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Analysis of dyestuff degradation products by capillary electrophoresis

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Abstract

Capillary electrophoresis (CE) with two different detection methods, mass spectrometry (MS) and UV absorption spectroscopy with photodiode array detection (UV/DAD), was used for the analysis of the degradation products of dyestuffs. We have studied wet oxidation with solid catalyst as the treatment method of wastewaters containing dyestuffs. When the Orange II (C.I. Acid Orange 7) solution was used as the model wastewater, treated solution contained unknown highly polar degradation products. We were able to determine the molecular masses of some products by CE–MS. From this clue, we tried to identify these products by CE–UV/DAD. By means of the comparison of the migration time and UV spectra of standard samples, three degradation products were identified. The separation of degradation products was successful within 15 min.

Keywords: Dyes

1. Introduction

Colored wastewater discharged from factories especially in the dyeing industry contains refractory coloring compounds such as dyestuffs. If this sort of wastewater is exhausted in the source area of a public water supply, serious environmental problem may arise. Furthermore, colored wastewater gives people unpleasant feelings [1]. Some local governments have imposed stringent controlling measures on the color of effluent from the industrial facilities in Japan.

Since there have been many difficulties in treatment of colored wastewater with conventional methods such as flocculation, we have studied a novel degradation method based on wet oxidation with solid catalyst [2]. The wet oxidation with the catalyst of platinum supported on titania was applied to a degradation of dyestuffs. We selected Orange II as a model dye because its structure is simple. After the treatment of the Orange II solution, it became colorless and some degradation products were generated. The products could not be identified by conventional HPLC method because their polarity was very high [3].

Recently, capillary electrophoresis (CE) has been applied to the analysis of dyestuffs [4–10]. CE is more suitable for the analysis of charged dyestuffs than HPLC because of its separation principle, higher separation efficiency and simpler method development. The combination of CE and mass

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spectrometry (MS) is a powerful technique to determine dyestuffs in wastewater [4,10].

In this paper, we demonstrated the identification of dyestuff degradation products by CE–MS and CE with UV absorption spectroscopy with photodiode array detection (UV/DAD). These two detection methods were complimentary used with each other. We were able to obtain information about molecular mass of unknown degradation products by CE–MS using a pneumatically assisted electrospray (ionspray) interface [11]. The comparison of peak spectra obtained by CE–UV/DAD was also a useful technique for identification.

2. Experimental

2.1. Apparatus

CE–MS was performed a Hewlett-Packard 3D CE instrument (Yokogawa, Tokyo, Japan) and a Perkin-Elmer Sciex API-300 triple quadrupole MS instrument (Perkin-Elmer, Yokohama, Japan). The CE instrument control was performed with a Hewlett-Packard Vectra XM Series 3 (5/120) computer. The MS instrument control and data collections were performed with a Macintosh computer (Model 8500/120). An ionspray interface supplied by Perkin-Elmer Sciex was employed for the coupling of CE and MS. For the delivery of a sheath liquid, a Harvard Apparatus syringe pump (Model 11, South Natick, MA, USA) was used. A fused-silica capillary of 50 μm I.D.×180 μm O.D. (Supelco, PA, USA) was used as untreated or coated with linear polyacrylamide by the method reported by Nakatani et al. [12]. The total length of the capillary was 75 cm.

CE–UV/DAD was performed with a CAPI-3000 automated CE System (Otsuka, Osaka, Japan). An untreated fused-silica capillary of 75 μm I.D.×375 μm O.D. (GL Sciences, Tokyo, Japan) was used. Its total length was 62 cm and the effective length was 50 cm to the detector. The instrument control and data collections were performed with a PC-9801 personal computer (NEC, Tokyo, Japan).

2.2. Reagents and samples

Orange II of guaranteed reagent grade was obtained from Nacalai Tesque (Kyoto, Japan). Other reagents were of analytical grade and were used without further purification. Distilled water for buffer preparation was purchased from Kanto (Tokyo, Japan) or prepared by Milli-Q Jr. (Millipore, CA, USA).

2.3. Procedure

Wet oxidation of 1000 mg/l Orange II solution was performed at 150°C in a stirred autoclave. The aliquot of treated solution was withdrawn through a cooling pipe of autoclave at 20, 30, 40, 50, 60, 70, 80, 110, 140 and 170 min.

In CE–MS, a 40 m*M* ammonium acetate buffer (pH 6.0) and a 50 m*M* ammonium carbonate buffer (pH 8.5) were used as running solutions. As a sheath liquid, a mixture of each running solution–methanol (1:1) was used. The sheath liquid was delivered at 4 μl/min. The capillary was rinsed with a running solution for 5 min at 94 kPa prior to each run, and a sample solution was injected at 5 kPa for 8 s. When the acetate buffer was used, a coated capillary was used and a constant CE voltage of −25 kV was applied. An ionspray voltage was not applied during sample injection and for 1 min from each start of the run, and then −4.5 kV was applied at another end of the capillary. When the carbonate buffer was used, an untreated fused-silica capillary was used and a constant CE voltage of 25 kV was applied. An ionspray voltage of −4.5 kV was applied after 1 min from the start of the run at another end of the capillary. The MS instrument was set at the single stage mode and the MS detection was performed in the selected ion monitoring mode for each negative quasimolecular ion.

In CE–UV/DAD, a 50 m*M* ammonium carbonate buffer (pH 9.5) were used as running solution. When the running solution was changed, the capillary was rinsed with 0.1 *M* NaOH for 5 min using a vacuum at the detector reservoir, followed by subsequent rinses of distilled water for 3 min and running buffer for 4 min. After each run, the capillary was rinsed with running buffer for 4 min. Sample injections were made hydrodynamically, 20 mm×30 s. The injection volume was about 1.7 nl. The set-up voltage and temperature were 20 kV and 30°C, respectively, throughout all experiments. Migrated

samples were detected by on-column measurement of UV absorption with photodiode array detection at the range of 200 nm to 600 nm.

3. Results and discussion

3.1. CE–MS

First, we used a 50 m*M* ammonium carbonate buffer (pH 8.5) as a running solution. Two samples of treated solution, No.4 (reaction time: 50 min) and No.10 (170 min) were used for the analysis. The peak of one component was not observed with No.10 sample since the electroosmotic velocity was too slow and the anionic mobility of the component was too large to detect on the cathodic end within 60 min. The use of coating capillary and 40 m*M* ammonium acetate buffer (pH 6.0) allowed the detection on the anodic end. When No.4 sample were analyzed, four peaks were observed at m/z 327.0, 172.8, 164.8 and 200.8, respectively. The pherograms are shown in Fig. 1. The peak at m/z 327.0 was easily identified to Orange II. The pherograms of No.10 at the same m/z are shown in Fig. 2. Main degradation products were observed at m/z 200.8. Two small peaks were observed at m/z 164.8 and m/z 172.8, respectively. No peak was observed at m/z 327.0.

Bandara et al. described the degradation of Orange II by Fenton oxidation [13]. Orange II was degraded into two compounds, *p*-phenolsulfonate and 1,2-dihydroxynaphthalene as shown in Fig. 3. The peak at m/z 172.8 in Fig. 1 was estimated to be *p*-phenolsulfonate. The peak of 1,2-dihydroxynaphthalene could not be observed because of further degradation. We inferred that other two peaks in Fig. 1 were *o*-phthalate (m/z 165.1) and *p*-sulfobenzoate

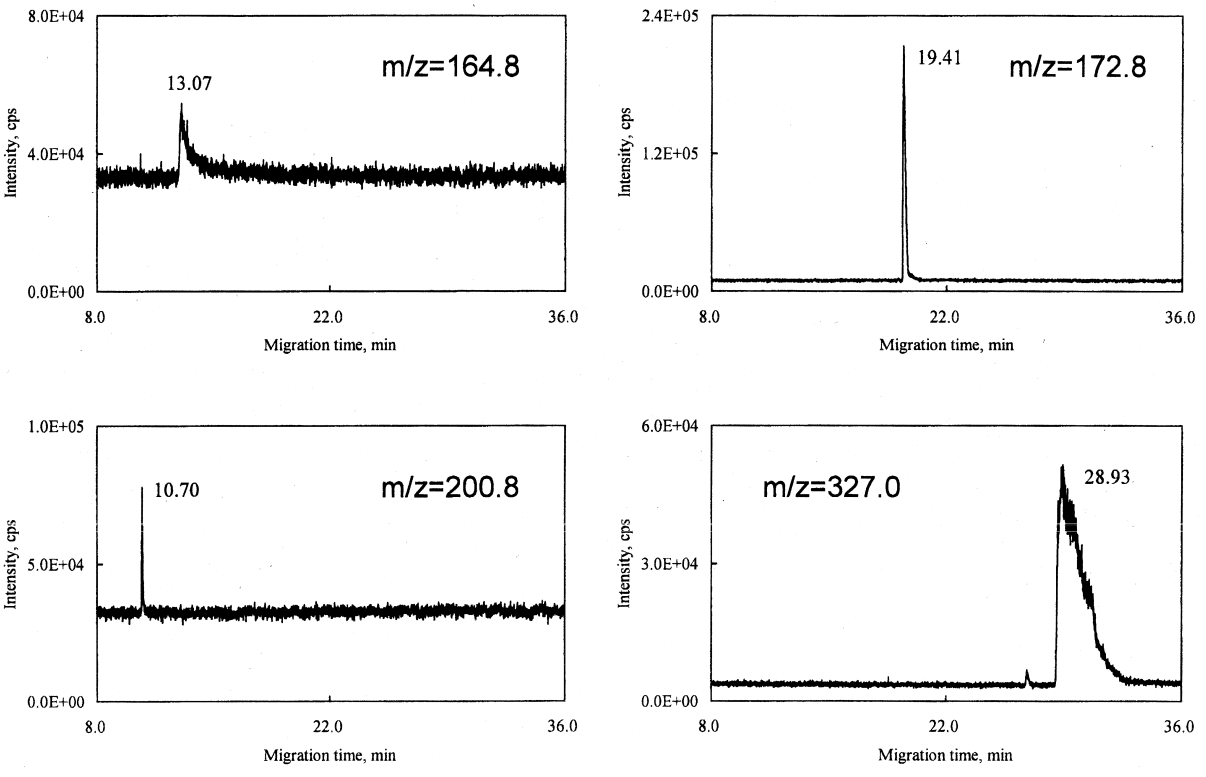

Fig. 1. Single ion pherograms of sample No.4 (reaction time: 50 min) by CE–MS. Conditions: sample injection, 5 kPa×8 s; capillary, 75 cm×50 μm I.D. coated with polyacrylamide; running solution, 40 m*M* ammonium acetate buffer (pH 6.0); sheath liquid, a mixture of running solution–methanol (1:1); flow-rate of the sheath liquid, 4 μl/min; CE voltage, −25 kV; ionspray voltage, −4.5 kV.

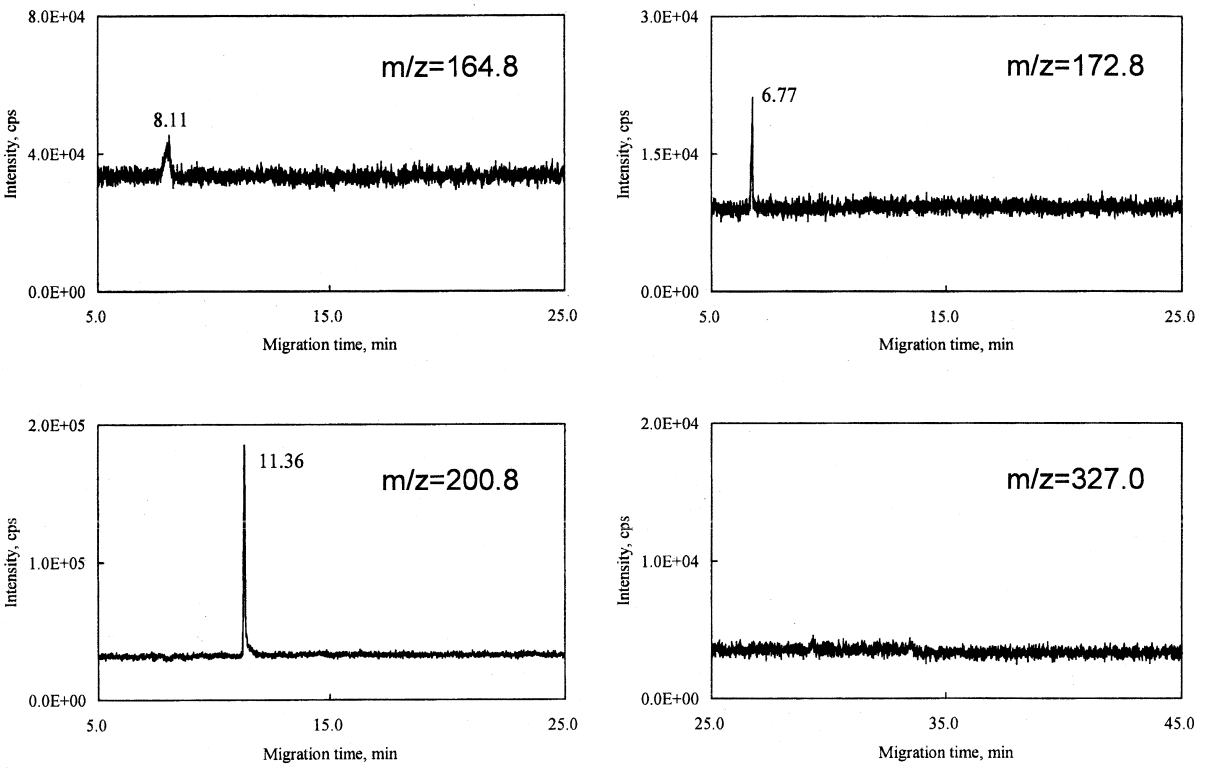

Fig. 2. Single ion pherograms of sample No.10 (reaction time: 170 min) by CE–MS. Other conditions as in Fig. 1.

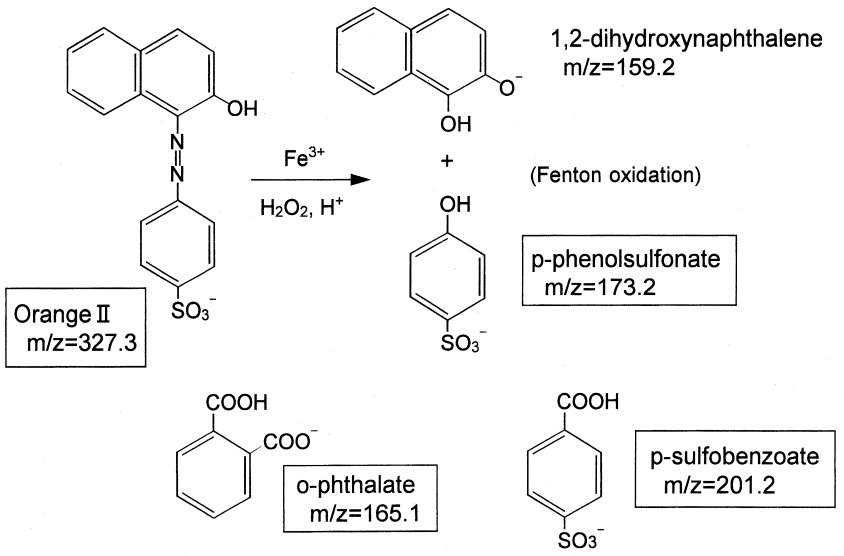

Fig. 3. The structure and molecular mass of Orange II and estimated degradation products.

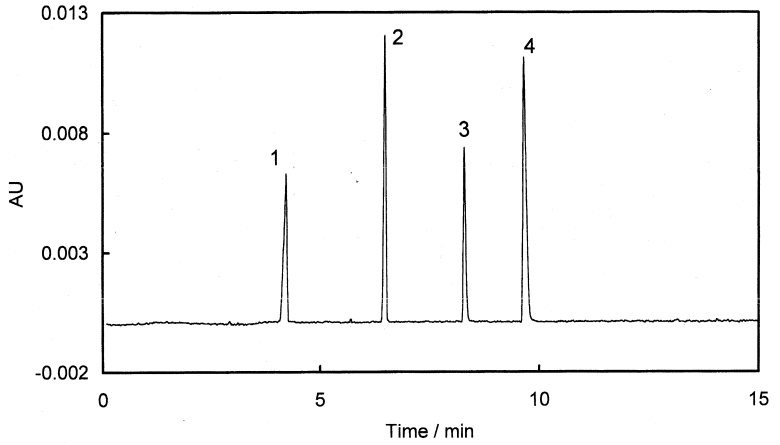

Fig. 4. Pherogram of standard solution by CE–UV/DAD. Conditions: sample injection, 20 mm×30 s; capillary, 62 cm×75 μm I.D. untreated fused-silica (50 cm to the detector); running solution, 50 m*M* ammonium carbonate buffer (pH 9.5); CE voltage, 20 kV; detection wavelength, 240 nm; temperature, 30°C. Peaks: 1, Orange II; 2, *p*-phenolsulfonate; 3, *o*-phthalate; 4, *p*-sulfobenzoate (100 mg/l of each).

(*m*/*z* 201.2) from the structure and molecular mass. Their structures are also shown in Fig. 3. The identification was confirmed by the standard addition method. In Fig. 2, the peak at *m*/*z* 200.8 was also estimated to be *p*-sulfobenzoate, however, the small peaks at *m*/*z* 164.8 and at *m*/*z* 172.8 were considered to be other unknown products because their migration time was different from that of the peaks in Fig. 1.

3.2. CE–UV/DAD

As another identification method, we used UV absorption spectroscopy as the detection method for CE. When a 50 m*M* ammonium carbonate buffer (pH 9.5) as a running solution was used for CE–UV/DAD, the peaks of degradation products were migrated within 15 min. Therefore, this buffer was used in CE–UV/DAD for the rapid separation and experimental simplicity.

The separation of standard compounds shown in Fig. 3 was performed by CE–UV/DAD. Orange II and three compounds were successfully separated within 15 min as shown in Fig. 4. The separation of the treated samples are shown in Figs. 5 and 6. The same samples (Nos. 4 and 10) were analyzed as in the case of CE–MS. Numbered peaks were identified with corresponding compounds shown in Fig. 4 by

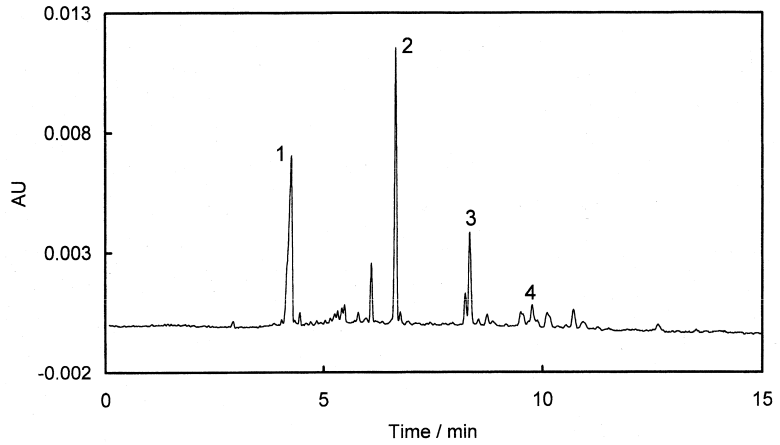

Fig. 5. Pherogram of sample No.4 (reaction time: 50 min) by CE–UV/DAD. Other conditions as in Fig. 4.

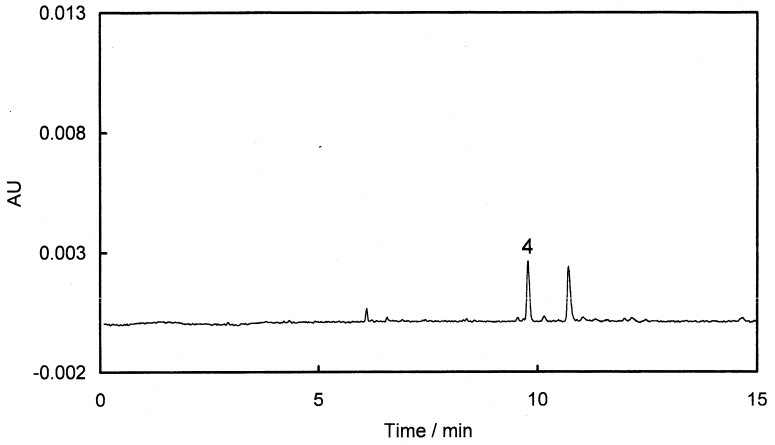

Fig. 6. Pherogram of sample No.10 (reaction time: 170 min) by CE–UV/DAD. Other conditions as in Fig. 4.

the comparison of the migration time and UV spectra of each peak with standard compounds. Their peak spectra are shown in Fig. 7. The identification was easily performed by use of the spectra library search system equipped with CAPI-3000. The matching factors for these spectra were 97.4% for *p*-phenol-

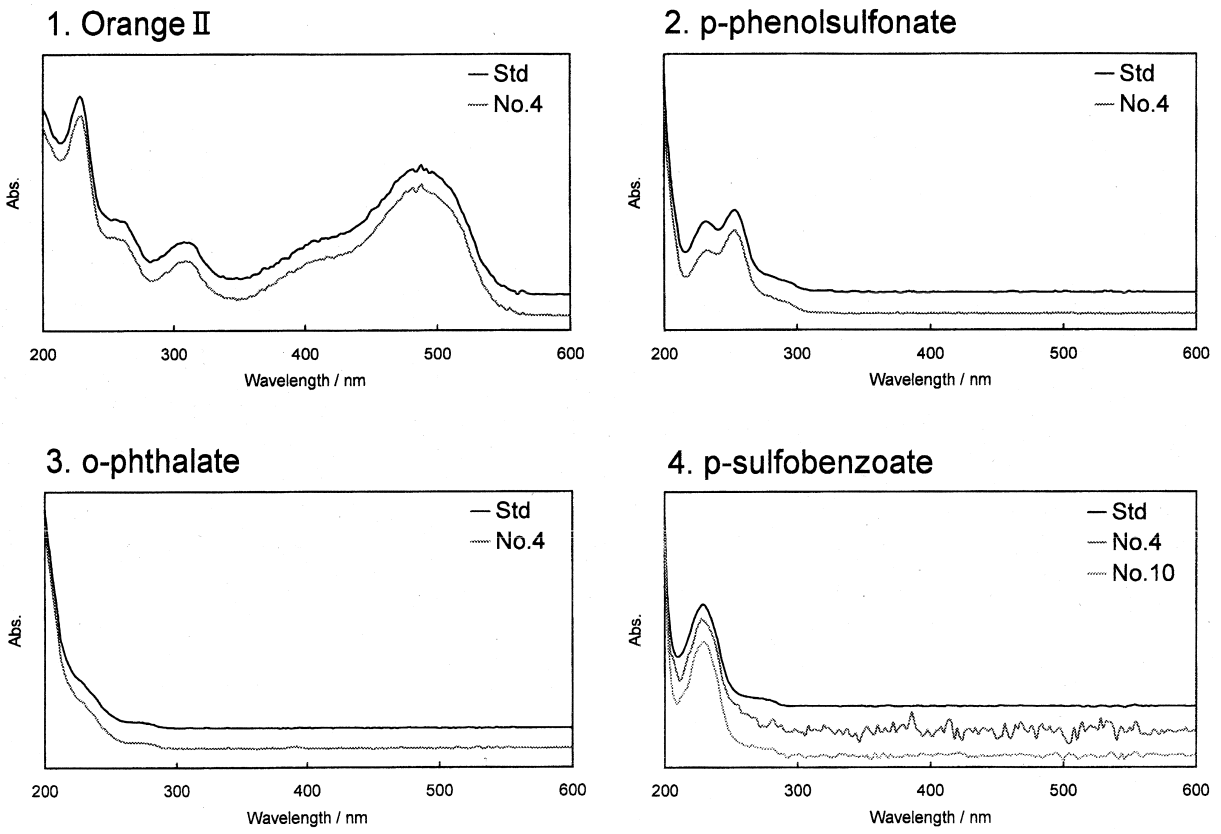

Fig. 7. Peak spectra of standard compounds and components of sample Nos. 4 and 10.

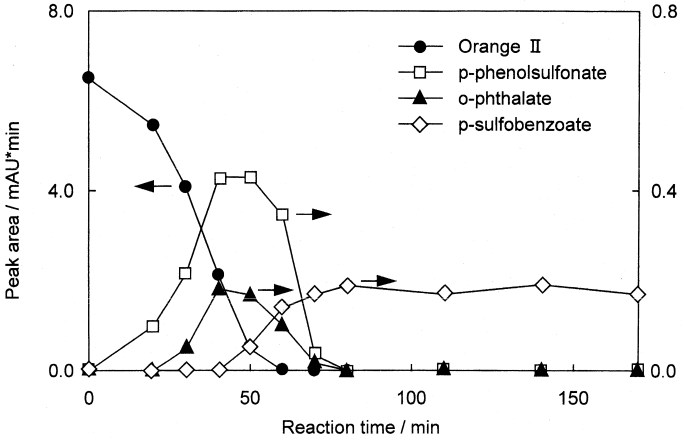

Fig. 8. Degradation and formation of components in the model solution (Orange II, 1000 mg/l) treated with wet oxidation. Reaction conditions: catalyst, 5% Pt/TiO_2; temperature, 150°C.

sulfonate, 97.8% for *o*-phthalate, and 94.7% for *p*-sulfobenzoate (No.10).

The preliminary results of the changes of Orange II and degradation products are shown in Fig. 8. Orange II was completely degraded at 70 min. *p*-Phenolsulfonate and *o*-phthalate were intermediates, whereas *p*-sulfobenzoate remained at 170 min. The relative standard deviations of the peak area of standards were within 6.4% ($n=3$). Therefore, for the precise determination of these products, the application of the standard addition method seems to be necessary.

4. Conclusions

The use of CE–MS and CE–UV/DAD enabled the identification of some unknown products in the samples treated with wet oxidation. These methods provided useful information for the analysis of the degradation process. The results were rapidly and easily obtained, and no pretreatment was necessary. We are proceeding with further identification of the undefined peaks and application to the diluted wastewaters.

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