

PRODUCT ANALYSIS OF THE PHOTO-OXYGENATION OF *tert*-BUTYLGUAIAICYLCARBINOL SENSITIZED BY 4-HYDROXY-3-METHOXY ACETOPHENONE

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Summary

The product formation in the photosensitized reaction of a lignin model compound *tert*-butylguaiacylcarbinol in the presence of acetoguaiacone (4-hydroxy-3-methoxyacetophenone) or polymer-bound acetoguaiacone was studied in dimethoxyethane solutions saturated with air. Volatile products were carried off and trapped. Peroxidic compounds were quantitatively analysed by iodometric titration and the other products from the reaction mixture were fractionated using chromatographic methods. The following products were identified: formaldehyde, isobutene, pivalaldehyde and the dimer 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-bis(1-hydroxy-2,2-dimethylpropyl)biphenyl. The reaction mixture was found to be very complex but nevertheless the quantitative analysis showed that more than 50% of the products were characterized. It is concluded that at least one-quarter of the products results from the oxidative bond cleavage between the side-chain and the aromatic ring, yielding primarily pivalaldehyde and acidic compounds formed by further cleavage of the aromatic ring. Another one-quarter is a result of a coupling reaction of intermediate phenoxyl radicals, leading to biphenyl structures. The mechanism of the reaction is discussed in terms of the formation of products.

1. Introduction

The photochemical degradation of wood specimens, high yield pulps and paper products is characterized by a change in colour and in deterioration of the product quality. Earlier studies [1-6] have revealed that chromophoric structures, particularly aromatic α carbonyl structures originated from lignin, acting as photosensitizers, in addition to oxygen, play an active role in the light-induced process. The total carbonyl content in lignin has been evaluated to be about 0.2 carbonyl groups per monomer unit, 30% of which was considered to be in the α position [7]. The results ob-

tained by direct or indirect methods from experiments with lignin model compounds have shown that radical intermediates are formed in the reaction [3, 4, 6, 8, 9]. The intermediate formation of singlet oxygen [10 - 13] has also been suggested in photoreactions of aromatic carbonyls and phenolic lignin model compounds. Many pathways for further reactions of these intermediates are available leading to different products and colour generation. Earlier product studies [4, 9, 10] indicate that these reaction mixtures after irradiation are indeed very complex containing a variety of products.

Product studies have often been performed in experiments with carbonyl compounds such as benzophenone [9, 10, 12] which are not exactly analogous to the α carbonyl structures of lignin and the reactivity of which may not be the same as that of the alkyl aryl ketone fragments found in lignin. Consequently, the products from irradiations of a lignin model compound *tert*-butylguaiacylcarbinol **1** in the presence of acetoguaiacone (4-hydroxy-3-methoxyacetophenone) **2** were analysed in the present study. Acetoguaiacone has been found to be present in kraft pulping liquors as a lignin degradation product [14]. Therefore, it represents a suitable aromatic α carbonyl sensitizer for the study of lignin photochemistry. In some of the experiments polymer-bound acetoguaiacone ($\text{\textcircled{P}}$ -AG) [13] was used instead of the free sensitizer in order to facilitate the work-up of the reaction mixture. The lignin model compound **1** was chosen as a substrate because it contains some typical structure elements found in lignin, the guaiacyl group and the benzyl alcohol group. The coupling of the monomer unit to the three-dimensional network in lignin is simulated in the model compound **1** by introduction of the *tert*-butyl group.

2. Experimental details

2.1. Methods

Irradiations were performed in dimethoxyethane solutions in 100 ml cylindrical reaction vessels (Pyrex) containing a cold-finger and a reflux condenser in a Rayonet photochemical reactor (RPR-208) fitted with eight UV lamps (RUL; 350 nm) yielding light of wavelengths 305 - 420 nm with one maximum centred at 350 nm. The reaction mixtures were stirred with a stream of dried air.

Gas-liquid chromatography (GLC) analyses were performed with a Perkin-Elmer 990 gas chromatograph and recorder 159 equipped with flame ionization detectors and two 2 m \times 3 mm packed columns (5% SE-30 on Varaport 30; 80 - 100 mesh) and a Hewlett-Packard 3373 B integrator. The rate of flow of nitrogen was 30 ml min⁻¹. GLC analyses of low molecular weight compounds were performed isothermally at subambient temperatures. The column was cooled with dry ice (CO₂) to keep the temperature between 0 and 5 °C. GLC analyses of higher molecular weight compounds were performed with temperature programming between 90 and 260 °C (16 °C min⁻¹) using dodecane as an internal standard.

Thin layer chromatography (TLC) analyses of the 2,4-dinitrophenylhydrazones of carbonyl compounds were performed with a 3:7 mixture of (ethyl acetate):toluene (eluent 1) or with toluene (eluent 2) on silica gel plates (HF₂₅₄ (Merck)). Column chromatography was performed using the same eluents or a 1:2 mixture of (ethyl acetate):cyclohexane (eluent 3), unless otherwise stated, on silicic acid 60 (70 - 230 mesh (Merck)). IR spectra were recorded on a Pye-Unicam SP 1100 spectrometer and nuclear magnetic resonance (NMR) spectra were recorded on a JEOL PMX 60 spectrometer. The total peroxide content was determined by iodometric titration according to refs. 15 and 16.

2.2. Materials

Peroxide-free dimethoxyethane was prepared by eluting the purum grade solvent (Fluka) through a column containing Al₂O₃ after which it was dried over 4 Å molecular sieves and distilled just before use.

tert-Butylguaiacylcarbinol 1 was synthesized according to ref. 17, purified by column chromatography using eluent 3 and recrystallized (melting point, 73 - 74 °C) from diethyl ether-ligroin (boiling point, 60 - 95 °C). Acetoguaiacone 2, obtained from Koch-Light, was recrystallized from water and (P)-AG was prepared according to ref. 13. Isobutene 3 was synthesized by dehydration of *tert*-butanol in the presence of an acid ion-exchange polymer (Amberlite IR-20 (Fluka)) according to ref. 18. Pivalaldehyde (trimethylacetaldehyde) 4 was prepared via a Grignard reaction from methyl formate, prepared from formic acid and methanol, and *tert*-butylmagnesium bromide at -40 °C according to ref. 19. Isobutyraldehyde 5 was synthesized from isobutanol by sodium dichromate dihydrate oxidation according to ref. 20. The 2,4-dinitrophenylhydrazones of 5 and 4 melted at 180 - 186 °C and at 210 - 211 °C (210 - 211 °C [21]).

Dehydrodivanillin 6 was prepared from vanillin according to ref. 22. Diacetyldehydrodivanillin 7 was prepared from 6 via acetylation according to ref. 22 and purification by column chromatography (eluent 3) raised the melting point to 134.5 - 135.5 °C (117 °C [22]).

Dehydrodi-*tert*-butylguaiacylcarbinol (2,2'-dihydroxy-3,3'-dimethoxy-5,5'-bis(1-hydroxy-2,2-dimethylpropyl)biphenyl 8 was synthesized by a modification of the procedure in ref. 23 from 7 and *tert*-butyl bromide via a Grignard reaction in LiAlH₄-treated tetrahydrofuran. The molar ratio of 7 to the Grignard reagent was 1:28. The reaction mixture containing at least five compounds according to TLC was subjected to column chromatography (eluent 3) and the dimer product was collected from a fraction with an *R_f* value of 0.15 and was recrystallized (melting point, 233 - 235 °C (229 - 232.5 °C [23])). The yield was 6% and the structure was confirmed by NMR analysis. GLC analysis of the product showed a retention time 2.4 times longer than that of the corresponding monomer (302 s).

5(1-Hydroxy-2,2-dimethylpropyl)-3-methoxy-*o*-quinone 9 was prepared according to ref. 24 by oxidation of 1 (105 mg) with Fremy's salt. Recrystallization of the obtained violet oil gave 60 mg of violet crystals (yield,

54%) melting at 136 - 138 °C (136 - 138 °C [24]). From TLC, $R_f = 0.48$ (eluent, 4:6 (ethyl acetate):toluene).

2.3. Isolation and identification of products

2.3.1. Volatile compounds

tert-Butylguaiacylcarbinol **1** (325 mg, 1.54×10^{-2} M) was irradiated in the presence of (P)-AG (1.250 g) in air-saturated dimethoxyethane and possible volatile products were trapped in a dimethoxyethane solution cooled in dry ice (CO₂). According to GLC analysis of the reaction mixture the consumption of the substrate **1** was 80%. GLC analyses of the solution in the trap after 3 and 6 h of irradiation showed only the presence of one peak (retention time, 32 s) but after irradiation for 22 h a second peak was observed with a retention time of 60 s (solvent retention time, 94 s). The most volatile product was tentatively identified as isobutene **3** by comparison with a synthesized reference (identical retention times of the two compounds). Support for the presence of an olefinic product was further gained from the fact that the solution in the trap discoloured a bromine water solution and a solution of KMnO₄. The amount of isobutene was greatest after 3 h of irradiation and decreased with prolonged reaction time.

The solution from the trap was also treated with a solution of 2,4-dinitrophenylhydrazine hydrochloride in order to precipitate derivatives of possible volatile carbonyl compounds. After the precipitate had been washed with ethanol and water, needles melting at 212 °C could be collected. The needles were identified as the 2,4-dinitrophenylhydrazone of pivalaldehyde **4** by comparison with a synthesized reference compound (melting point, 210 - 211 °C) using GLC, IR and mixed melting point measurements. The second volatile product from the trap was thus identified as pivalaldehyde.

Volatile compounds were also studied by absorbing them directly in a trap containing a solution of 2,4-dinitrophenylhydrazine hydrochloride protected from light. After 22 h of irradiation the solution in the trap was filtered and crystals were obtained which were washed with hydrochloric acid, water and ethanol. The melting point was not sharp and TLC of the crystals showed the presence of two spots (R_f values of 0.95 and 0.85 (eluent 1)), the first of which was identified as the derivative of **4**. The second carbonyl compound was identified as the 2,4-dinitrophenylhydrazone of formaldehyde. An IR spectrum of a 1:1 mixture of the hydrazones of formaldehyde and **4** was identical with that obtained of the crystals isolated from the irradiation experiment.

2.3.2. Products from the irradiated solution

1 (325 mg, 1.54×10^{-2} M) was irradiated for 5 h in the presence of acetoguaiacone **2** (166 mg, 10^{-2} M) in dimethoxyethane (100 ml). Because of the slowness of the conversion of the substrate in the presence of (P)-AG the experiment was performed with free sensitizer to permit shorter irradiation times. Approximately the same degree of consumption was obtained with free sensitizer after 5 h as with (P)-AG after 22 h. The low reaction rate

is thought to be due to a much lower mobility in comparison with the free sensitizer. The primary photochemical event takes place in a thin layer close to the wall of the reaction vessel and the efficiency therefore crucially depends on mixing and on the geometry of the experimental set-up.

Quantitative GLC analyses of the irradiated solution showed the presence of 21% unreacted 1. The consumption of the sensitizer was negligible. The presence of pivalaldehyde in the reaction mixture was demonstrated by low temperature GLC. During irradiation the substrate suffers weight loss as a result of escape of volatile degradation products and in compensation oxygen uptake results in a gain in weight. This was checked with gravimetric analysis. 10 ml of the total reaction mixture of 100 ml was evaporated to dryness. The weight of the residue was 49 mg (see Section 3).

The total peroxide content of the irradiated solution was determined by iodometric titration of a 10 ml sample and was found to be 0.80×10^{-2} M. Iodometric titration of a blank containing only dimethoxyethane, which had been irradiated for 5 h, was found to contain 0.12×10^{-2} M peroxides.

The remaining four-fifths of the reaction mixture (80 ml) was treated with 50 ml of 2 M HCl saturated with 2,4-dinitrophenylhydrazine. After extraction with chloroform and the usual work-up an oil was obtained which gave several spots on TLC. The oil was fractionated on a silicic acid column with eluent 1. Refractionation with eluent 2 gave 12 mg of the 2,4-dinitrophenylhydrazone of 4 and 45 mg of the 2,4-dinitrophenylhydrazone of formaldehyde. Unidentified products were compared with the 2,4-dinitrophenylhydrazones of acetone, acetaldehyde, propionaldehyde, ethyl methyl ketone and isobutyraldehyde but none of these carbonyl compounds could be detected in the reaction mixture.

The formation of acidic products was studied by irradiating 1.050 g (5.0×10^{-2} M) of 1 in the presence of (P)-AG (2.500 g) in 100 ml aerated dimethoxyethane for 23 h. After the irradiation the polymer was filtered off from the dark red solution and the solvent was evaporated to dryness. The residue was dissolved in diethyl ether and extracted three times with 5% sodium hydrogen carbonate solution. After acidification of the combined extracts and further work-up a mixture of 117.5 mg acidic products was isolated. GLC analysis of the irradiated solution before the work-up showed a 58% consumption of 1. The mixture was found to be very complex according to TLC and to GLC analysis of the acetylated mixture and was not studied further.

The experiment was repeated (49% consumption of 1) and this time the residue was fractionated on a silicic acid column (5 cm \times 30 cm) with methylene chloride as eluent. Study of the fractions subjected to TLC showed that the mixture was very difficult to fractionate because of the large amount of unreacted substrate and of the presence of many products with similar R_f values in much lower concentrations.

After the fractions containing mainly the starting material had been collected, the eluent was changed to an 8:2 mixture of methylene chlo-

ride:dimethoxyethane and the elution was continued. Refractionation, with methylene chloride and subsequently with the eluent ethyl acetate-cyclohexane-methanol (45:45:5), gave 73 mg of a compound with a melting point of 228 - 235 °C ($R_f = 0.34$) and 46 mg of a compound ($R_f = 0.55$) which could not be identified. Both compounds gave a similar brown colour on a thin layer sprayed with diazotized *p*-nitroaniline, suggesting the presence of phenolic compounds. The IR spectra of the two compounds were also very similar showing the presence of *tert*-butyl groups in addition to phenolic groups. The phenolic compound ($R_f = 0.34$) was identified as the dimer of 1, 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-bis(1-hydroxy-2,2-dimethylpropyl)biphenyl 8, by comparison with a synthesized reference compound. The identification was further confirmed with the aid of melting point, IR and NMR analyses.

Prolonged irradiation for 81 h showed that the dimer products were not stable under the irradiation conditions. Aliquots taken from the solution at different times were analysed by visual judgment of the intensity of the brown spots developed on TLC. This analysis showed that the yield of dimers, which increased at the beginning of the reaction, gradually levelled off and decreased.

An attempt to detect the corresponding *o*-quinone of 1, namely 5(1-hydroxy-2,2-dimethylpropyl)-3-methoxy-*o*-quinone 9, in the reaction mixture was also made by comparison with a synthesized reference substance. TLC studies were performed after different times of irradiation but no *o*-quinone formation could be detected.

3. Results and discussion

The results of the product analysis of the photoreaction of 1 in the presence of sensitizer are shown in Table 1. The calculation of the amounts of formaldehyde and pivalaldehyde 4 was based on the isolated amounts of the corresponding dinitrophenylhydrazones determined from four-fifths of the reaction mixture. Thus 6.4 mg formaldehyde and 3.9 mg pivalaldehyde were formed in the solution, corresponding to 8.0 mg and 4.9 mg formed from the total solution and equivalent to 22 mol.% and 5 mol.% (3 wt.% and 2 wt.%) respectively calculated on the basis of the amount of substrate consumed. Both aldehydes were also detected as volatile products in the trap. Pivalaldehyde is known to degrade via autoxidation and it is photochemically unstable. It decomposes in daylight to low molecular weight compounds including isobutene and formaldehyde [25]. Isobutene was also detected as a volatile product, the concentration of which decreased with prolonged reaction times. The reason for this decrease may be that it is generated at the beginning of the reaction and that it gradually disappears from the solution trap because of its volatile properties. Isobutene may also be formed by cleavage of the bond between the α and β carbons of the side-chain. Nevertheless, on the assumption that all the formaldehyde is derived

TABLE 1

Products from the photosensitized oxygenation of *tert*-butylguaiacylcarbinol **1** by free or polymer-bound acetoguaiacone **2** in air-saturated dimethoxyethane

<i>Products</i>	<i>Isolated or determined</i> (mol.% (wt.%))	<i>Calculated</i> ^a (mol.% (wt.%))
Formaldehyde ^{b, c}	22 (3)	
Isobutene ^b	— ^d	
Pivalaldehyde ^{b, c}	5 (2)	9 ^e (4) ^e 26 ^f (11) ^f
Acidic compounds ^c	(19)	
8 ^c	14 (14)	
Unknown dimer ^c	9 (9)	
Dimers (totally) ^c	23 (23)	
Peroxidic compounds ^c	56 (9) ^g	

^a Calculated on the basis of the amount of **1** consumed.

^b Also identified as a volatile product.

^c Determined from the reaction mixture.

^d Tentatively identified; the absolute amount has not been quantitatively determined.

^e Calculated on the assumption that all the isolated formaldehyde originated from pivalaldehyde (see text).

^f Calculated on the assumption that all the volatile products or the weight loss determined by gravimetry and iodometry were pivalaldehyde (see text).

^g Calculated from the oxygen content in the peroxidic compounds.

from the side-chain the total amount of **4** formed in the photoreaction increases to 9 mol.% (4% is due to the formation of formaldehyde). The possibility of formaldehyde formation from the methoxyl group in **1** should perhaps also be considered because the methoxyl content in wood and lignin has been shown to decrease under irradiation [1, 26]. However, the corresponding demethoxylation of lignin model compounds has been found to be a slow process in solution [27]. GLC analyses of the irradiated solutions showed no consumption of the sensitizer **2**. Consequently, the guaiacyl structure is stable towards demethoxylation under the prevailing conditions. Another small increase in the formaldehyde content might originate from the solvent. Finally, if all the weight loss (27 mg) after irradiation is hypothetically taken as **4**, an assumption which may be valid before **4** is photochemically destroyed, a molar yield as high as 26% can be calculated for the pivalaldehyde formation.

Analogous reactions to the formation of pivalaldehyde in the photochemical reaction of **1** in the presence of a triplet carbonyl sensitizer have been observed earlier. The formation of methanol and formaldehyde has been observed from vanillin [3], methanol [3, 5] and acetaldehyde [4] from acetoguaiacone and methanol and acetaldehyde from methyl vanillyl alcohol (apocynol) [4, 27]. Further, when apocynol was irradiated in the presence of benzophenone formation of acetaldehyde was observed but the yield was only 1% after 24 h [27]. **1**, with its much bulkier side-chain, seems to

undergo oxidative breakage of the side-chain more easily than apocynol, a fact which is also demonstrated in the present work by the much higher yields of products from cleavage. The differences in reactivity can also be caused by the different sensitizing behaviour of a diaryl ketone and of an alkyl aryl ketone. Nevertheless, the bond breaking in both lignin model compounds occurs between the ring and the carbon chain generating intermediates of which methoxy-*p*-benzoquinone seems to be a possible candidate [4, 12] (Fig. 1). Intermediates of the hydroquinone type are also probable because of the observed interconversion between *p*-quinones and the corresponding hydroquinones [28]. The formation of peroxidic compounds demonstrated in this work strongly indicates the critical role of these unstable compounds in the ultimate product formation. A probable primary product may be the hydroperoxide of 1. Hydroperoxides as well as dialkyl peroxides are generally both photochemically and thermochemically unstable, which means that further reactions are probable, such as the formation of methoxy-*p*-benzoquinone by breakage of the side-chain bond as visualized in Fig. 1.

The photochemical instability of methoxy-*p*-benzoquinone in dimethoxyethane solution has earlier been demonstrated and the formation of strongly coloured dimers such as 4,4'-dimethoxybiphenyl-2,5,2',5'-bisquinone and 8-hydroxy-3,7-dimethoxydibenzofuran-1,4-quinone has also been

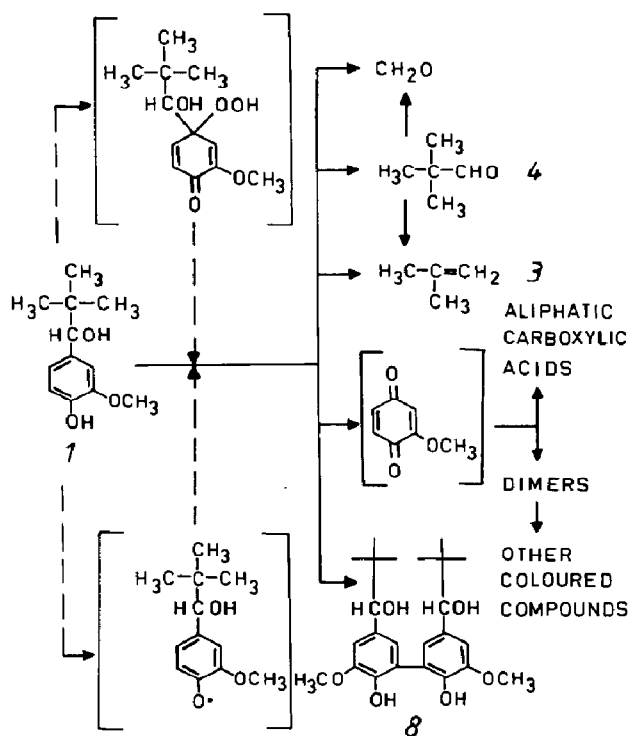


Fig. 1. Proposed reaction scheme for the photoreaction of *tert*-butylguaiacylcarbinol 1 sensitized by acetoguaiacone 2 in air-saturated dimethoxyethane.

observed [28]. The rate of consumption of methoxy-*p*-benzoquinone was found to be high. After 6 h of irradiation almost all the substrate was consumed. The dimers were also found to be photochemically unstable, undergoing further reactions [28]. These results make it almost impossible to succeed in isolating the postulated intermediate, methoxy-*p*-benzoquinone, from the reaction mixture under the prevailing conditions.

The formation of acidic compounds amounted to 19 wt.% calculated on the basis of the amount of 1 consumed. The acidic products are thought to be formed from the unstable methoxy-*p*-benzoquinone in a reaction where the aromatic ring is oxidatively degraded. Possible intermediates in this reaction are hydroxylated *p*-quinone structures [27] but unstable epoxidated methoxy-*p*-quinone structures [29, 30] seem to be more probable under the present conditions. The degradation of quinone structures is an important reaction in terms of the amount of isolated acidic compounds (see Table 1). The formation of highly unstable intermediate *o*-quinone structures is also possible, but these structures are also degraded by aromatic ring cleavage, generating acidic compounds. These reactions cannot be differentiated from those of the corresponding *p*-quinones.

The yield of the dimer 8 was calculated to be 14% on both molar and weight bases. Because of the almost identical IR spectrum of the unknown compound ($R_f = 0.55$) in comparison with that of 8 and also because of its gas chromatographic characteristics it is thought to be a dimer, although it could not be identified. Whether it is just a stereoisomer or a structurally very similar compound is at this stage unclear but the structure is under further investigations. Nevertheless, the total yield of the dimers amounted to 119 mg, *i.e.* 23 mol.% (23 wt.%), on the assumption that the molecular weight of the unknown dimer is the same as that of 8. Moreover, prolonged irradiation studies showed that the biphenyl dimers formed by radical coupling of phenoxy radicals were not the ultimate products but that they were consumed further in the reaction.

The formation of biphenyl structures in the photosensitized reactions of other lignin model compounds has also been previously demonstrated. Such dimers have been isolated from vanillin [4], from ethylguaiacylcarbinol after KMnO_4 oxidation [6] and from vanillyl alcohol [4]. The results from this work confirm that the dimerization of phenolic compounds is an important reaction in addition to the oxidative breakage of the side-chain. Numerous studies of chemical oxidation of 4- or 2,4-substituted phenolic lignin model compounds also show that a dominating pathway of the reaction of intermediate phenoxy radicals is a coupling reaction leading to biphenyl structures [31].

It is evident from Table 1 that at least one-quarter of the photosensitized oxygenation reaction of *tert*-butylguaiacylcarbinol 1 by acetoguaiacone or (P)-AG in air-saturated dimethoxyethane results in oxidative side-chain breakage giving primarily pivalaldehyde and acidic products and another one-quarter results in dimerization of the phenolic substrate to biphenyl structures.

3.1. Mechanistic implications

The results from the product analysis of the photoreaction of **1** clearly show that many reaction pathways are available for the substrate. Competing as well as consecutive reactions contribute to the complexity of the reaction, which is demonstrated by the variety of products formed after irradiation and detected by TLC and GLC. Many of the products may also be photochemically active as was observed with the isolated dimers. Because the concentration of the carbonyl sensitizer was found to be constant during the reaction (see also ref. 32) some kind of regenerative loop must be operative which restores the sensitizer. This is in accordance with the results of Brunow and Sivonen [11] who found that as long as there is a certain amount of substrate containing free phenolic hydroxyl groups the sensitizer is not consumed. Obviously, this threshold concentration was not reached in the present work. In contrast with the oxygen-containing system the sensitizer was unstable under oxygen-free conditions both in the absence and in the presence of substrate [33]. The reaction sets proposed for these two systems consisted of 15 and 33 elementary reactions respectively [33]. To describe the mechanism of the present oxygen-containing system the number of elementary reactions is thought to be much higher because of the involvement of oxygen.

In addition to the elementary processes operating in oxygen-free solutions the energy transfer from the excited triplet sensitizer to the ground state oxygen generating singlet oxygen must be considered [32]. Further reactions of singlet oxygen with substituted phenols yield peroxidic compounds such as hydroperoxides which may also arise from reactions between radicals and ground state oxygen. This is exemplified in one of the two major pathways found in the present work, *i.e.* oxidative side-chain elimination which is thought to proceed via an intermediate hydroperoxide (Fig. 1). The second major pathway is a radical coupling reaction of two phenoxyl radicals formed from the substrate via hydrogen abstraction from the phenolic hydroxyl group by the excited carbonyl sensitizer or by participation of some other active radical species.

After prolonged irradiation a more pronounced tendency to radical reactions caused by the increasing amount of thermochemically and photochemically unstable peroxidic compounds formed in the solution is expected. By homolytic cleavage of the peroxidic bond alkoxy and hydroxyl radicals are formed which initiate new radical chains. The formation of hydrogen peroxide in the reaction medium during irradiation is also suggested to contribute to these radical reactions. Hydrogen peroxide may be formed in oxidation-reduction reactions involving hydroquinones, semiquinone radicals and quinones. The proposed intermediate methoxy-*p*-benzoquinone is likely to take part in these reactions. The ultimate product distribution depends largely on the reactions and the possible interconversion of the oxygen-containing radicals and the activated oxygen species in the solution [28, 34]. The photoinduced process at a certain time is thus to a great extent dependent on the prevailing conditions at that instant, *i.e.* the

concentrations and the properties of the participating compounds, intermediates and products.

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