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GAS CHROMATOGRAPHY AS A TOOL FOR THE STUDY OF THE PRODUCTS OF PHOTOSENSITIZED PHENOL DECOMPOSITION

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SUMMARY

The decomposition of phenol photosensitized by trivalent iron was studied using gas chromatography and gas chromatography–mass spectrometry. The photooxidation entails hydroxylation and dimerization which provide hydroxylated benzenes, biphenyls and diphenyl ethers. The reactions of the photoactive complex ions $FeOH^{2+}$ and $FeOPh^{2+}$ are strongly influenced by the concentrations of both Fe(III) and phenol, pH and radiation dose and wavelength.

INTRODUCTION

Phenolic compounds occur in nature as various plant pigments, as components of the aromas of many plant and animal products, etc. They are also introduced into the biosphere by man in the form of industrial wastes, pesticides, herbicides, etc.

Recently, the interaction of phenolic compounds with radiation in the gamma, ultraviolet and visible regions has been used for the study of these substances and for regulation of their occurrence in nature, especially in waste waters. In view of the complicated reactions involved, attention has been centred mainly on phenol, the simplest of these substances.

Gamma and ultraviolet radiation with a wavelength of 254 nm decompose phenol in aqueous solutions with the formation of many products; phenol is hydroxylated to form di- and trihydroxybenzenes[1–3], and dimerizes either through the C–C or C–O bond, yielding dihydroxybiphenyls[3,4] or hydroxylated diphenyl ethers[3]. In the presence of oxygen, phenol is oxidized to *o*-benzoquinone[1,2,5]. Using high energy ^{60}Co radiation, the aromatic ring itself is destroyed[6,7]; this has been successfully used

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for purification of waste waters polluted by phenol[7–9].

In all these reactions it is assumed that the phenoxyl radical $C_6H_5O^\cdot$ and/or the radical $HO^\cdot$ is formed[3,10–16], their mutual reactions or reactions with phenol molecules leading to the observed products. The formation of the phenoxyl radical is also assumed in the eosine-photosensitized phenol oxidation[17–20].

Photochemical reactions sensitized by compounds of trivalent iron also have radical mechanisms[21–26]. The primary radical is generated by the reaction sequence[21,27,28]:

$$FeX^{2+} \xrightarrow[\text{excitation}]{h\nu} [FeX^{2+}]^* \xrightleftharpoons[\text{ion-pair formation}]{} [Fe^{3+}X^-] \xrightleftharpoons[\text{charge transfer}]{} [Fe^{2+}X] \xrightarrow[\text{dissociation}]{} Fe^{2+} + X^\cdot \tag{1}$$

Radical $X^\cdot$ then reacts with substrate R–H to yield the radical $R^\cdot$, which is oxidized in the next step by the ion-pair $Fe^{3+}X^-$:

$$X^\cdot + R\text{–}H \rightarrow R^\cdot + HX \tag{2}$$

$$R^\cdot + Fe^{3+}X^- \rightarrow R\text{–}X + Fe^{2+} \tag{3}$$

In this way, the radicals $HO^\cdot$, $Cl^\cdot$ and $SCN^\cdot$ are generated from $FeOH^{2+}$[23,27,29], $FeCl^{2+}$[24,27] and $FeSCN^{2+}$[30]; for $FeOH^{2+}$, the use of radiation with a wavelength of 300–400 nm is advantageous, while 436 nm is suitable for $FeSCN^{2+}$.

The present work is based on the assumption that $FeOPh^{2+}$ (Ph = phenyl), which is responsible for the intense mauve colouration of phenol solutions in the presence of Fe^{3+} and whose composition has been confirmed by Job's method of continuous variations[31] at constant pH = 1.00 and 1.60[32], behaves analogously to the above ions.

The complicated reaction mixtures obtained after photolysis or radiolysis of phenol solutions have so far been analysed using only spectrophotometric methods[2], thin-layer chromatography (TLC)[3,16] and column chromatography[16]. However, gas or high-performance liquid chromatography, possibly combined with mass spectrometry, seems to be the optimal method for this purpose.

For gas chromatographic (GC) analysis of phenols, both solid adsorbents, such as graphitized carbon black, Separon SDA and Tenax and, chiefly, liquid stationary phases, *e.g.*, silicones SE-30, OV-101, SE-52, OV-17, etc., have been recommended. Packed and capillary columns have been used for the separations. Some higher phenols require conversion into volatile derivatives, usually trimethylsilyl (TMS) derivatives, heptafluorobutyrates, flophemesyl derivatives, pentafluorobenzoyl derivatives, etc. Derivatization leads to improvement in separation and sometimes also in detection, but may be a source of error in quantitations. Therefore, high-performance liquid chromatography (HPLC) has recently been used, both on solid adsorbents based on silica gel and on chemically bonded phases, *e.g.*, C_{18}, NH_2, phenyl and CN. Chromatographic methods used in the analysis of phenols have been reviewed, *e.g.*, in refs. 33 and 34.

During a study of the GC behaviour of mono- and dihydroxybiphenyls on silicone stationary phases[35] it was found that OV-17 gave the best separations and thus this phase was also used in the present work for identification of the products of phenol decomposition.

EXPERIMENTAL

Materials

Ferric perchlorate was prepared by dissolving iron powder in 10% $HClO_4$ (Lachema, Brno, Czechoslovakia) and oxidizing the $Fe(ClO_4)_2$ formed with H_2O_2. Phenol (Lachema) was purified by redistillation *in vacuo*. These chemicals were of reagent grade purity. Pyrocatechol and hydroquinone were recrystallized from diethyl ether. 2,2′- and 4,4′-dihydroxybiphenyls were kindly provided by Dr. P. van der Jagt of the Free University, Amsterdam, The Netherlands. 2,4′-Dihydroxybiphenyl was prepared by Dr. B. Černý of the Institute of Nuclear Biology and Radiochemistry, Prague, Czechoslovakia, according to the procedure given in ref. 36.

Methods

The UV spectra were obtained on a Unicam SP-800 instrument (Unicam, Cambridge, Great Britain). Radiation was provided by a high-pressure mercury discharge lamp Tesla RVL, 1000 W (Tesla, Prague, Czechoslovakia). Using this lamp, two sources of radiation were available: source I with a filter consisting of a polystyrene plate 1.20 mm thick, having a 50% transparence at 320 nm and an absorption edge at 400 nm; source II with a filter consisting of a 1-cm layer of a 1% solution of $FeCl_3$, having an absorption edge at 560 nm and 50% transparence at 450 nm (see Fig. 1).

For dosimetry, a YSI Model 65 Radiometer (Yellow Springs Instrument, Yellow Springs, OH, U.S.A.) was employed. With the given irradiation arrangement, a value of 460 erg/m^2 · sec was found, corresponding to a dose of 1175 J/h.

An 100-ml volume of the test solution was placed in a glass vessel (diameter 10 cm) and irradiated with constant stirring and water cooling. After irradiation the solutions were acidified with 5 ml 2 *N* H_2SO_4, extracted three to five times into 50 ml diethyl ether and evaporated to dryness, the unreacted phenol being distilled off *in vacuo*. The residue was dissolved in 1 ml methanol and 10 μl were injected into the

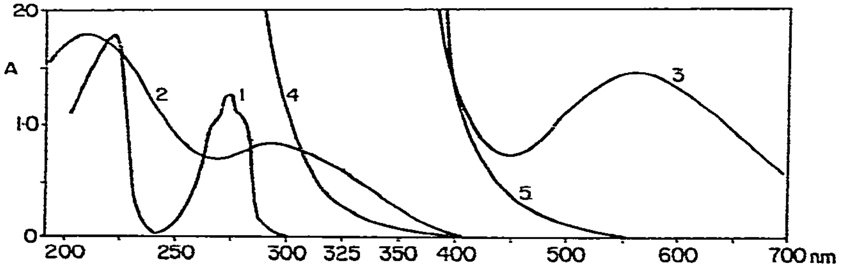


Fig. 1. UV and visible spectra: 1, aqueous phenol solution, $c = 10^{-4}$ *M*; 2, $Fe(ClO_4)_3$, $c = 5 \cdot 10^{-4}$ *M*, pH = 3.0; 3, $FeOPh^{2+}$, $c_{Fe(III)} = 1.34 \cdot 10^{-2}$ *M*, $c_{phenol} = 8.04 \cdot 10^{-2}$ *M*, pH = 2.1; 4, radiation source I; 5, radiation source II.

gas chromatograph. The photodecomposition yield was evaluated from the ratio of the total amount of products after distilling off the phenol to the initial amount of phenol.

The analyses were carried out on a Varian Model 3700 gas chromatograph with a FID and nitrogen as carrier gas (20 ml/min). A glass column (200 cm × 2 mm I.D.) was packed with 3% OV-17 on Varaport 30 (100–120 mesh). The gas chromatographic–mass spectrometric (GC–MS) analyses were kindly carried out by Dr. P. A. Leclercq of the Technical University, Eindhoven, The Netherlands.

RESULTS AND DISCUSSION

The oxidation of phenol photosensitized by trivalent iron is a complex reaction that is affected by many factors, see Table I.

The reaction products were analysed using GC–MS to give a general picture of the substances formed. A chromatogram of a typical sample and a survey of the products identified by this method are given in Fig. 2 and Table II respectively. With a few exceptions, the MS spectra do not permit conclusions to be drawn concerning the position of the hydroxyl groups; however, in view of the electron densities on the individual phenol carbons, OH groups are expected to be present in the *ortho*- and *para*-positions. This assumption was verified by isothermal GC using a packed column.

For the analysis of the reaction mixtures obtained after irradiation, our method of separation of hydroxylated biphenyls, published elsewhere[35], was modified. On the basis of agreement of the retention data with those for standards it was demonstrated that the samples contained pyrocatechol, hydroquinone and 2,2′-, 2,4′- and 4,4′-dihydroxybiphenyls (see Fig. 3). The retention indices of the products on the OV-17 stationary phase are given in Table III.

The formation of the products given in Tables II and III can be explained by assuming that the primary reaction intermediate is the phenoxyl radical, which is formed in the photo- and radiochemical oxidation of phenol[3,10–16]. Although we have not demonstrated the presence of this radical experimentally, it is highly probable that it is formed, since the same products were formed as in those reactions in which its existence was confirmed.

TABLE I

PARAMETERS OF THE IRRADIATED SOLUTIONS

Parameter	*Range studied*
$c_{Fe(III)}$	10^{-4}–1.0 M
c_{phenol}	5×10^{-3}–1.0 M
Ratio $c_{Fe(III)}:c_{phenol}$	10:1–1:1000
pH	0.7–3.3
Radiation source	I ($\lambda \geqslant$ 320 nm)
	II ($\lambda \geqslant$ 450 nm)
Irradiation time	3–24 h
Presence of other substances	Passage of nitrogen or oxygen through the solution during irradiation

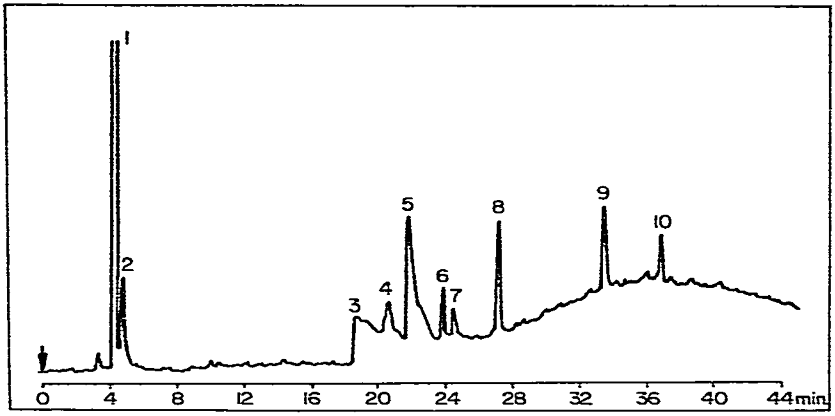


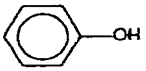
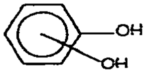
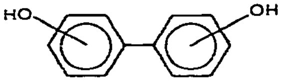
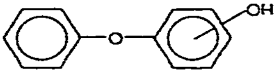
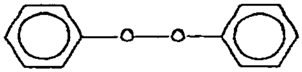
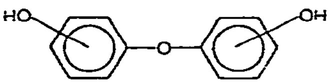
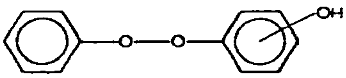
Fig. 2. GC–MS analysis of a sample containing $c_{\mathrm{Fe(III)}} = 3.33 \cdot 10^{-2}$ *M*, $c_{\mathrm{phenol}} = 10^{-1}$ *M*, pH = 3.0, with passage of oxygen during irradiation from source I for 20 h. Capillary column: 48 m × 0.25 mm I.D., OV-101. Temperature gradient: 3°C/min from 150 to 230°C. For peak identification see Table II.

One of the possible mechanisms of formation of the phenoxyl radical is analogous to the photochemical generation of $HO^{\bullet}$, $Cl^{\bullet}$ and $SCN^{\bullet}$ radicals[23–30]:

$$FeOPh^{2+} \xrightarrow{h\nu} [FeOPh^{2+}]^{*} \rightarrow [Fe^{3+}OPh^{-}] \rightarrow [Fe^{2+}OPh] \rightarrow Fe^{2+} + OPh^{\bullet} \quad (4)$$

TABLE II

PRODUCTS OF THE PHOTOSENSITIZED DECOMPOSITION OF PHENOL FOUND BY GC–MS

Molecular mass (m/e)	*Composition*	*Probable structure*	*No. of peak in Fig. 2*
94	C_6H_6O		1
110	$C_6H_6O_2$		2
186	$C_{12}H_{10}O_2$	  	3–7
202	$C_{12}H_{10}O_3$	 	8–10

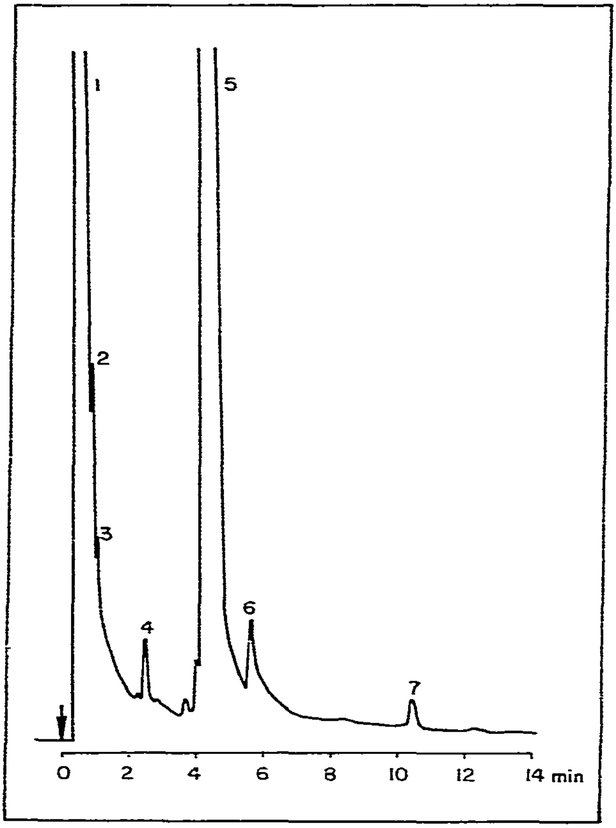


Fig. 3. Chromatogram of the products of phenol decomposition on OV-17 at 170°C. Sample: $c_{Fe(III)} = c_{phenol} = 10^{-2}$ M, pH = 3.0, Radiation source; II, irradiation time 12 h. Peaks: 1 = solvent + phenol; 2 = pyrocatechol; 3 = hydroquinone; 4,6 = unidentified substances; 5 = 2,2′-dihydroxybiphenyl; 7 = 2,4′-dihydroxybiphenyl.

TABLE III

RETENTION INDICES OF THE IDENTIFIED PRODUCTS OF PHOTOSENSITIZED OXIDATION OF PHENOL OBTAINED ON OV-17 AT VARIOUS TEMPERATURES

Substance	$I_{140°C}$	$I_{170°C}$	$I_{197°C}$	$I_{220°C}$
Phenol	1146	1186	1200	*
Pyrocatechol	1406	1416	1444	1475
Hydroquinone	1545	1555	1558	1583
Pyrogallol**	***	1625	1667	1709
2,2′-Dihydroxybiphenyl	***	1951	2004	2018
2,4′-Dihydroxybiphenyl	***	2192	2226	2241
4,4′-Dihydroxybiphenyl	***	***	2441	2486

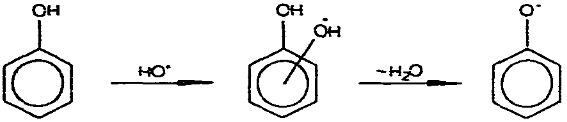
* Eluted simultaneously with the solvent.

** The retention data of pyrogallol were measured for the sake of completeness; its presence in the sample was not detected by GC.

*** Not eluted under the given conditions.

This is apparently a classical example of charge transfer to metal (CTTM) de-excitation[37], which has not yet been described for this complex ion.

During irradiation of the Fe(III)–phenol system in water at wavelengths absorbed by the photoactive $FeOH^{2+}$ (300–400 nm), *i.e.*, using radiation source I, the phenoxyl radical can also be formed by the reaction of the ensuing $HO^{\bullet}$ radical with a phenol molecule with abstraction of a water molecule:



(5)

The phenoxyl radical then yields hydroxylated biphenyls and diphenyl ethers or diphenyl peroxides by reaction with $FeOPh^{2+}$, and hydroxylated benzene derivatives by reaction with $FeOH^{2+}$. These products have actually been found by GC or GC–MS. It follows from the analyses that hydroxylation in the *ortho*-position is preferred over that in the *para*-position; pyrocatechol and 2,2′-dihydroxybiphenyl are formed preferentially. No formation of pyrogallol and *p*-benzoquinone was observed.

The above products can react further according to an analogous radical mechanism with formation of polymeric products. The mechanism of these reactions was studied in more detail with 2,6-dimethylphenol[38]. Similar tar-like substances were actually observed during irradiation of our samples, but were not analyzed. The mechanism proposed is also supported by the formation of Fe(II), whose presence in the samples after irradiation was detected by reaction with *o*-phenanthroline.

In addition to photochemical reactions, chemical oxidation of phenol by iron(III) takes place in the solution. This competing reaction is particularly important in samples with high concentrations of Fe(III); the analysis of such a sample stored in the dark showed a major product, 2,2′-dihydroxybiphenyl, in addition to traces of some unidentified substances. However, the yields of the photochemical reactions are much larger than that of this competing reaction.

The course of the photosensitized oxidation of phenol is significantly affected by the pH, component concentrations, radiation wavelength, time of irradiation and by the presence of oxygen or nitrogen.

The pH influences the hydrolysis of iron(III) salts according to the following equilibria:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K_{11} = 8.9 \cdot 10^{-4} \qquad (6)$$

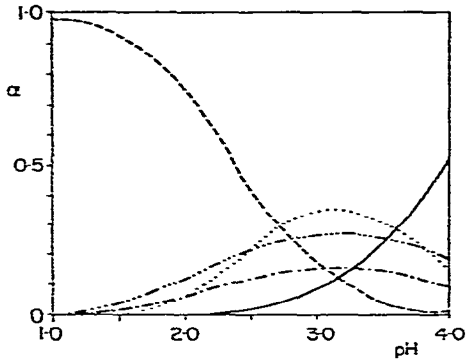
$$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+ \qquad K_{12} = 5.5 \cdot 10^{-4} \qquad (7)$$

$$2\,Fe^{3+} + 2\,H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \qquad K_{22} = 1.23 \cdot 10^{-3} \qquad (8)$$

Further, the pH affects the dissociation of phenol

$$PhOH \rightleftharpoons PhO^- + H^+ \qquad K_a = 1.05 \cdot 10^{-10} \qquad (9)$$

and thus also the formation of the complex cation $FeOPh^{2+}$:



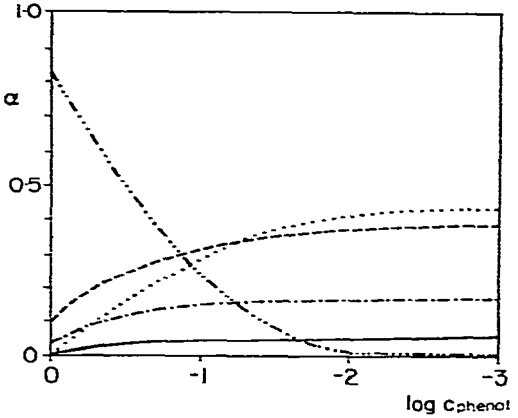


Fig. 4 Dependence of the equilibrium amounts of individual complex ions of Fe(III) on pH. $c_{Fe(III)} = 10^{-2}$ *M*. $c_{phenol} = 10^{-1}$ *M*. ---, Fe^{3+}; –.–.–, $FeOH^{2+}$; ———, $Fe(OH)_2^+$; ·········, $Fe_2(OH)_2^{4+}$; –···–···–, $FeOPh^{2+}$.

Fig. 5. Dependence of the equilibrium amounts of the iron(III) comples ions on total phenol concentration. $c_{Fe(III)} = 10^{-2}$ *M*, pH = 2.7. Symbols as in Fig. 4.

$$Fe^{3+} + PhO^- \rightleftharpoons FeOPh^{2+} \qquad K = 1.58 \cdot 10^8 \qquad (10)$$

The mass balance in solutions containing phenol and Fe(III) is then given by:

$$c_{Fe(III)} = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^+] + [Fe_2(OH)_2^{4+}] + [FeOPh^{2+}] \qquad (11)$$

$$c_{phenol} = [PhOH] + [PhO^-] + [FeOPh^{2+}] \qquad (12)$$

On inserting the above equilibria into the Guldberg–Waage law and considering the mass balances 11 and 12, seven non-linear equations with seven unknowns are obtained, the solution being a cubic equation. On the basis of this equation, a distribution diagram was constructed for the dependence of the equilibrium amounts of the individual complex ions on pH (see Fig. 4). It is seen that pH = 3 is optimal for the studied reaction, as the concentrations of the photoactive ions, $FeOPh^{2+}$ and $FeOH^{2+}$, are maximal. In agreement with this, it was found experimentally that the reactions proceed to a lesser extent in more acidic solutions.

The effect of the initial phenol concentration follows from the distribution of the individual ions at pH = 2.7 and $c_{Fe(III)} = 10^{-2}$ *M* (see Fig. 5). At lower phenol concentrations the concentration of $FeOH^{2+}$ increases, which leads to an increase in the yield of the products and to the formation of dihydroxybenzenes. The fact that pyrocatechol and hydroquinone were found only in samples with initial phenol concentrations equal to or less than 10^{-2} *M* and that the reaction yield increased with decreasing c_{phenol} confirms the proposed mechanism.

On the other hand it seems that $FeOPh^{2+}$ plays no significant rôle in the formation of the phenoxyl radical (eqn. 4), as according to this reaction the yield should increase with increasing concentration of $FeOPh^{2+}$ and thus also with increasing c_{phenol}; the experiments showed an opposite trend. However, at higher phenol concentrations greater amounts of tar-like polymeric products were formed.

The total concentration of Fe(III) at constant pH and c_{phenol} has little effect on the distribution of trivalent iron among the individual complexes, but an increase in $c_{\mathrm{Fe(III)}}$ leads to an increase in the total reaction yield. However, the competing chemical oxidation of phenol by iron(III) cannot be neglected, especially at higher iron(III) concentrations.

Passage of oxygen or nitrogen through the solutions during the irradiation also affects the reaction yield and the contents of the individual products. With nitrogen the yield is higher, but the number of products is smaller. Oxygen apparently participates in the formation of substances that readily undergo side and subsequent reactions, possibly even with destruction of the aromatic nucleus; the products of this reaction remained in the aqueous phase and thus were not included in the reaction yield.

In accordance with theory, longer irradiation leads to higher yields. The radiation wavelength also affects the course of the reaction; radiation from source I, *i.e.*, at wavelengths longer than 300 nm, provides higher product yields, especially of pyrocatechol and hydroquinone, due to excitation of the $FeOH^{2+}$, whereas radiation from source II with wavelengths greater than 450 nm, which is not absorbed by the $FeOH^{2+}$, leads to an increased formation of dimers and tar-like substances.

It follows from the results of the photosensitized oxidation of phenol that the amounts and number of the products increase with increasing iron(III) concentration, irradiation time and pH, and with decreasing concentration of phenol.

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