

# DEGRADATION OF PHENOL AND SALICYLIC ACID BY ULTRAVIOLET RADIATION/HYDROGEN PEROXIDE/OXYGEN

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Abstract—Based on the oxidation reactions of u.v. radiation/hydrogen peroxide/oxygen with either phenol or salicylic acid a spectra library was established. The reaction products contain hydroxylated phenols, benzoquinone and aliphatic acids with up to six carbon atoms. Many of the substances have been identified by means of chromatography and spectra comparison. From the observed concentrations of the substances and the known reaction mechanisms the following course of reaction has been postulated. The first reaction step is the hydroxylation of the aromatic ring. Further oxidation occurs via abstraction of a hydrogen atom to form 1,2-benzoquinone which is cleaved to form muconic acid. The cleavage of the muconic acid by u.v. radiation/hydrogen peroxide/oxygen leads to maleic acid, fumaric acid and oxalic acid. The degradation of oxalic acid leads to formic acid and finally to carbon dioxide. The hydroxylation of the double bond of the maleic or fumaric acid and the abstraction of a hydrogen atom produces malic acid. The reactions can be seen as essential step in the photochemical transformation of refractory substances into biodegradable ones.

Key words—phenol, salicylic acid, degradation, u.v. radiation, hydrogen peroxide, humic substances, HPLC, spectra library, advanced oxidation process, oxidation products

## INTRODUCTION

Humic substances (HS) are spread all over the biosphere and account for a large part of the mass of organic substances on earth. More than half the total organic matter in surface waters are HS. The following list represents some of the main reasons why water treatment plants have to remove HS from water:

(1) The yellow colour of HS is incompatible with the requirement that drinking water is colourless.

(2) HS have a potential for bacterial growth.

(3) Application of disinfectants in water treatment processes can lead to toxic disinfection by-products (DBPs), e.g. when chlorine is used, humic substances in the water form chlorinated compounds which have a potential for toxicity.

(4) HS can complex and remobilize heavy metals which, as a consequence, cannot be precipitated in a water treatment plant and reach the consumer.

The removal of HS from waters can be achieved by total oxidation to  $CO_2$  and other inorganic products. A common method of advanced oxidation processes is u.v. irradiated hydrogen peroxide and/or ozone. This process has also been used to degrade pollutants which have an unfavourable effect on biological treatment (Glaze *et al.*, 1987); e.g. trichloroethylene,

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tetrachloroethylene and the disinfectant formic acid have been successfully destroyed by advanced oxidation (Glaze and Kang, 1988; Brunet *et al.*, 1984).

It should be kept in mind that total oxidation is always very energy consuming. Therefore, it is not reasonable to try to achieve total oxidation of organic matter by chemical or physical means in water treatment. Partial degradation with subsequent microbiological degradation, however, seems to be feasible, but might produce undesirable toxic and biodegradable substances such as some particular aldehydes.

Moreover, the oxidation processes with u.v. radiation/hydrogen peroxide/oxygen may occur in nature itself. Studies of flash light photolysis of "humic" chromophores suggest the formation of a superoxide ion-radical ( $O_2^-$ ) from reduction of oxygen by a hydrated electron (Cooper and Zika, 1983; Zafiriou *et al.*, 1984). The superoxide disproportionates to hydrogen peroxide and oxygen. For example, the concentration of hydrogen peroxide in a lake in North America was measured to be 400 (200) × 10<sup>-9</sup> M on a sunny day (Cooper and Lean, 1989).

A direct investigation of the oxidation mechanism of u.v. radiation/hydrogen peroxide/oxygen on HS is hampered by the complex structure of humic substances. Therefore, it is appropriate to use well defined humic specific model compounds and to investigate the oxidized intermediate substances. The present choice of substances is based on previous studies by Mehta *et al.* (1963) and Griffith and Schnitzer (1977). In the first study, soil humic substances were degraded by hydrogen peroxide to carbon dioxide, oxalic acid and benzoic acid. In the second study, other soil humic substances were treated with hydrogen peroxide (30% wt) in a steam bath. A large amount of the carbon in the initial organic matter was oxidized to volatile and water-soluble products. Among the latter, various phenols, phenolic acids and aromatic carboxylic acids were identified.

These results suggest that phenol and salicylic acid play an essential role in u.v. radiation/hydrogen peroxide/oxygen degradation of HS.

The aim of this work was to use phenol and salicylic acid as typical building blocks of aquatic HS and to investigate their advanced oxidative degradation in the millimolar concentration range by

(1) application of a technical scale photoreactor

(2) identification of stable intermediate products.

Further it was intended to suggest a degradation pathway including all identified compounds.

#### MATERIALS AND METHODS

## Photoreactor system

The reaction system consisted of a photoreactor, a supply container, a pump and tubes (Fig. 1). The photoreactor and the pump were made of stainless steel. The supply container and the tubes were made of glass and PTFE plastic material. For protection against diffuse daylight, they were wrapped in aluminium foil.

The irradiation in the photoreactor was done by a low-pressure mercury lamp (JR 50; Katadyn Co.) positioned in the centre of the tube. Emission wavelengths of the lamp were 185, 254 and 313 nm with a maximum of intensity at  $\lambda = 254$  nm. The lamp tube was made of synthetic quartz which absorbed wavelengths below 230 nm. The photon flow of the lamp was evaluated by iron oxalate actinometry (Parker and Hatchard, 1956). The wavelength of 313 nm produced only about 3% of the total photon flow and therefore it was considered negligible. The data of the photoreactor are listed in Table 1.



Fig. 1. Reaction system.

Table 1. Dimensions and technical data of the photoreactor		
Diameter of the lamp	30 mm	
Internal diameter of the photoreactor	45 mm	
Path length of the u.v. radiation in solution	7.5 mm	
Total length of the radiation source	750 mm	
Total irradiation volume	0.66 litre	
Flow of the solution	0.026 l s - I	
Average residence time	25 s	
Electric power	40 W	
Radiation flux	16 W	

## Chemical substances

The selected model compounds were dissolved in double-distilled water by means of ultrasonic agitation. The concentration of these substances was in the  $10^{-3}$  M range and had to be a compromise: high concentrations are good for easy detection on the one hand but on the other hand they can absorb too much of the u.v. radiation (filter effect). The pH was maintained at 6.2 by a 0.065 M phosphate buffer (7.97 g  $1^{-1}$  potassium dihydrogenphosphate and 1.14 g  $1^{-1}$  disodium hydrogenphosphate). Hydrogen peroxide was added as a concentrated solution (30% wt). The total volume of the solution was 5 litres and the oxygen concentration during the irradiation process was maintained at 8 ( $\pm 0.5$ ) ×  $10^{-3}$  g  $1^{-1}$ , close to air saturation.

#### Irradiation procedure

The reaction was carried out at a temperature of 23  $(\pm 2)^{\circ}$ C. The initial solution was pumped from the supply container into the photoreactor, where the irradiation occurred. Having passed the photoreactor, the solution was pumped into the supply container and thoroughly mixed with the rest of the supply solution. The circulation flow of the reaction mixture was maintained constant for the whole reaction time. Samples were taken at defined intervals.

#### Analytical procedures

The selected model compounds and their reaction products were measured by HPLC analysis using an ion exchange resin (Aminex HPX-87H column; Bio-Rad Co.) and a mobile phase of 50% wt methanol and 50% wt diluted sulphuric acid (pH 2) at a flow rate of  $6 \times 10^{-4}$  l min<sup>-1</sup>. The chromatograph was a LC 1090 (Hewlett-Packard Co.) with a diode array detector and a computer for data processing. The u.v. spectra of the substances (phenols, benzoquinone and aliphatic acids) were recorded and stored in a spectra library. The retention times, which have been determined in triplicate for each substance, are given in Table 2. The irradiated solutions were analysed by means of chromatography and the peaks were identified by the retention time and spectra matching.

The amount of oxygen was measured using an oxygen membrane electrode (EQ 200; Wissenschaftliche-Technische Werkstätten Co.). The pH values were measured by a glass electrode (N 61; Schott Co.).

The concentration of hydrogen peroxide was quantified using a reaction with a titanium salt forming a coloured complex (Eisenberg, 1943).

## RESULTS

#### Oxidation of phenol

The initial concentration of phenol c(t = 0) was  $1.43 \times 10^{-3}$  M and the initial concentration of hydrogen peroxide was 0.26 M. Whereas the concentration of hydrogen peroxide was hardly affected by the irradiation procedure, there was a significant decrease in the concentration of phenol. This was caused by an excess of hydrogen peroxide in comparison to phenol (182 mol:1 mol) and the

Table 2. Retention times of selected model compounds and their products

				Average retention time
	Retention time			
Substance	$r_1$ (min)	r1 (min)	$r_{\rm t}$ (min)	$r_1$ (min)
Maleic acid	8.11	8.16	8.15	8.14
D,L-Malic acid	9.75	9.78	9.81	9.78
Malonic acid	10.24	10.23	10.22	10.23
Succinic acid	11.22	11.21	11.23	11.22
Glutaric acid	12.16	12.17	12.18	12.17
Fumaric acid	13.22	13.28	13.22	13.24
Adipic acid	13.55	13.56	13.57	13.56
Formic acid	13.93	13.93	13.88	13.91
Acetic acid	14.54	14.52	14.51	14.52
Ketomalonic acid	16.89	16.45	16.74	16.69
E.E-Muconic acid	18.86	18.85	18.86	18.86
Oxalic acid	23.23	22.65	22.88	22.92
Z,Z-Muconic acid	23.37	23.30	23.22	23.30
Z.E-Muconic acid	24.81	24.80	24.80	24.80
1,4-Dihydroxybenzene	24.94	24.93	24.95	24.94
1,4-Benzoquinone	25.11	24.99	25.04	25.05
1,3-Dihydroxybenzene	25.67	25.87	25.84	25.79
1,2-Dihydroxybenzene	27.60	27.53	27.55	27.56
2,3-Dihydroxybenzoic acid	35.47	35.49	35.55	35.50
Phenol	40.12	40.10	40.25	40.16
Vanillic acid	46.93	46.87	46.17	46.66
Salicylic acid	62.45	63.51	63.39	63.12

low rate constant of the dissociation of hydrogen peroxide.

Figure 2 shows the concentration ratio c(t)/c(t = 0)(on a logarithmic scale) as a function of irradiation time (on a linear scale). The concentration ratios of phenol form approximately a straight line from t = 0to t = 30 min indicating a pseudo-first-order reaction.

The concentration of phenol decreased during the first 30 min, the concentration of 1,2-dihydroxybenzene and 1,4-dihydroxybenzene increased. The concentration of 1,2-dihydroxybenzene or 1,4-dihydroxybenzene exceeded the concentration of phenol at an irradiation time of approx. t = 20 min (Fig. 3). Muconic acid appeared at approx. t = 10 min and disappeared after approx. t = 30 min. The other acids, with the exception of oxalic acid, became measurable at a reaction time of approx. t = 10 min (Fig. 4). Fumaric acid disappeared after 40 min and oxalic acid after 240 min. Formic acid was the main reaction product over the whole irradiation time.







Fig. 3. Oxidation of phenol (concentration of the aromatic substances and muconic acid). Detection limit (phenol or 1,2-dihydroxybenzene or 1,4-dihydroxybenzene or muconic acid) =  $1.0 \times 10^{-6}$  M.

## Oxidation of salicylic acid

The initial concentration of salicylic acid c(t = 0)was  $4.46 \times 10^{-3}$  M and the concentration of hydrogen peroxide at the start of the reaction c(t = 0) was 0.26 M. The concentration ratio c(t)/c(t = 0) of salicylic acid and hydrogen peroxide is plotted against the irradiation time in a semi-logarithmic scale in Fig. 5.

Because of the excess of hydrogen peroxide (58 mol of hydrogen peroxide for each mole of salicylic acid) and the low rate constant of the dissociation of hydrogen peroxide, its concentration decreased only slightly during the experiment.

Plotting the concentration ratios of salicylic acid over time gives a fairly straight line between 0 < t < 30 min, again indicating reaction kinetics of pseudo-first-order (Fig. 5).

The concentration of salicylic acid approached zero after 150 min irradiation, the concentration of 2,3-dihydroxybenzoic acid, 1,2-dihydroxybenzene, 1,4-dihydroxybenzene and muconic acid could be detected after approx.  $t = 6 \min$  (Fig. 6). Maleic acid, fumaric acid and D,L-malic acid became measurable at approx.  $t = 20 \min$  (Fig. 7). Oxalic acid appeared at approx.  $t = 120 \min$ , malonic acid at approx.  $t = 210 \min$ . Oxalic acid and malonic acid were degraded after  $t = 240 \min$ . Formic acid was found after a reaction time of approx.  $t = 6 \min$  and vanished after  $t = 240 \min$ .



Fig. 4. Oxidation of phenol (concentration of the aliphatic substances). Detection limit (fumaric acid or maleic acid) =  $1.0 \times 10^{-6}$  M. Detection limit (oxalic acid) =  $1.0 \times 10^{-5}$  M. Detection limit (D,L-malic acid or formic acid) =  $1.0 \times 10^{-4}$  M.



Fig. 5. Oxidation of salicylic acid (concentration of salicylic acid and hydrogen peroxide). Detection limit (salicylic acid) =  $1.0 \times 10^{-6}$  M.

## DISCUSSION

The primary reaction resulting from the irradiation of hydrogen peroxide in aqueous solution is its photo-decomposition. The excited hydrogen peroxide molecule is thereby cleaved into two hydroxyl radicals [equation (1)]. The hydroxyl radicals initiate the chain decomposition [equations (2)–(4)].

$$H_2O_2 \xrightarrow{h^{v}} 2 \cdot OH$$
 (1)

$$OH + H_2O_2 \longrightarrow OOH + H_2O$$
 (2)

$$\cdot OOH + H_2O_2 \longrightarrow \cdot OH + H_2O + O_2 \qquad (3)$$

$$2 \cdot OOH \longrightarrow H_2O_2 + O_2 \tag{4}$$

Phenol as a radical scavenger reacts with the hydroxyl radicals as oxidizing species.

## **Reaction kinetics**

The semi-logarithmic graphs of the concentration of phenol and salicylic acid yield straight lines for reaction times t < 30 min indicating in both cases reactions of pseudo-first-order [equation (5)].

$$-\frac{\mathrm{d}}{\mathrm{d}t}(c(X)) = k \times (c(X)) \tag{5}$$

where c (M) is the concentration and k (s<sup>-1</sup>) is the reaction rate constant of the substance X.



Fig. 6. Oxidation of salicylic acid (concentration of the aromatic substances and muconic acid). Detection limit (salicylic acid or 2,3-dihydroxybenzoic acid or 1,2-dihydroxybenzene or 1,4-dihydroxybenzene or muconic acid) =  $1.0 \times 10^{-6}$  M.





Fig. 7. Oxidation of salicylic acid (concentration of the aliphatic substances). Detection limit (fumaric acid or maleic acid) =  $1.0 \times 10^{-6}$  M. Detection limit (oxalic acid) =  $1.0 \times 10^{-5}$  M. Detection limit (D,L-malic acid or malonic acid or formic acid) =  $1.0 \times 10^{-4}$  M.

The reaction rate constants as calculated from experimental data (Figs 2 and 5) are given in Table 3. In addition, an analogous experiment with hydrogen peroxide and vanillic acid was carried out under analogous condition (Fig. 8, Table 3).

Vanillic acid has the highest reaction rate constant and salicylic acid the lowest under these experimental conditions. This can be explained by the stabilizing effect of the methoxy- and the hydroxyl group and the destabilizing effect of the carboxyl group with respect to the reactivity of the aromatic ring with hydroxyl radicals.

## Reaction products

There are two possible mechanisms to explain hydroxylation (Omura and Matsuura, 1968):

(1) The hydroxyl radical attacks the phenolic ring R forming a cyclohexadienyl radical (intermediate), which is converted by further abstraction of a hydrogen atom to the hydroxylated product [equation (6)].

$$\mathbf{R}-\mathbf{H} \xrightarrow{+ \mathbf{HO}} \mathbf{HO} \cdot \mathbf{R} - \mathbf{H} \xrightarrow{- \mathbf{H}} \mathbf{R} - \mathbf{OH}$$
(6)

(2) The hydroxyl radical abstracts a hydrogen atom from the phenolic compound R yielding a phenoxyl radical (intermediate). This, in turn adds a hydroxyl radical, giving the hydroxylated phenolic product [equation (7)].

$$\mathbf{R}-\mathbf{H} \xrightarrow[-H_{2O}]{+OH} \mathbf{R} \cdot \xrightarrow[-H_{2O}]{+HO} \mathbf{R} - OH$$
(7)

Reaction of u.v. radiation/hydrogen peroxide/oxygen with phenol

Phenol is hydroxylated by the use of u.v. radiation/hydrogen peroxide to 1,2- and 1,4 dihydroxybenzene [Fig. 3; equations (8) and (9)]. There

Table 3. Reaction rate constants k for the photo-degradation of model substances X

Substance (X)	Reaction rate constant $(k)$ $(s^{-1})$		
Phenol	$0.136 \pm 0.010$		
Salicylic acid	$0.058 \pm 0.014$		
Vanillic acid	$0.378 \pm 0.106$		



Fig. 8. Oxidation of vanillic acid (concentration of vanillic acid and hydrogen peroxide). Detection limit (vanillic acid) =  $1.0 \times 10^{-6}$  M.

may be a further hydroxylation reaction on the aromatic ring. It is of minor yield and was not investigated.

Oxidation of the dihydroxybenzenes to benzoquinones was analysed [equations (10) and (11)]. These reactions are caused by the high oxidation potential of hydroxyl radicals ( $E_o = +2.80$  V; Prengle and Mauk, 1978). In our experiments, however, we have not been able to detect benzoquinone. There may be two principle reasons for this:

(1) Benzoquinone is fairly unstable when in contact with strong oxidants and is easily cleaved into aliphatic compounds.

(2) Benzoquinone and dihydroxybenzene are in a redox equilibrium, which shifts to the dihydroxybenzene side during sampling and HPLC analysis.

Once 1,2-benzoquinone is formed, ring tension and oxidizing agents force a fission. One of the fission products is muconic acid (Pospisil *et al.*, 1957). In our experiments the formation of muconic acid occurred approximately at the same time as the formation of 1,2-dihydroxybenzene. This suggests that the reaction of 1,2-dihydroxybenzene resulting in muconic acid takes place readily (Fig. 3).



For a more detailed investigation, 1,2-dihydroxybenzene was used as the starting material, and a reaction with u.v. radiation/hydrogen peroxide/oxygen was carried out. The main product was Z,Z-muconic acid and no benzoquinone was detected (Fig. 9). These data can be explained by the assumption that benzoquinone produced by oxidation reacts rapidly under ring cleavage. The bond between the carbon atoms carrying the oxygen atoms of benzoquinone is cleaved, and the unsaturated diacid is formed [equation (12)]. Consequently other compounds are created by photochemical isomerization.

Maleic acid was detected as a further product of the oxidation process (Figs 4 and 9). Its isomer, fumaric acid, was found in lower concentration (Fig. 4). The maleic and fumaric acid were probably formed by an oxidation process of hydroxyl radicals and oxygen at a double bond of muconic acid. It has been shown that hydrogen peroxide, under the influence of u.v. light, reacts with double bonded compounds, e.g. with maleic acid to form 2,3-dihydroxysuccinic acid (Milas et al., 1937) and that the oxidation process from a hydroxyl group to a carboxyl group may take place (Bothe and Schulte-Frohlinde, 1978). The higher concentration of maleic acid [equation (13)] in contrast to fumaric acid [equation (14)] is in accordance with the higher concentration of Z,Z-muconic acid to E,E-muconic acid if the configuration is maintained in this reaction.



Another reaction path to maleic acid may be the degradation of 1,4-dihydroxybenzene. One double bond may be hydroxylated and then cleaved by an oxidation process yielding maleic acid. An indication for this is the high concentration of maleic acid shown in Fig. 4, whereas the concentration of muconic acid shown in Fig. 3 is rather low. As the concentration of 1,4-dihydroxybenzene is rather high, it is reasonable to assume that maleic acid comes from 1,4-benzoquinone [equation (15)].

The occurrence of malic acid can be explained by an addition of a hydroxyl radical to the double bond of maleic or fumaric acid followed by an abstraction of a hydrogen atom. This type of reaction [equation (16)] has also been observed by the reaction of maleic acid with hydrogen peroxide/ferrous ions (Fenton's reagent; Walling and El-Taliawi, 1973).



Fig. 9. Oxidation of dihydroxybenzene. Detection limit (1,2-dihydroxybenzene or isomers of muconic acid or maleic acid) =  $1.0 \times 10^{-6}$  M.

(15)



## HOOC-HC=CH-COOH

Oxalic acid may have been produced by the cleavage of muconic acid [equations (13) and (14)] and by the cleavage of 1,4-dihydroxybenzene [equation (11) and (15)].

The concentration of oxalic acid was lower than the concentration of formic acid during the whole reaction process. This was probably caused by a quick cleavage of the carbon–carbon bond of oxalic acid giving two molecules of formic acid [equation (17)].

$$HOOC-COOH - - - > 2 HCOOH$$
(17)

Finally, formic acid is oxidized by hydroxyl radicals to carbon dioxide [equation (18); Weeks and Matheson, 1956]. Because phenol has six carbon atoms, a complete oxidation should result in six molecules of carbon dioxide. This however could not be experimentally verified because the degradation reaction was not completed during the time of the experiment and the system was not completely air-tight.

$$\text{HCOOH} - - - > \text{CO}_2 \qquad (18)$$

## Reaction of u.v. radiation/hydrogen peroxide/oxygen with salicylic acid

A part of salicylic acid is hydroxylated to 2,3-dihydroxybenzoic acid. This corresponds to the first step of the reaction with phenol (Fig. 6). Nevertheless, this seems to be a side reaction when compared to the amount of 1,2-dihydroxybenzene being formed [equation (19); Fig. 6]. The appearance of dihydroxybenzene may be explained by the substitution of the carboxyl group by a hydroxyl group.



The reaction of 4-hydroxybenzoic acid with hydroxyl radicals to 1,4-dihydroxybenzene has been described by Matsuura and Omura (1974).

Starting from the intermediate product dihydroxybenzene, the reaction path of salicylic acid is similar to that of phenol with one exception (Figs 6 and 7):

Malonic acid is found after the disappearance of malic acid. This may be caused by the higher molar concentration of salicylic acid. The following reaction path can be concluded.

Malic acid is oxidized to oxalacetic acid [equation (20)]. This  $\alpha$ -keto-acid decarboxylizes [equation (21)] and is oxidized to malonic acid [equation (22)].

 $- - - > HOOC - H_2C - CO - COOH$  (20)

HOOC-H<sub>2</sub>C-CO-COOH

$$- - - > HOOC-CH_2-CHO + CO_2$$
 (21)

$$-$$
 HOOC-CH<sub>2</sub>-COOH (22)

## CONCLUSIONS

This investigation of the degradation of phenol and salicylic acid by u.v. radiation/hydrogen peroxide/ oxygen highlights only one part of a complex reaction system. The experiments were not intended to analyse all intermediate products, e.g. hydroxylated maleic acid and aldehydes have been omitted and will be the subject of further work.

The results obtained in this work correspond well with the current data of the oxidation of phenolic substances. The model compounds phenol, salicylic acid, and vanillic acid are typical building blocks of aquatic humic matter. Therefore the obtained results can add to the understanding of the reactivity of natural organic matter in aquatic systems.

Aliphatic diacids were the main intermediate products obtained by advanced oxidation processes (AOPs). The ecological and technological relevance of these intermediates can be derived from the improved biodegradability compared with the starting compounds. Increased microbial growth potential can be technically used in water treatment. In drinking water supply it has to be controlled carefully to avoid hygiene problems.

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