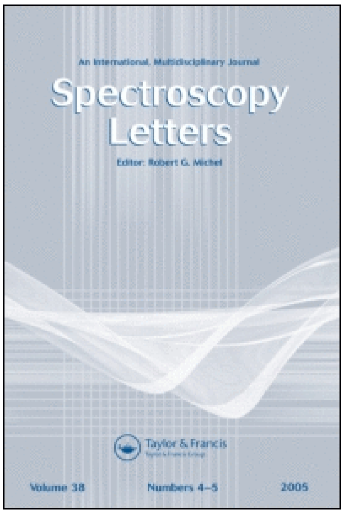

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Spectrophotometric Study of Catechol Oxidation by Aerial O_2 in Alkaline Aqueous Solutions Containing Mg(II) Ions.

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SPECTROPHOTOMETRIC STUDY OF CATECHOL OXIDATION BY AERIAL O_2 IN ALKALINE AQUEOUS SOLUTIONS CONTAINING Mg(II) IONS

Keywords: catechol oxidation, spectrophotometry

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ABSTRACT

Electronic absorption spectroscopy was employed to study the aerial oxidation of catechol (1,2-benzenediol) in alkaline aqueous solution containing an excess of Mg(II) ions. Graphical analysis by the matrix method of UV spectra recorded at regular time intervals gave a good fit for two absorbing species in solution. Based on this result and our earlier ESR spectroscopic investigations we concluded that two main absorbing species in this system are Mg(II)-spin stabilized *o*-benzosemiquinone anion radical and C-C dimer formed by the nucleophilic attack of catecholate anion on *o*-benzoquinone. Although the formation of 1,2,4-benzenetriol during the catechol oxidation has been detected in some ESR studies its presence was not indicated by this analysis probably because of the low and/or stable steady state concentration throughout the experiment.

INTRODUCTION

Oxidation of catechols and related compounds has been studied for many years due to the toxicity of their oxidation products. This is important as catechols are widespread in nature, both in plants and animal systems, and some of them are used clinically. Either chemical or enzymatic oxidation of these materials could produce *ortho*-semiquinone free radicals which are involved in the formation of highly reactive species capable of damaging living cells, like *o*-quinones and oxygen free radicals[1]. On the other side, antioxidant activity of some flavonoids and phenolic acids has been attributed to the presence of *o*-diphenolic groups in their molecules[2].

Electronic spectroscopy has been mainly used to study the oxidation of catechol(amine)s[3-5] and reactions of their oxidation products with some nucleophilic molecules[6,7]. However, the influence of diamagnetic metal ions on the catechols oxidation has been scarcely investigated by electronic spectroscopy[8] although ESR spectroscopic studies demonstrated that the oxidation of catechols and their reactions may be greatly influenced by the presence of diamagnetic metal ions through the spin stabilization of *o*-semiquinone free radicals[8-10]. We therefore performed the spectrophotometric study of catechol oxidation by aerial O_2 in alkaline aqueous solutions containing an excess of Mg(II) ions.

EXPERIMENTAL

All the chemicals used in this study were of analytical (p.a.) grade. Catechol (1,2-benzenediol) was used without additional purification. Solutions were prepared just prior the use by dissolving exactly weighted amount of catechol in distilled water saturated with ambient air. Catechol oxidation was stimulated by mixing catechol solution (0.5mmol dm^{-3}) with equal volume of either Tris or Tris-Mg buffer. Tris-Mg buffer was obtained by dissolving magnesium chloride in Tris buffer (100mmol, pH 8.4) up to the final concentration of 0.2mol dm^{-3} Mg(II) ions.

A Specord UV/VIS spectrophotometer (Carl Zeiss, Jena) with 0.5cm quartz cuvettes was employed for recording UV spectra.

RESULTS AND DISCUSSION

Catechol oxidation was followed spectrophotometrically at pH 8.4 in the presence and absence of Mg(II) ions. In Fig. 1 UV spectra of aqueous solution of catechol and mixtures of catechol solution with Tris and Tris-Mg buffers recorded immediately after mixing are presented.

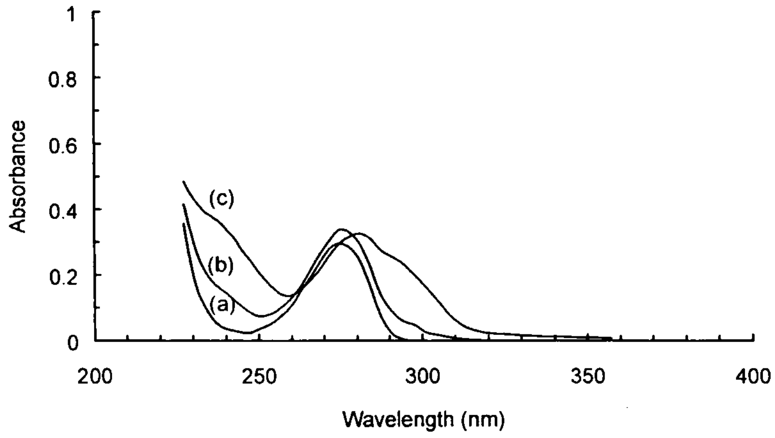

FIG. 1. Electronic absorption spectra of :
a) aqueous solution of catechol, 0.25mmol dm^{-3}.
b) catechol+Tris buffer (pH 8.4).
c) catechol+Tris-Mg buffer.
Spectra (a) and (b) are recorded immediately after mixing of catechol solution (0.5mmol dm^{-3}) with equal volume of buffer solutions.

While mixing of catechol solution with Tris buffer alone produced relatively small immediate changes in the UV spectrum of catechol, the addition of Tris-Mg buffer caused very fast appearance of new absorption peaks.

In Fig. 2 UV spectra of catechol+Tris buffer and catechol+Tris-Mg buffer mixtures after 90min of standing (with occasional shaking) in open glass cups are presented together with the difference spectrum. This difference spectrum (curve (c) in Fig. 2) clearly demonstrates that the presence of Mg(II) ions greatly enhanced the absorbance increase around 235 and 340nm with pronounced shoulders at around 250 and 295nm, respectively. These absorbance changes were followed by an increase in visible green color of the solution.

In Fig. 3 the UV spectra of catechol+Tris-Mg buffer mixture recorded at 15min intervals are overlaid to accentuate spectral changes. The first scan was performed immediately after mixing of catechol solution with Tris-Mg buffer and the last one after 90min.

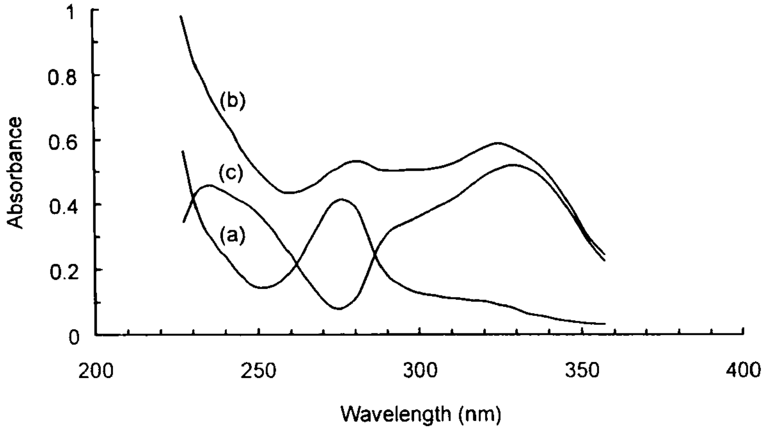

FIG.2. Electronic absorption spectra of:
a) catechol+Tris buffer (pH 8.4).
b) catechol+Tris-Mg buffer.
c) difference spectrum.
Spectra (a) and (b) are recorded 90min after mixing of catechol solution (0.5mmol dm^{-3}) with equal volumes of buffer solutions.

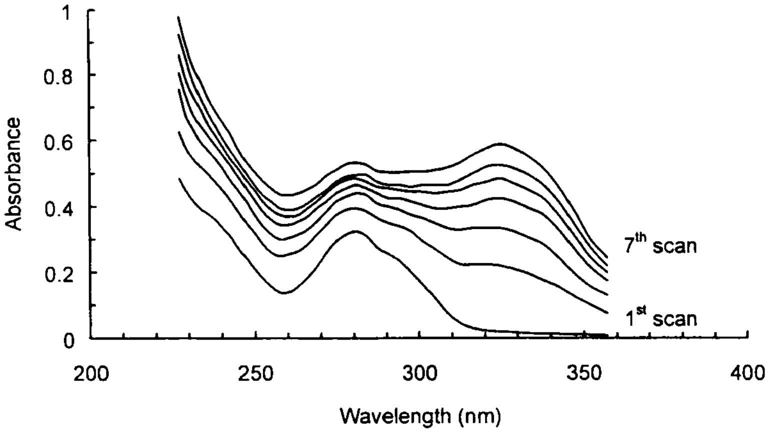

FIG.3. Oxidation of catechol in the presence of Mg(II) ions at pH 8.4 and room temperature. Spectra were taken at 15min intervals.

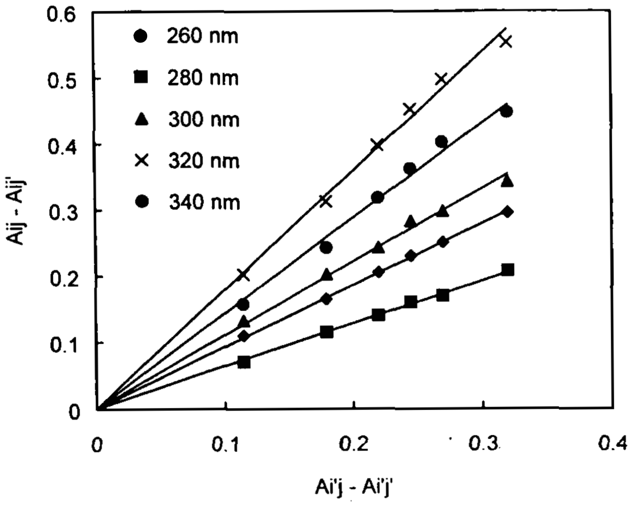

FIG.4. Graphical analysis by the matrix method of recordings of Fig.3. The test for two absorbing species was applied, being i'=240nm and j'=first scan.

UV spectra from Fig. 3 were subjected to the graphical analysis by the matrix method of Coleman *et al.*[11] in order to determine the number of absorbing species in solution. Although there is no isobestic point in UV spectra the graphical analysis of the recordings gave a good fit for two absorbing species in solution, as is shown in Fig. 4.

Based on the results of our ESR spectroscopic studies of catechol oxidation in alkaline aqueous solutions containing an excess of Mg(II) ions[12,13] we could suggest that these two absorbing species are Mg(II)-spin stabilized *o*-benzosemiquinone anion radical and C-C dimer formed by the nucleophilic attack of catecholate anion on *o*-benzoquinone[14]. Although ESR studies provided some evidence that 1,2,4-benzenetriol may also be formed during the aerial oxidation of catechol in alkaline aqueous solutions[13,15] the graphical analysis of our UV spectra does not give a good fit for three absorbing species in solution (data not shown). However, the concentration of 1,2,4-benzenetriol may be low enough and/or stable throughout the experiment thus going undetected by the matrix analysis of UV spectra.

CONCLUSIONS

We performed a spectrophotometric study of aerial oxidation of catechol in alkaline aqueous solution containing an excess of Mg(II) ions.

Comparison of UV spectra recorded during the catechol oxidation in the presence and absence of Mg(II) ions revealed that the presence of Mg(II) ions greatly influenced the catechol oxidation.

Graphical analysis by the matrix method of UV spectra recorded at regular time intervals during the catechol oxidation in the presence of Mg(II) ions gave a good fit for two absorbing species in solution. Based on this result and our earlier ESR spectroscopic investigations we concluded that two main absorbing species in this system are Mg(II)-spin stabilized *o*-benzosemiquinone anion radical and C-C dimer formed by the nucleophilic attack of catecholate anion on *o*-benzoquinone.

It is suggested that these results could be of some use for the interpretation of spectrophotometric data in the studies of catechol(amine)s oxidation.

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