtained from the reaction solution with pyrocatechol, sodium thiosulfate and iron oxide

Fe^{3+} high spin in a rhombic environment and the other with $g = 2.003$, assigned to the organic free radical *o*-semiquinone. In the solid complex six weak signals around $g = 2$ characteristic of Mn^{2+} could be observed, probably present as trace impurities in the iron oxide. However, the presence of soluble Mn^{2+} in the mixture was tested and it had no influence on the oxidative process.

The literature reports that iron(III)-SQ complexes show strong antiferromagnetic spin-spin coupling of Fe-SQ or SQ-SQ, therefore they should be EPR silent^{14,17}. A more recent paper, however, reports that unlike the previously characterized mixed valence semiquinone-catecholato-iron(III) complexes, the complex [Fe(III) (bispicen) (Cl_4Cat) (Cl_4SQ)]₂DMF (bispicen = *N,N*-bis (2-pyridylmethyl) -1,2-ethanediamine) is EPR active, presenting at room temperature two broad transitions centered at $g = 1.92$ and 2.53 , and a strong signal appears at 77 K of $g = 4.3$ typical for the high spin Fe(III) complexes²⁰. We believed that the mixed nature of the complex, with SQ⁻ and Cat²⁻, resulted in weaker spin-spin coupling at room temperature and iron EPR signal appearing.

The presence of Fe^{3+} in the complex can be explained by the slow released of Fe^{3+} from the oxide into solution. Jewett *et al.*²¹ observed the formation of Fe^{3+} :catechol, in the proportion 1:3 in aqueous solution in $\text{pH} > 8.0$, and of the compound Fe^{2+} :catechol, in the proportion 1:2, below that value. As the pH in the reacting solution was always > 8.0 , increasing even more around 100 h (Figure 1B), the Fe-SQ-CAT complex had the physical chemical conditions to be present. The UV-vis spectrum of the complex in chloroform, Figure 3, presents one transition at 313 nm assigned to internal ligand electronic transitions and at 514 nm assigned to an interligand charge transfer (SQ⁻ → Cat), or a ligand to metal charge transfer (LMCT).

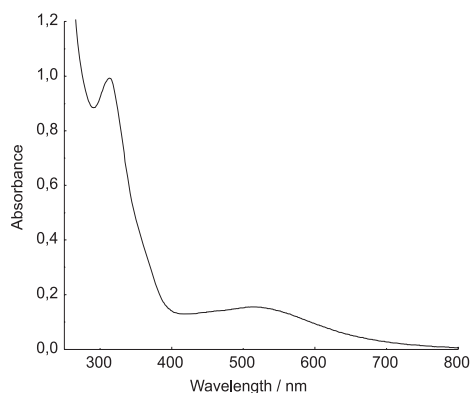


Figure 3. UV-Vis spectrum of [CTA][Fe(SQ)₂(Cat)] complex in CH_3Cl

The spectrum was very similar to $\text{LFe}^{\text{III}}(\text{DBSQ})$, where L is a phenolate and DBSQ a semiquinone, showing a band at 560 nm assigned as LMCT phenolate → Fe(III) and a intense band at 290 nm assigned to $\pi \rightarrow \pi^*$ transition in the ligand²². The UV-Vis spectrum of [LFe^{III}(DBC)]₂, however, showed bands at 620 and 420 nm, typical of catecholate complexes. Therefore, the UV-Vis spectral pattern indicated that the solid compound contained a semiquinone derivative from pyrocatechol and coordinated to high spin iron(III).

The iron complex bands in the infrared spectrum can only be observed from 1000 to 1450 cm^{-1} due to the predominance of cetyltrimethylammonium cation bands between 400 and 4000 cm^{-1} , Figure 4. Furthermore, Table 1 presents the observed frequencies and a tentative assignment for the compound. Intense bands were observed at 636, 1027, and 1220 cm^{-1} and a medium band at 1439 cm^{-1} for the compound obtained in the presence of iron oxide. The bands at 1220 and 1439 cm^{-1} are characteristic for the ligand based mixed valence semiquinone-catecholate transition metal complexes,

while bands at 1100 and 1480 cm^{-1} were generally observed for catecholates based transition metal complexes²². The presence of the band at 1439 cm^{-1} can be assigned to C-O stretching (νCO) with the iron bonded to the pyrocatechol oxygen.

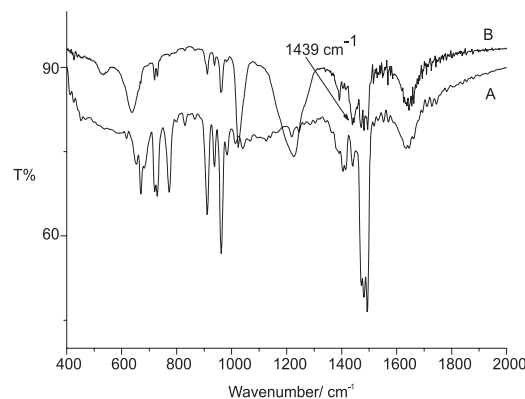


Figure 4. IR spectra of (A) CTAB salt, and (B) [CTA][Fe(SQ)₂(Cat)] complex in KBr pellets

Table 1. Observed frequencies (cm^{-1}) and a tentative assignment for the most characteristic bands of [CTA][Fe(SQ)₂(Cat)]

Assignment	Frequency/ cm^{-1}
$\nu(\text{CO}) + \nu(\text{CC})$	1439 m
$\nu(\text{CO}) + \nu(\text{CH})$	1387 w
$\nu(\text{CO})$	1220 s
$\nu(\text{CO}) + \nu(\text{CC})$	1164 sh
$\nu(\text{CC})$	1027 s
$\nu(\text{CC})\text{ring} + \nu(\text{CO-Fe})\text{ring}$	636 s
$\nu(\text{CC})\text{ring} + \nu(\text{C-O-Fe})\text{ring}$	530 w

m=medium, w=weak, s=strong, sh=shoulder

The thermal analysis of the complex was obtained, Figure 5, and the thermal decomposition mechanism below was proposed:

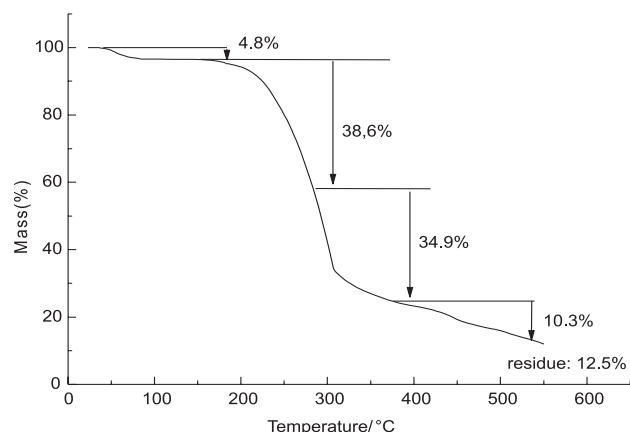
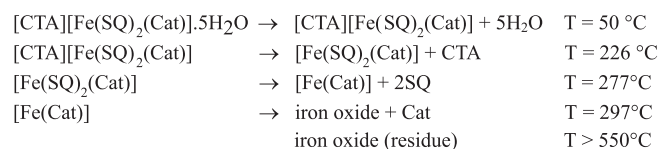


Figure 5. Thermogravimetric curves (TG) for the compound [CTA][Fe(SQ)₂(Cat)]

The mass loss percentages calculated based on the proposed mechanism and experimental results obtained were, respectively, 11.9 and 4.8%; 37.6 and 38.6%; 42.9 and 45.3% and 7.6% (calculated as Fe_2O_3) and 12.5%. Steps 3 and 4 steps were summed because the differences between the two mass losses were not well defined. The differences among the calculated and experimental values were due to imprecision in the step interval measurements. The mass loss mechanism reinforced the definition of the proposed structure as presented in Figure 6.

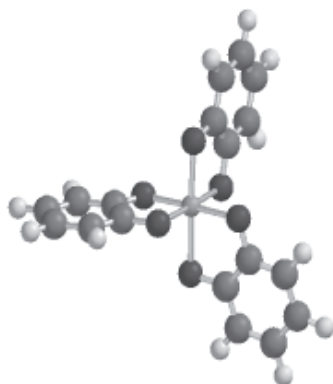


Figure 6. A schematic structure proposed for the anion complex $[\text{Fe}(\text{SQ})_2(\text{Cat})]^-$

CONCLUSION

The results of pyrocatechol oxidation in the presence of Fe_2O_3 and sodium thiosulfate indicated that pyrocatechol was oxidized by a more complex mechanism compared to catecholamine oxidation (dopamine or L-dopa) with MnO_2 . The presence of $\text{S}_2\text{O}_3^{2-}$ was fundamental to generate and stabilize the *o*-semiquinones in solution. The presence of the iron oxide provided Fe^{3+} to stabilize the radical by complex formation and had little action as an oxidizing agent. The complex isolated in solid state through CTAB precipitation indicated the presence of free radicals and Fe^{3+} , and the formulae was proposed as $[\text{CTA}][\text{Fe}(\text{SQ})_2(\text{Cat})]$. The complex structure should be close to an hexacoordinate arrangement with Fe^{3+} high spin due to the $g = 4.3$ characteristic signal. The structure proposed was coherent with the thermal decomposition analysis of the solid complex and associated thermal mechanism.

ACKNOWLEDGEMENTS

The authors thank Dr. O. R. do Nascimento (Laboratório de Biofísica UFScar, São Carlos, Brazil) for EPR spectra. The authors thank the CNPq and Fundação Araucária for financial support and Dr. R. Dekker for the manuscript revision.

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