Reaction behavior of curcumin and its analogues with active oxygen species in a polyaniline / oxygen / aqueous system

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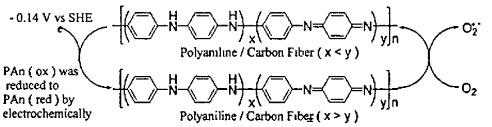
Abstract

Since the discovery that superoxide production proceeds simply from the contact of polyaniline (PAn) with oxygen, an apparatus was developed for its continuous production. This apparatus enables us to examine the environmental dynamics of reactions between organic compounds and oxygen. We conducted studies into the reaction of both ß-diketone, which was recently reported as a new antioxidant reagent, and its analogues, with active oxygen species in a PAn / oxygen system.

Keywords 2,4-pentanedione, curcumin, ß-diketone, polyaniline, active oxygen

Introduction

Recently, there have been concerns over the effects of organic compounds on organisms. We previously discovered that superoxide is produced simply by the contact of polyaniline (PAn) with oxygen (Scheme 1).[1,2] In this reaction system, the production of different active oxygen species is possible without adding a reagent to an aqueous system, making it advantageous for studying the environmental dynamics of organic compounds. Therefore, the aim of this research is to study the reactions of curcumin, which has antioxidant properties, and its analogues, with active oxygen species in an aqueous system.



Scheme. 1. Mechanism for the reaction of polyaniline with dissolved oxygen.

Method

Active oxygen was produced using a PAn electrode as a working electrode, a titanium plate as a counter electrode, and a saturated calomel electrode as a 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℃ using curcumin (1), tetrahydrocurcumin (2) and 2,4-pentadione (3) as substrates. After the reaction, a

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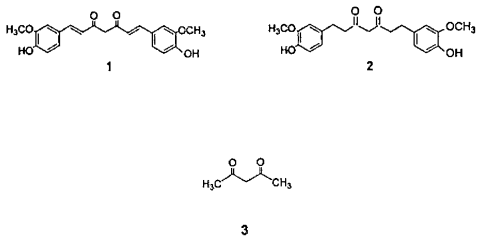

UV spectrum of the reaction system was measured directly.

The products of the oxidation reaction were identified using HPLC, IR, and NMR. In order to investigate the active species involved in the reaction, the substrates were reacted with superoxide in a KO_2 / THF system, with hydrogen peroxide in a H_2O_2 system, and with hydroxyl radicals in a H_2O_2 / $FeCl_2$ system.

Results and Discussion

The results for the reactions of 1 and 2 in the PAn / O_2 system (A) and the KO_2 system (B) are shown in Fig. 1. As

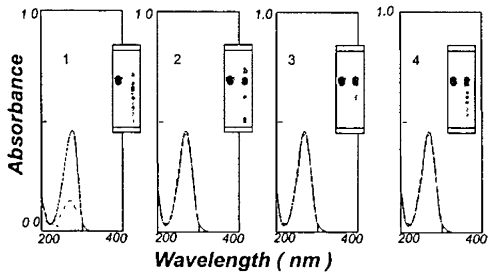

Fig. 1. Results of TLC and UV spectra of curcumin and tetrahydrocurcumin (—) and after oxidative reaction (-----:24h) by PAn/O_2 system (1) , KO_2/THF (2) .

can be seen from the graphs, 1 exhibited high reactivity in the PAn / O_2 system and with the superoxide. Judging from the patterns of UV changes, in the case of 1, it is believed that the double bond reacted first. Since the reaction products of 1 in the PAn / O_2 system and the KO_2 system exhibited different patterns, it can be

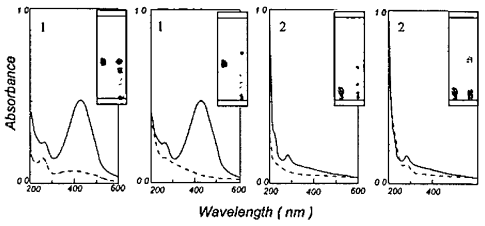

Fig. 2. Results of TLC and UV spectra of 2,4-pentanedione (—) and after oxidative reaction (-----:21h) by PAn/O_2 system (1) , KO_2/THF (2) , H_2O_2/$FeCl_2$ (3) , H_2O_2 (4) .

presumed that 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 the PAn / O_2 system. On the other hand, it was found that the reactivity of 2 was low compared to 1 in both the PAn / O_2 and the KO_2 systems. Further reactions were performed with 3 using the various active oxygen species (Fig. 2). Although no 3 was found to remain in the PAn / O_2 system after being allowed to react for 21 hours, the reaction with hydrogen peroxide had progressed only by 20% and the Harber-Weiss reaction (i.e., the reaction with hydroxyl radicals) had hardly progressed at all. Moreover, in the hydrogen peroxide system after the reaction time of 21 hours, TLC and HPLC analysis showed that the three components had the same Rf values and retention times as did the reaction products in the PAn / O_2 system after 5 hours. After these components were isolated and re-oxidized with hydroxyl radicals, HPLC analysis showed that a number of components that had the same retention time as the reaction products in the PAn / O_2 system after 21 hours were included. From these results and considering that only in the PAn / O_2 system was 3 mostly oxidized after

21 hours, it can be presumed that in this system, the reactions with the superoxide and hydrogen peroxide were preferred and took place initially, followed by the progression of the reaction with hydroxyl radicals.

In the PAn / O_2 system, the production of different active oxygen species is possible without adding a reagent to the aqueous system. Consequently, this system provides an interesting reaction field for investigating which active oxygen species react preferentially, depending on the structure of the substrate. This system, in which oxygen is activated under conditions similar to those in nature, may have advantages in studying environmental dynamics of reactions of organic compounds.

References

1) S. Otsuka, K. Saito and K. Morita, *Chem. Lett.*, 1996, 615.

2) Proceedings of The 40th Symposium on Chemical and Biochemical Oxidation 1222 (2007).