

Reaction behavior of 3,5-Di-*tert*-butylcatechol with active oxygen species using polyaniline / oxygen / aqueous system

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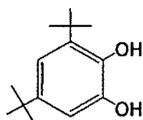
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Abstract — Following the discovery at this laboratory that superoxide can be produced simply by placing polyaniline (PAn) in contact with oxygen, studies have been conducted into the application of this to organic reactions in an aqueous system. As a result, it was revealed that an oxidation reaction of the substrate progresses, including the aromatic ring cleavage. This research was conducted in order to make observations of the properties of the oxidation reactions in a polyaniline / oxygen / aqueous system, as an oxidation reaction field with 3,5-Di-*tert*-butylcatechol.

Keywords — 3,5-Di-*tert*-butylcatechol, epinephrine, polyaniline, active oxygen

I. Introduction

Perviously, we found that polyaniline (PAn) reduces dissolved oxygen to generate superoxide in water¹⁾, and we



3,5-Di-*tert*-butylcatechol
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have been investigating the continuous generation of active oxygen species by reducing PAn electrochemically in aqueous solution and applying this system to organic reactions. We have been able to confirm the presence of superoxide and hydroxyl radicals in this system. In addition, we demonstrated that in a reaction with benzoic acid as a substrate, aromatic rings are cleaved. These findings suggest that this reaction system involves not only Fenton-type reaction pathways, but also other reaction pathways.

The purpose of this research was to study the process of ring cleavage reactions in greater detail, 3,5-Di-*tert*-butylcatechol (1, 3,5-DTBC), as used in the catechol oxygenase model reaction, was selected as the substrate. 1 can suppress nucleophilic substitution, a side reaction, due to the steric effects of the butyl group. It was decided to track the oxidation reactions of 1, in an attempt to isolate and identify intermediate products.

Table 1. Oxidation of 3,5-Di-*tert*-butylcatechol with various active oxygen species.

Run	Reaction condition ^{a)}		Recovery (%)	Yield of product (mol %)				Unknown
	Oxidation methods	Time		2	3	4		
1	PAn/O ₂ /FeCl ₃ ^{b)}	10 min	96	4	-	-	-	Tr
2	PAn/O ₂ /FeCl ₃	1 h	46	-	46	8	-	Tr
3	PAn/O ₂ /FeCl ₃	24 h	0	-	57	9	-	35
4	H ₂ O ₂ ^{c)}	24 h	68	2	25	5	-	Tr
5	H ₂ O ₂ ^{d)} /FeCl ₃ ^{e)}	24 h	34	3	63	-	-	Tr
6 ^{f)}	KO ₂ /MeCN ^{g)}	1 h	23	16	-	4	-	-

^{a)} 3,5-Di-*tert*-butylcatechol · 2.52 × 10⁻³ mol. All runs except 6 were at room temperature

^{b)} Moro-oka, Y., Foote, C. S. *J. Am. Chem. Soc.*, 1976, 98, 1510

^{c)} Continuous generation

^{d)} H₂O₂ · 1.46 × 10⁻³ mol ^{e)} FeCl₃ · 0.86 mg

^{f)} 3,5-Di-*tert*-butylcatechol · 3 × 10⁻³ mol, KO₂ 3 × 10⁻³ mol, MeCN 25 ml

II. Method

The active oxygen was produced using a PAn electrode for the working electrode, a titanium plate as the counter electrode, and a saturated calomel electrode for the reference electrode. A constant potential of -0.14 V vs SHE was applied in a 0.9 wt% NaCl solution. The oxidation decomposition reaction was performed at 25°C using 1, epinephrine and adrenochrome as substrates. After the reaction, the reaction system's UV spectrum was measured directly, and the oxidation reaction products were identified using HPLC. Moreover, in order to investigate the active species involved in the reaction, the reactions with potassium superoxide, hydrogen peroxide and hydroxyl radicals were also performed.

III. Results and Discussion

The results of the reactions with 3,5-DTBC (1) are summarized in Table 1. A PAn/O₂ system was used in Runs 1, 2 and 3, a hydrogen peroxide system was used in Run 4, Fenton reaction system was used in Run 5, and KO₂ system was used in Run 6. In the initial stages of the reaction using the PAn / O₂ system, a blue tint was seen in the reaction system,

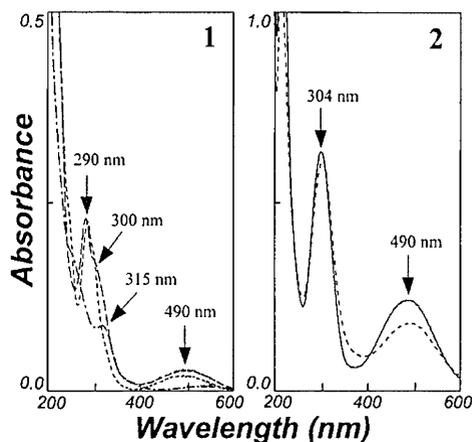


Figure 1. UV spectra of epinephrine(1), adrenochrome(2) (—), and after oxidation reaction for 20 min. (-----), 50min. (----), 3h (-----) by PAn/O₂/H₂O system.

confirming the production of 3,5-Di-*tert*-benzoquinone (2). In one hour, half of 1 reacted, and a further reaction to form 3 had progressed. Furthermore, after sufficient reaction time of 24 hours, the reactant did not contain 1 but a component, indicating that the reaction progressed further to 4. Since the respective recovery rates in Runs 4 and 5 were 68 % and 34 %, respectively, it can be presumed that the reactivity with hydrogen peroxide and hydroxyl radicals was not high. It was also shown that the reaction with hydroxyl radicals did not produce 4. Moreover, the reaction with KO₂ quickly provided 2. The above results demonstrate that in the PAn / O₂ system, a number of active oxygen species, including the superoxide produced by the one-electron reduction of the oxygen dissolved in the water, were involved in the reaction. In order to confirm this, the reaction was performed with epinephrine as the substrate. Epinephrine is known to react with superoxide to produce adrenochrome²⁾. The results of the epinephrine oxidation reaction are shown in

Fig. 1. The adrenochrome results are also given for comparison. As can be seen from the graphs, after 20 minutes from the start of the reaction, a shoulder was observed at around 300 nm, and a peak in absorbance occurred at around 490 nm. After 50 minutes, the shoulder at around 300 nm had become more pronounced, and the peak in absorbance at 490 nm had increased (Figure 1(1)). These two absorbance wavelengths correspond to the peak absorbance wavelengths of adrenochrome (2), confirming the presence of superoxide. Moreover, as the reaction continued over a long time, the absorbance at 490 nm gradually faded, and a new peak appeared at 315 nm. Meanwhile, the absorbance peak at 490 nm for adrenochrome reduced by 25 % after 20 minutes, showing a faster change than in the epinephrine system. This is presumed to be due to the competition between the adrenochrome oxidation reaction and the reaction of epinephrine with superoxide that produces adrenochrome. Based on these results, it is believed that the continuous production of superoxide is closely connected with the oxidation reactions of organic compounds in a PAn / oxygen / aqueous system.

References

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