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Oxidative decomposition of organic water pollutants with UV-activated hydrogen peroxide Determination of anionic products by ion chromatography

Claudia Scheuer[a,*], Birgit Wimmer[a], Heidrun Bischof[a], Le Nguyen[a], Jürgen Maguhn[b], Peter Spitzauer[c], Antonius Kettrup[c], Dietrich Wabner[a]

[a]*Arbeitsgruppe Angewandte Elektrochemie und Chemische Umwelttechnik, TU München, Lichtenbergstrasse 4, 85748 Garching, Germany*

[b]*GSF-Institut für Ökologische Chemie, Schulstrasse 10, 85356 Freising, Germany*

[c]*Lehrstuhl für Ökologische Chemie, TU München, 85350 Freising, Germany*

Abstract

Organic water pollutants are decomposed by UV-activated hydrogen peroxide. Using ion chromatography, inorganic and organic anions formed by the oxidative treatment can simultaneously be determined at trace levels without any sample preparation. For identification of anionic metabolites of 2,4-dichlorophenoxyacetic acid (2,4-D), 2-nitrobenzoic acid and nitrobenzene, an ion chromatographic system with a combination of two detectors based on physically different principles, conductivity and UV absorption, is used. Hence the anionic water components can reliably be identified by two parameters: retention time and the concentration-independent specific ratio of conductivity and UV absorption response.

1. Introduction

The increasing pollution by pesticides and other organic compounds endangers drinking water supplies worldwide. In addition to removal by adsorption, methods for the oxidative degradation of persistent compounds are gaining more and more importance. Mainly combinations of ozone, hydrogen peroxide and UV radiation (O_3–H_2O_2, O_3–UV, H_2O_2–UV) have been tested for water treatment [1]. These methods are based on the formation of hydroxyl radicals, which are the strongest oxidants (+2.85 V) in aqueous media apart from fluorine. They are able to decompose and even mineralize organic components in water by oxidation. H_2O_2–UV has turned out to remove several pesticides effectively from water on laboratory and pilot-plant scales.

2,4-Dichlorophenoxyacetic acid (2,4-D), 2-nitrobenzoic acid and nitrobenzene were treated with UV-activated hydrogen peroxide. Carboxylic acids such as acetic, fumaric, formic, glycolic, maleic, malonic and oxalic acid and the inorganic ions chloride and nitrate were found to be formed during the oxidative treatment [2]. The organic decomposition products can be identified by GC–MS and HPLC, but by employing ion-exchange chromatography the inorganic and organic anions can be determined simultaneously without further sample preparation steps. As co-elution of organic and inorganic ions is pos-

* Corresponding author.

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sible, the retention time is not sufficient for reliable identification. For this purpose, a second indicator is obtained by installing two detectors (conductivity and UV absorption) in series. The response ratio for conductivity and UV detection is independent of concentration and is specific for each compound. The combination of the respective retention time with the corresponding response ratio allows reliable peak identification. Elucidation of the mechanisms and quantification of all products are required for the official approval of oxidative treatment to improve the quality of drinking water.

2. Experimental

2.1. Chemicals

All chemicals were of analytical-reagent grade and used without further purification. Deionized water was used for preparing the model solutions for the degradation experiments and ultra-pure water (conductivity <0.07 μS) for ion chromatography. Hydrogen peroxide (35% technical grade, non-stabilized) was purchased from Peroxidchemie (Höllriegelskreuth, Germany).

2.2. Procedures

All irradiation experiments were carried out in a stirred batch reactor at 20°C. To aqueous solutions containing 2,4-dichlorophenoxyacetic acid (0.186 m*M*), 2-nitrobenzoic acid (0.155 m*M*) or nitrobenzene (0.130 m*M*) hydrogen peroxide was added so that its initial concentration ranged from 1.45 to 5.88 m*M*. The mixture was irradiated for 1 h with a TNN 15/32 low-pressure mercury lamp (Heraeus, Hanau, Germany) with emission maxima at 185 and 254 nm.

The determination of anions was performed with a Dionex (Sunnyvale CA, USA) 4506i ion chromatographic system with Dionex AI 450 external PC control software. The injection volume was 50 μl. Separation was performed on an AS 5 A column (250 × 4 mm I.D., alkanol quaternary amine, 5 μm, 20°C) from Dionex. The eluents were prepared under a helium atmosphere. For eluent A (0.75 m*M* NaOH) 39 μl of 50% NaOH were added to 1000 ml of water and for eluent B (200 m*M* NaOH) 10.4 ml of 50% NaOH were added to 990 ml of water. The water was previously thoroughly degassed with helium to remove traces of dissolved CO_2. Gradient elution was applied as follows: 0.0–5.0 min, 100% A; 25.0 min, 85% A + 15% B; 35.0 min, 57% A + 43% B; 35.1 min, 100% A. The flow-rate was 1.0 ml/min. The regenerant for micromembrane suppression was 25 m*M* sulfuric acid. Two detectors in series (conductivity and UV absorption, 200 nm) were used for identification. Retention times and responses were determined by the analysis of external standards. The quantification limits for the identified anionic fragments ranged from 0.001 to 0.006 m*M*.

3. Results

3.1. Identification of anionic metabolites

Some inorganic and organic ions could not be separated under the chosen analytical conditions (e.g., glyoxylate–chloride, tartrate–sulfate, malonate–sulfite). For a reliable identification, the retention times and the specific ratio of conductivity and UV absorption response were determined for each compound of the external standard (see Table 1). The measurements demonstrated a deviation of the response ratio from 1 to 14% for the same compound, depending on the degree of overlapping by neighbouring peaks. A deviation of more than 15% indicates a wrong identification or co-elution with another substance. The procedure was applied to the anionic decomposition products of 2,4-D (Figs. 1 and 2), 2-nitrobenzoic acid and nitrobenzene. Thus the inorganic ions chloride and nitrate and also the organic ions acetate, glycolate, malonate and oxalate could be unequivocally identified. Owing to the constant distance of the two detectors, the retention time difference of pure substances has to be constant, here 0.11–0.14 min, deviations point to impurities. Concerning

Table 1
Identified substances, retention times and specific response ratios (conductivity/UV absorption)

No.	Substance	Retention time (min)	Response ratio		Deviation (%)
			Standard	Sample 2,4-D	
1	Acetate	4.88	16219	–	–
2	Glycolate	5.45	16671	18538	11
3	Formate	7.24	60256	63706	6
4	Chloride	13.82	42368	45059	6
5	Nitrate	20.77	668	677	1
6	Malonate	23.33	21524	22186	3
7	Maleate	24.25	543	1015	46
8	Oxalate	25.73	3671	3836	4
9	Fumarate	28.85	690	1117	61
10	2,4-D	33.27	–	–	–

fumarate, a difference of 0.21 min and the deviation of the response ratio indicated co-elution with another compound. Maleate also turned out to be overlapped. Further, an unknown UV-active substance was formed after 15-min irradiation of 2-nitrobenzoic acid and nitrobenzene, overlapping the formate peak.

3.2. Decomposition of 2,4-D

Ion chromatographic analysis shows that the degradation rate depends on the hydrogen peroxide concentration; the decomposition rate is enhanced by increasing the initial hydrogen peroxide concentration. Almost complete degradation was attained after 20-min irradiation with an initial H_2O_2 concentration of 1.45 m*M*, after 10 min with 2.96 m*M* H_2O_2 and after 5 min with 5.88 m*M* H_2O_2 (Fig. 3). Increasing the H_2O_2 concentration seems to accelerate the dechlorination. With 5.88 m*M* hydrogen peroxide, 0.366 m*M* chloride was formed. Fig. 4 shows the degradation of 2,4-D and the concentration course of the main fragments. In all experiments the formation of acetate, fumarate and maleate was observed. The concentration of acetate was always close to the quantification limit. Small amounts of fumarate and maleate were detected

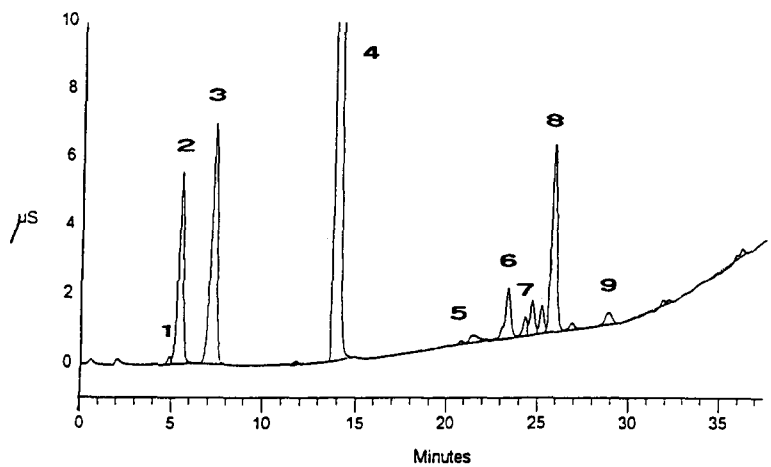

Fig. 1. Conductivity chromatogram: decomposition of 2,4-D, 2.96 m*M* H_2O_2, 10-min irradiation. For identification of peaks, see Table 1.

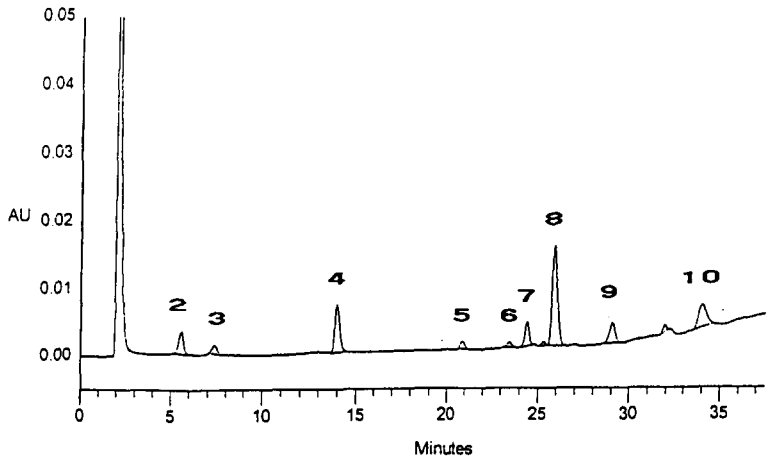

Fig. 2. UV absorption chromatogram: decomposition of 2,4-D, 2.96 m*M* H_2O_2, 10-min irradiation. For identification of peaks, see Table 1.

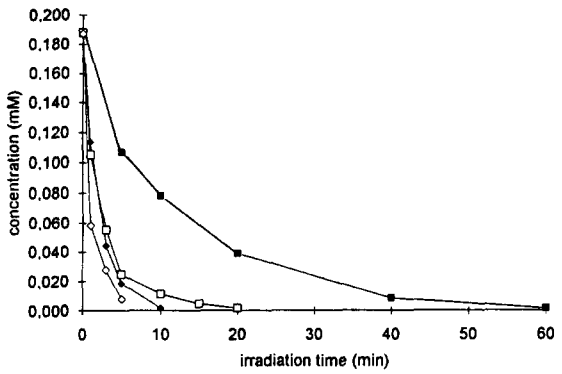

Fig. 3. Decomposition of 2,4-D with different initial H_2O_2 concentrations: ■ = 0.00 m*M*; □ = 1.45 m*M*; ◆ = 2.90 m*M*; ◇ = 5.88 m*M*.

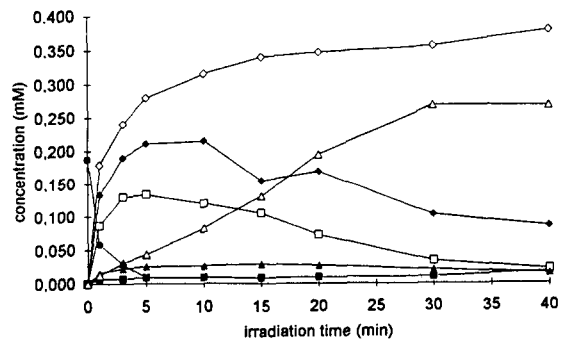

Fig. 4. Decomposition of 2,4-D with 5.88 m*M* H_2O_2. ■ = Acetate; □ = glycolate; ◆ = formate; ◇ = chloride; ▲ = malonate; △ = oxalate; ● = 2,4-D.

during the first 15 min of irradiation. The concentration of malonate reached about 0.020–0.040 m*M* in the first 20 min. After 5 min of irradiation with an initial H_2O_2 concentration of 5.88 m*M* the concentrations of formate and glycolate reached maxima of 0.210 and 0.130 m*M*, respectively. Oxalate was detected with concentrations up to 0.270 m*M* after 30 min. The formation of formate, glycolate and oxalate increased with increasing H_2O_2 concentration. All of the detected carboxylic acids decomposed on further irradiation.

3.3. Decomposition of 2-nitrobenzoic acid and nitrobenzene

Fig. 5 shows the degradation of 2-nitrobenzoic acid and the concentration course of the main anionic metabolites. With an initial H_2O_2 concentration of 5.88 m*M* the concentration of 2-nitrobenzoic acid was reduced to 5% within 25 min of irradiation. Nitrobenzene was decomposed to 5% within 60 min with an initial H_2O_2 concentration of 4.00 m*M*. Its concentration was determined spectrophotometrically by measuring the absorbance of the solution at 266 nm.

Fig. 6 shows the concentration course of the main anionic degradation products of nitrobenzene. The nitro group was split off from both

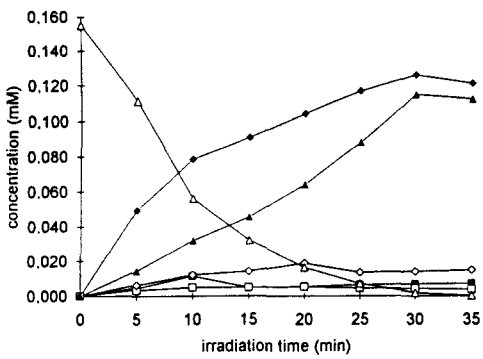

Fig. 5. Decomposition of 2-nitrobenzoic acid with 5.88 m*M* H_2O_2. ■ = Acetate; □ = glycolate; ◆ = nitrate; ◇ = malonate; ▲ = oxalate; △ = 2-nitrobenzoic acid.

compounds, yielding 0.126 and 0.095 m*M* nitrate, respectively. During the oxidative decomposition acetate and glycolate reached concentrations of 0.005–0.012 m*M*, close to their quantification limits. In both instances maleate was formed in concentrations up to 0.005 m*M*; fumarate was not detected. The formation of formate could only be quantified during the first 15 min of irradition because the formate peak was subsequently overlapped by another UV-active substance. The maximum concentration of malonate was 0.019 m*M* for 2-nitrobenzoic acid and 0.010 m*M* for nitrobenzene. Oxalate again turned out to be the main organic decomposition product, 0.115 m*M* being formed from 2-nitrobenzoic acid and 0.080 m*M* from nitrobenzene.

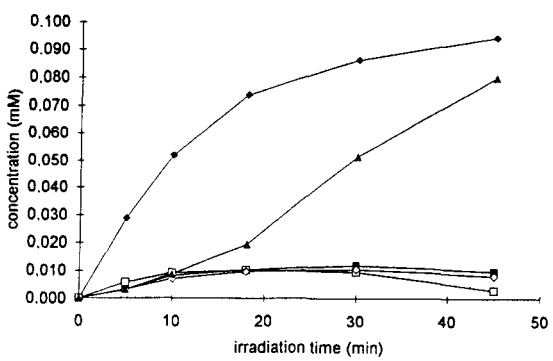

Fig. 6. Decomposition of nitrobenzene with 4.00 m*M* H_2O_2. ■ = Acetate; □ = glycolate; ◆ = nitrate; ◇ = malonate; ▲ = oxalate.

4. Discussion

The oxidative treatment of the investigated organic compounds in dilute aqueous solutions leads to a rapid decrease of the parent compound, yielding a variety of decomposition products. The analytical method applied allows the simultaneous observation of the degradation of the pollutant, except for nitrobenzene, and the formation of anionic products. 2,4-D was reduced to the detection limit within 10 min of irradiation and 2-nitrobenzoic acid to 5% within 25 min. Anionic C_3 and C_4 fragments such as malonate, maleate and fumarate were found to be formed by the oxidative treatment. The detection of malonate and maleate in all experiments, and in some instances of fumarate, confirms the destruction of the aromatic ring soon after the start of irradiation. The degradation of the aromatic ring proceeds either by direct ring opening or via quinoid intermediates [3,4]. Generally, the concentration of carboxylic acids increases with increasing the initial H_2O_2 concentration. Concerning the degradation of 2,4-D, however, the malonate concentration was lower when the initial concentration of H_2O_2 was 5.88 m*M* than it was with an initial H_2O_2 concentration of 2.96 m*M*. The reason may be a faster degradation to smaller fragments. In all experiments 10–20% of malonate were formed relative to the initial concentration of the substrate. The amounts of C_4 fragments were also very low compared with glycolate and oxalate. It is presumed that they are rapidly oxidated to C_2 and C_1 fragments (oxalate, formate) and finally CO_2. The experiments show that oxalate is one of the main products of the decomposition process and that the concentrations of acetate, glycolate, formate and oxalate were also reduced by further irradiation. This was additionally demonstrated by treating an acetate solution, yielding formate and oxalate. After 60 min of irradiation acetate was decomposed completely, and 30 min later the oxalate also. Formate seems to be a short-lived metabolite, being oxidized to CO_2. It is presumed that glycolate decomposes in a similar way [5]. The nitro group and the Cl atom are to a great extent rapidly split off from the

aromatic ring, forming nitrate and chloride; 73% and 81% of the nitro groups were detected as nitrate on decomposing nitrobenzene and 2-nitrobenzoic acid, respectively, and with 98.5% of chlorine split off from 2,4-D, almost complete dechlorination was observed.

5. Conclusions

In order to apply oxidative treatment to improve the quality of drinking water, investigations had to be made concerning the degradation rates and degradation products of organic pollutants. The results presented show an almost complete decomposition of the investigated compounds; even aromatic ring systems were decomposed and finally mineralized to CO_2. Hence oxidative treatment results in an effective detoxification of polluted water. Once approved officially, the technique can be installed in water works without further scaling up because units of pilot-plant scale can simply be run in parallel according to the output of water.

Ion chromatography is a suitable technique for determining inorganic and small organic anions at concentrations down to 0.001 to 0.006 m*M*. As the concentrations of these anions will be lower in real water samples compared with the model solutions, it has to be proved whether installing an on-line accumulation technique results in lower detection limits.

Acknowledgement

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