ASPECTS OF PHOTOSENSITIZED LIGNIN OXYGENATION[†]

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Summary

The light-induced oxygenation of lignin was studied with the aid of lignin model compounds in dimethoxyethane solution saturated with air or oxygen. The results are obtained from experiments with *tert*-butylguaiacyl-carbinol and aromatic α carbonyl compounds (acetoguaiacone, polymer-bound acetoguaiacone, *p*-methoxyacetophenone, *p*-methoxypropiophenone and benzophenone), and aromatic compounds containing ring-conjugated double bonds (anethole and isoeugenol) and the biphenyl compound bicreosol were added as sensitizers. The rates of disappearance of the reactants were determined by gas chromatography and the formation of peroxides was measured by iodometric titration. The kinetics were also studied in the presence of β-carotene and diazabicyclo[2.2.2]octane. The reactivity of the non-phenolic lignin model compound *tert*-butylveratrylcarbinol was also examined. The importance of the different chromophoric structures in lignin is discussed. The results indicate that the mechanism for photo-oxygenation is very complicated, with many pathways operating simultaneously, one of which is attributed to a reaction involving singlet oxygen. The relative significance of the different pathways is discussed.

1. Introduction

The photodegradation of wood, high yield pulps and paper products is accompanied by a change in colour and in deterioration of the product quality. Earlier studies [1 - 6] have revealed that the yellowing process is a light-induced oxidation of lignin and that the presence of oxygen is essential. The decreasing supply of wood has made industrial processes in which all the raw material is used, *e.g.* mechanical pulps, more attractive. Thus, today there are more paper mills making mechanical pulps, *i.e.* pulps in which the lignin has not been removed, than there are mills making chemical pulps,

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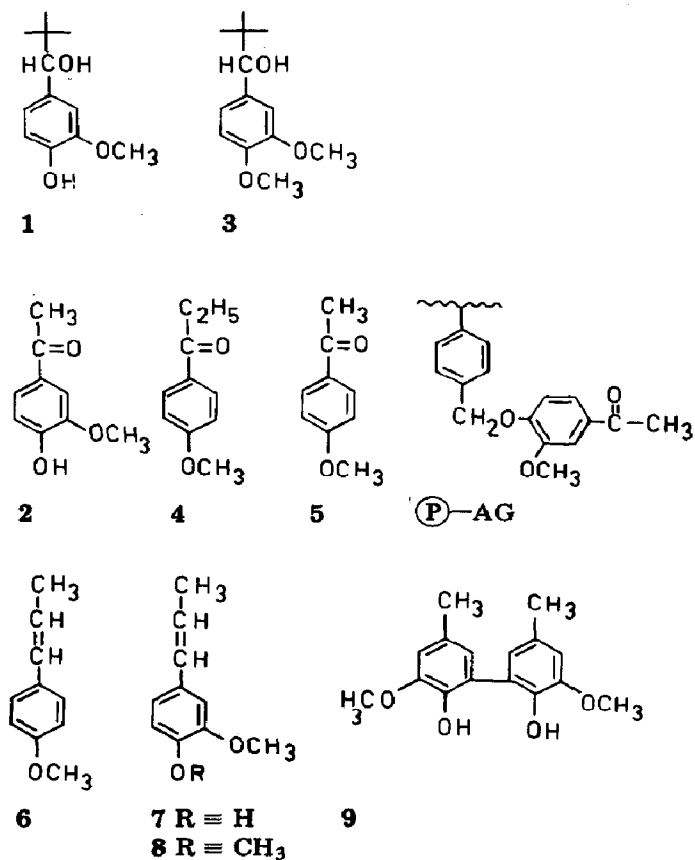
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Fig. 1. The structures of the substrates and sensitizers.

although the world production of chemical pulp is still greater. It has been of interest to use lignin-retaining bleaching methods, to reduce the amounts of bleaching chemicals and to prevent re-yellowing of the products.

A substantial knowledge of the chromophoric structures in native lignin and in degraded lignin has been accumulated. These structures, acting as sensitizers in the presence of light, are responsible for reactions leading ultimately to photodegradation of the material. Lignin is a complex macro-molecule and the three types of chromophoric structures of interest are the aromatic α carbonyl groups, the ring-conjugated double bonds and the biphenyl structures [2]. Of these three types the α carbonyl groups have been considered to be of the greatest importance because of their absorption characteristics in the daylight wavelength region.

The results obtained from experiments with lignin model compounds have shown that radical intermediates, i.e. phenoxy radicals, are formed in the reaction. The intermediate formation of singlet oxygen [7 - 10] has also been suggested in photoreactions of aromatic α carbonyl compounds and phenolic lignin model compounds.

This work is a contribution to the understanding of the mechanism of the yellowing process. The results are obtained from experiments with the lignin model compound *tert*-butylguaiacylcarbinol (*tert*-butyl-(4-hydroxy-3-methoxyphenyl)carbinol) **1** using as sensitizers lignin model compounds containing aromatic α carbonyl groups, ring-conjugated double bonds or biphenyl structures. The α carbonyl compound acetoguaiacone (1-(4-hydroxy-3-methoxyphenyl)ethanone) **2** was chosen to represent α carbonyl groups in lignin and has also been found in kraft pulping liquors [11]. The studied substrates and sensitizers are shown in Fig. 1. In some of the experiments the polymer-bound acetoguaiacone (Ⓟ-AG) [10] was used instead of the free sensitizer. A comparison of the reaction of **1** was also performed with benzophenone as sensitizer. The kinetics of the reaction were also studied in the presence of additives of so-called singlet oxygen quenchers.

2. Experimental details

The irradiations were performed, unless stated otherwise, in air-saturated dimethoxyethane in a Rayonet photochemical reactor (RPR-208) fitted with eight UV lamps yielding light of wavelength 305 - 420 nm with one maximum centred at about 350 nm. The rates of disappearance of the reactants were determined by gas chromatography and the formation of peroxides was measured by iodometric titration. Further details will be published elsewhere.

3. Results and discussion

When **1** (10.3×10^{-3} M) was irradiated in the presence of **2** (9.90×10^{-3} M) the substrate was consumed according to first-order kinetics (Fig. 2). The first-order rate constant k^{I} was calculated to be $(1.02 \pm 0.05) \times 10^{-4}$ s^{-1}
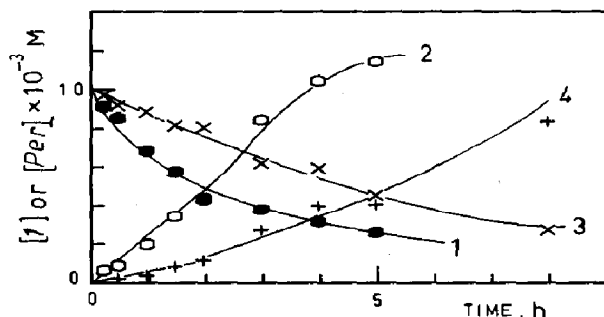

Fig. 2. Rate of disappearance of **1** (curves 1 and 3) and rate of peroxide formation (curves 2 and 4) in the photoreaction of **1** (initial [**1**] = 10.3×10^{-3} M; sensitized by **2** (9.90×10^{-3} M) in air-saturated dimethoxyethane in the absence (curves 1 and 2) and in the presence (curves 3 and 4) of β-carotene (2.53×10^{-3} M)).

(correction coefficient $r = 0.997$). Both light and the sensitizer were essential for the reaction. The consumption of the sensitizer was negligible during a run. The reaction mixture turned yellow during the irradiation and the formation of peroxides was observed and monitored by means of iodometric titrations of withdrawn samples. The amount of peroxides equals that of the initial concentration of 1 at about 4 h after which the peroxide content continued to increase, indicating a continuous oxygen uptake. The rate of formation of the peroxides followed first-order kinetics at the beginning of the reaction with a first-order rate constant equal to $(0.79 \pm 0.11) \times 10^{-4}$ s^{-1} ($r = 0.980$).

The experiment was repeated in the presence of β-carotene, which has been used in concentrations of about 10^{-3} M to demonstrate singlet oxygen participation in sensitized photo-oxidations [12, 13]. In this work a significant quenching effect both in the substrate disappearance and in the peroxide formation was observed. The rate of consumption of the substrate was still found to follow first-order kinetics in the presence of the quencher (2.53×10^{-3} M) with a rate constant $k^{I} = (4.57 \pm 0.02) \times 10^{-5}$ s^{-1} ($r = 0.994$). First-order kinetics were also observed in the peroxide formation during the first hours of the reaction with a rate constant equal to $(1.89 \pm 0.21) \times 10^{-5}$ s^{-1} ($r = 0.982$).

A problem met in the present work is that the absorption spectra of the sensitizers (absorbing at less than 400 nm) of interest in wood photochemistry often overlap at least partly the absorption spectra of many singlet oxygen quenchers. Thus the concentration of the quencher is crucial to the magnitude of this effect.

3.1. Evaluation of quenching rate constants

Because the quenching effect obtained with β-carotene indicated that singlet oxygen could be involved in the reaction, an approach was made to determine the rate constant k_A for total quenching of singlet oxygen by the phenol 1. The determination of the rate constants, both in the absence and in the presence of quenchers, was based on the assumption that the singlet oxygen pathway was the only way of reaction for the substrate and that the steady state approximation for singlet oxygen could be applied to the system. Thus, in the evaluation of the rate constants other pathways, such as direct hydrogen abstraction, quencher anomalies (such as internal filtering effects and quencher—sensitizer interactions) and the participation of peroxides and radicals in the initiating stage, have been omitted.

To determine the rate constants for the quenching of singlet oxygen by 1, the extent of the substrate disappearance in the photoreaction sensitized by p-methoxypropiophenone 4 was monitored in the presence of β-carotene in three different concentrations (2.50×10^{-3}, 0.50×10^{-3} and 0.25×10^{-3} M). The disappearance of 1 was found to follow first-order kinetics in the presence of β-carotene, at least during the first hours of the reaction. The quencher β-carotene is itself photolabile and deviations from linearity were already observed at low concentrations of quencher (0.25×10^{-3} M)

TABLE 1

Relative observed first-order rate constants for the disappearance of *tert*-butylguaiacylcar-binol 1 sensitized by triplet carbonyls in the presence of quenchers

Additive	Concentration ($\times 10^{-3}$ M)	Relative k_{obs}^{I}
None	0	1[a]
β-carotene	0.25	0.37 [a]
β-carotene	0.50	0.15 [a]
β-carotene	2.50	0.07 [a]
DABCO	2.50	0.46 [b]

DABCO, diazabicyclo[2.2.2]octane.
[a]Sensitizer, 4 (10^{-2} M); volume, 10 ml; [1] = 10^{-2} M; $k_{obs}^{I}([Q] = 0) = (1.70 \pm 0.01) \times 10^{-4} \, s^{-1}$ ($r > 0.999$).
[b]Sensitizer, (P)-AG (10^{-2} M); volume, 10 ml; [1] = 10^{-2} M; $k_{obs}^{I}([Q] = 0) = (0.93 \pm 0.06) \times 10^{-4} \, s^{-1}$ ($r = 0.994$).

after irradiation for 1 h. The instability of β-carotene was also visually observed by the relatively fast bleaching of the orange solution. The observed first-order rate constants for the disappearance of the substrate are shown in Table 1.

Quenching rate constants k_A for the reaction of the substrate 1 and singlet oxygen were calculated according to ref. 14 from the three disappearance curves obtained at different concentrations of β-carotene. A plot of the change in the substrate concentration without quencher divided by the change in the presence of quencher *versus* the concentration of quencher gives a straight line when certain criteria are fulfilled. The reaction has to be a singlet oxygen reaction, the quencher must quench only singlet oxygen and the reaction time has to be sufficiently short to permit conversions up to a maximum of 10%.

The calculations in the presence of β-carotene show that a straight line actually is obtained (Fig. 3). This implies that the reaction is a singlet oxygen reaction and that the qualifications made are correct. The line has a slope of 11 301 $\pm$ 71 M^{-1} ($r > 0.999$), giving a quenching rate constant k_A of 1.12 $\times$ $10^8 \, M^{-1} \, s^{-1}$. In the calculations a value of $1.30 \times 10^{10} \, M^{-1} \, s^{-1}$ was used for the rate constant for the total quenching of singlet oxygen by carotene [15 - 17]. The value for the rate constant for deactivation of singlet oxygen in the solvent was taken from the corresponding value determined in dioxane, *i.e.* $3.13 \times 10^4 \, s^{-1}$ [18].

Irradiation of 1 sensitized by (P)-AG [10] in the presence of 2.50×10^{-3} M diazabicyclo[2.2.2]octane (DABCO) [19] was also performed and first-order kinetics in 1 were again observed (see Table 1). The quenching rate constant k_A was calculated in the presence of DABCO using an integral form of the kinetic equation [20, 21]. These so called "one-point" experimental data were taken from the disappearance curve and the time was selected to give a maximum of 20% conversion of the substrate for [Q] = 0. The calcu-
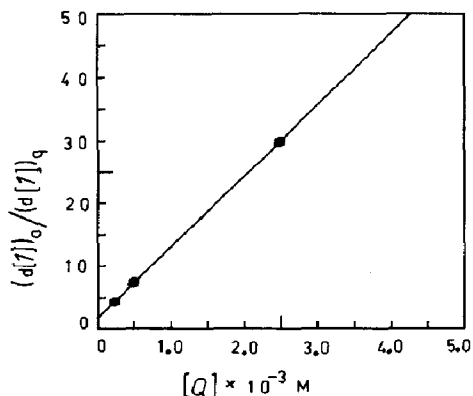
Fig. 3. Inhibitory effect of β-carotene on the photosensitized reaction of 1 (10^{-2} M) in the presence of 4 (10^{-2} M) in dimethoxyethane. The ordinate represents the quotient of the consumption of 1 in the absence and in the presence of β-carotene after 0.75 h of irradiation.

lated value of k_A in the presence of DABCO was 7.19×10^6 M^{-1} s^{-1} using the value of 44×10^6 M^{-1} s^{-1} for k_q^{tot}(DABCO) [17, 22]. Thus the value of k_A calculated in the presence of DABCO differs from that obtained in the presence of β-carotene by more than one order of magnitude.

3.2. Direct disappearance technique

More exact values for k_A are usually obtained by a more accurate technique, the substrate direct disappearance technique [21, 23]. This technique is also based on the steady state approximation and can be applied to the determination of k_A values both in the absence and in the presence of a quencher and to test whether a specific quencher also quenches the triplet sensitizer. When no triplet sensitizer quenching by Q occurs then plots of $1/\Phi$ or $1/\Delta[A]$ *versus* $1/[A]$ are found to be linear with constant intercepts after a given time of irradiation in the presence of different concentrations of Q. Thus oxygen-saturated dimethoxyethane solutions of various concentrations of 1 in the presence of 2 were photo-oxidized in a merry-go-round apparatus and the disappearance of 1 and the formation of peroxide were determined from these solutions. A plot of $1/\Delta[1]$ *versus* $1/[1]$ was linear ($r = 0.972$) with a slope of 2.48 ± 0.30 and an intercept of 98 ± 12 M^{-1} giving a β value defined as k_d/k_A equal to 0.025 ± 0.006 M. The value of k_A was calculated to be 1.24×10^6 M^{-1} s^{-1} (Fig. 4). A plot of $1/[\text{peroxide}]$ *versus* $1/[1]$ was also found to be linear ($r = 0.989$) and the calculated value of k_A from this plot was 8.52×10^5 M^{-1} s^{-1} ($\beta = 0.037 \pm 0.006$ M) (Fig. 5, curve 1). Deviations from linearity were found at low substrate concentrations which probably reflect the increasing contributions of small amounts of peroxides from the solvent when going to more dilute solutions.

Analogous plots from irradiation experiments in the presence of β-carotene in two different concentrations (1.03×10^{-3} and 5.25×10^{-4} M) were also found to be linear in the concentration interval $1/[1] < 100$ M^{-1} and the intercepts of the curves were the same as in the case without a
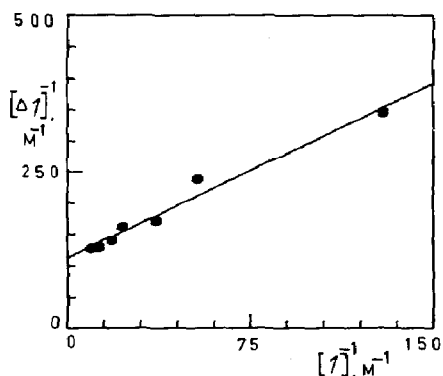
Fig. 4. Plot of the change in concentration of 1 at different initial concentrations of 1 in the photoreaction of 1 sensitized by 2 after 0.75 h of irradiation.
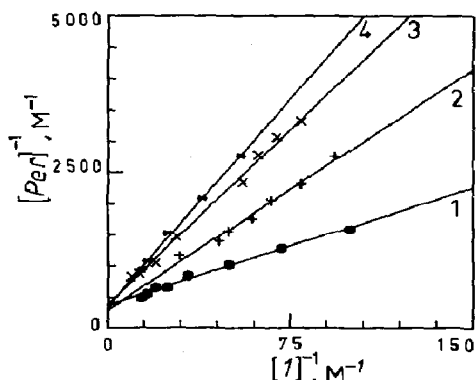
Fig. 5. Plots of the formation of peroxides from 1 in the reaction of 1 photosensitized by 2 (10^{-2} M) in the presence and in the absence of a quencher: curve 1, no quencher; curve 2, β-carotene (5.25×10^{-4} M); curve 3, β-carotene (1.03×10^{-3} M); curve 4, DABCO (5.00×10^{-4} M).

quencher (see Fig. 5). This could imply, if the applied kinetic scheme is correct, that β-carotene and 1 compete for the same intermediate, singlet oxygen [21]. By use of the same experimental data a rough estimate of k_A can be obtained by plotting the so-called β_{app} data (slope/intercept) versus [Q], which allows for the determination of k_d/k_A from the intercept of the new line with extrapolation to infinite dilution of the quencher. The intercept was found to be 0.031 giving $k_A = 1.01 \times 10^6$ M^{-1} s^{-1}. However, when k_A values were calculated from β_{app} values obtained from original plots of 1/[peroxide] versus 1/[1] where the β-carotene quenching constant is needed, the k_A values were found to be 1.10×10^8 M^{-1} s^{-1} and 0.98×10^8 M^{-1} s^{-1} for the higher and the lower concentrations of Q respectively. This gives an average value of k_A of 1.04×10^8 M^{-1} s^{-1}, which is again about two orders of magnitude greater than the value obtained without a quencher.

Results from studies in the absence and in the presence of DABCO (5.00×10^{-4} M) gave intercepts from a plot 1/[peroxide] versus 1/[1] which also were found to be of the same magnitude, implying exclusively singlet oxygen quenching (Fig. 5). The calculated value for k_A was in this case 3.43×10^5 M^{-1} s^{-1} ($\beta_{app} = 0.156 \pm 0.031$).

4. Mechanistic implications

When k_A values determined for 1 with the aid of different experimental set-ups and methods are compared, discrepancies in the rate constants are observed. In the absence of a quencher or when the quencher concentration is extrapolated to zero, the differences are not so great and the k_A values scatter from 8.52×10^5 to 1.24×10^6 M^{-1} s^{-1}. This implies a rate constant for the reaction of 1 and singlet oxygen of the approximate magnitude of
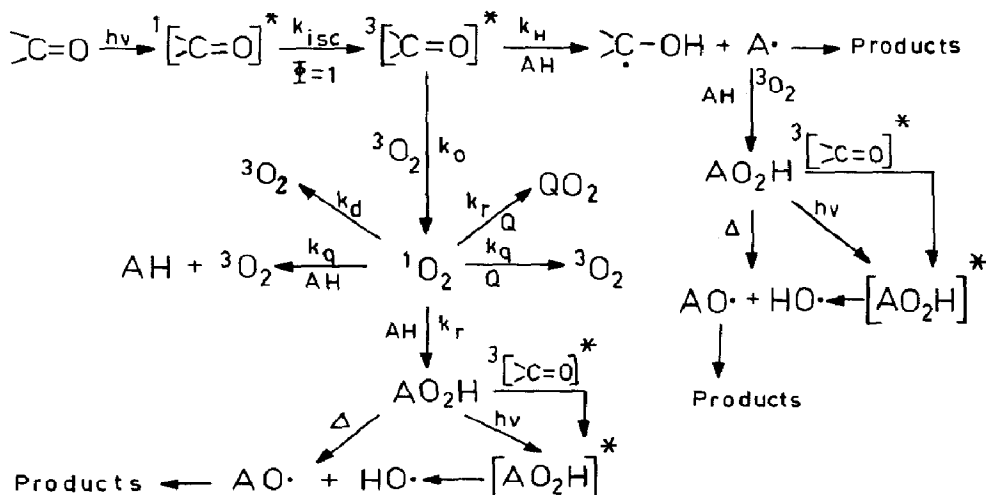
Fig. 6. Different pathways of the carbonyl-sensitized photo-oxidation of 1 ($\equiv$AH) in air-saturated dimethoxyethane. The products of the different routes need not be identical ($k_A = k_r + k_q$).

10^6 $M^{-1}.s^{-1}$. The fact that the values for the rate constant k_A are different in experiments with added quenchers implies *either* some anomalies in the quenching behaviour of the additives *or* that the working hypothesis is not valid and that more than one mechanism is operating in the reaction between the aromatic triplet carbonyl and the phenolic substrate.

Evidence is being accumulated that the so-called "singlet oxygen quenchers" are not so specific for singlet oxygen and that they can also react with free radicals and can influence the light absorption. The filter effect may be of importance with higher concentrations of β-carotene but not in the presence of DABCO which does not absorb light at the region of the sensitizer. Furthermore, β-carotene is also photolabile. Thus caution should be observed when these quenchers are used in mechanistic studies [24]. More useful results may be gained from the experiments without quenchers.

The peroxidic compounds formed as primary products are usually both thermochemically and photochemically unstable, decomposing into free radicals which can react along different pathways inducing new oxidation chains. This effect is thought to be of minor significance at the beginning of the irradiation but to increase gradually at longer reaction times, when the peroxide content increases.

The role of direct hydrogen abstraction from the phenolic substrate 1 by the sensitizer in its triplet state should also be considered as a possible competing process with singlet oxygen formation (Fig. 6), where different possible pathways are shown. The scarcity of experimental data in the literature [25, 26] makes it difficult to make any conclusive statement but the much larger reaction rates observed in the presence of oxygen compared with oxygen-free systems [8] suggest that the contribution from direct hydrogen abstraction is small, *i.e.* $k_H \ll k_O$.

The lack of experimentally measured rate constants for carbonyl compounds of interest to the photochemistry of wood makes it very difficult to make any final decision about the mechanism of the reaction studied.

5. Studies in other systems

5.1. Reaction of a non-phenolic lignin model compound

Recently, it has been shown by Kutsuki *et al.* [27] that some lignin model compounds with alkylated *para* phenolic groups were stable in the presence of singlet oxygen. We could confirm these results with the non-phenolic compound 3 (*tert*-butyl-(3,4-dimethoxyphenyl)carbinol) which was found to be stable when irradiated in the presence of 4 or 2 (Fig. 7). In the latter case the sensitizer itself was consumed so that only about 30% remained after irradiation for 5 h.
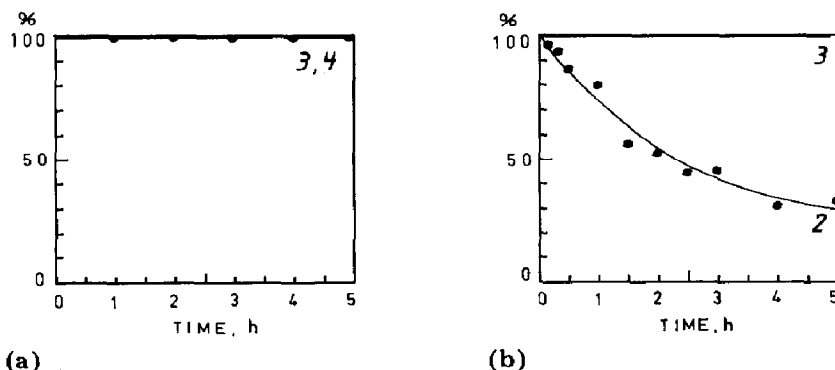

(a)   (b)

Fig. 7. (a) The rate of consumption of 3 (10^{-2} M) and 4 (10^{-2} M) in air-saturated dimethoxyethane (50 ml) during irradiation; (b) the rate of consumption of 3 (10^{-2} M) and 2 (10^{-2} M) in air-saturated dimethoxyethane during irradiation.

The conclusion which can be drawn, on the basis of these experiments, is that the presence of a free phenol group is essential for the reaction and that benzyl alcohol groups do not take part in the photoreaction.

5.2. Benzophenone as sensitizer

Benzophenone has often been used as a carbonyl sensitizer in studies of the photoinduced reactions of lignin model compounds. Although this sensitizer is among the most studied of all the carbonyl compounds, its sensitizing activity in the presence of phenols is not yet known in detail [26, 28]. Benzophenone is not exactly analogous to the α carbonyl structures in lignin and the reactivity of benzophenone may not be the same as that of the alkylarylcarbonyl groups found in lignin.

The benzophenone-sensitized reaction of the substrate 1 was performed to compare it with the reaction in the presence of 2. The results of the gas—liquid chromatography (GLC) analyses show that benzophenone was not
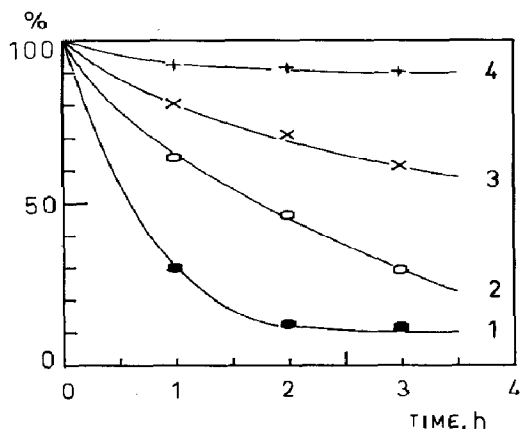
Fig. 8. Rate of disappearance of 1 (10^{-2} M) in the photoreaction of 1 in air-saturated dimethoxyethane sensitized by benzophenone (10^{-2} M) (curve 1), benzophenone (10^{-3} M) (curve 2), 2 (10^{-2} M) (curve 3) and benzophenone (10^{-2} M) in the presence of β-carotene (2.5×10^{-3} M) (curve 4).

consumed (by analogy with studies with 2) but instead the rate of disappearance of the substrate 1 was very fast, which can be seen in Fig. 8. Although the concentration of benzophenone was reduced by one order of magnitude the consumption of 1 was still faster than with 2. Strong inhibition of the consumption of 1 was further obtained in the presence of 2.5×10^{-3} M β-carotene.

Obviously benzophenone is a much more efficient sensitizer than the lignin model compound 2. Whether or not the difference in reactivity is a consequence of different modes of reaction of the triplet carbonyls is not yet known, but caution should nevertheless be employed when statements regarding the mechanism of the photosensitized reaction of lignin are made on the basis of experiments with benzophenone.

5.3. Ring-conjugated double bonds and biphenyl structures

It was also of interest to compare the sensitizing ability of aromatic ring-conjugated double bonds with that of α carbonyl compounds in the presence of the substrate 1. Thus 1 was irradiated in the presence of the olefinic sensitizers anethole (1-methoxy-4-propenylbenzene) 6 and isoeugenol (1-hydroxy-2-methoxy-4-propenylbenzene) 7 and the consumption of 1 was determined by GLC. The results are shown in Fig. 9(a), where the corresponding disappearance curve of 1 in the presence of p-methoxyacetophenone 5 is also shown. In comparison with the aromatic α carbonyl compound, 6 was a slightly inferior sensitizer. After 3 h 60% of 1 was left with 5 and 68% with 6. However, 7 did not sensitize the reaction of 1 at all. No consumption of 1 was detected in this case.

A striking difference in the behaviour of the α carbonyl and the olefinic sensitizers was found in the consumption of the sensitizers themselves. The α carbonyl compounds were stable during the irradiation but the olefinic compounds were consumed rather rapidly which is seen in Fig. 9(b). The

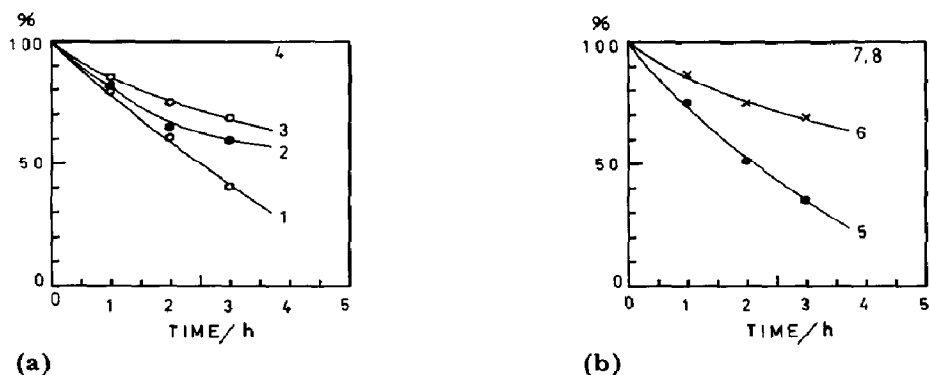Fig. 9. (a) Rate of disappearance of 1 (10^{-2} M) during irradiations in the presence of 2 (10^{-3} M) (curve 1), 5 (10^{-3} M) (curve 2), 6 (10^{-3} M) (curve 3) and 7 (4×10^{-3} M) (curve 4). (b) Rate of consumption of the sensitizers in the reactions in (a): curve 5, 7; curve 6, 6; curve 7, 2; curve 8, 5.

solutions with **6** and **7** were also in general less coloured after irradiation than the solutions obtained with carbonyl sensitizers. Although **7** had no sensitizing effect on **1** it was consumed even faster than **6**. Whether the mechanism of the sensitized reaction of **1**, in the presence of the double-bond structures, is similar to that in the presence of α carbonyl triplets is at this stage unclear, but there are significant differences in their observed behaviours although all reactions were inhibited to different degrees in the presence of β-carotene.

The prerequisite for the olefinic compounds to function as sensitizers seems to be that the structures do not contain free phenolic groups in the *para* position, a fact that does not apply to the α carbonyl compounds. Further proof of the correctness of this conclusion was gained from experiments with isoeugenolmethylether (1,2-dimethoxy-4-propenylbenzene) **8** which was consumed itself but which also sensitized the oxidation of **1**. The photochemical degradation of lignin model compounds containing ring-conjugated double bonds has been observed earlier [7] but their different sensitizing abilities with regard to the consumption of other lignin model compounds present have not been evaluated. Only from the small amount of discolouration after irradiation were the olefinic and the biphenyl structures judged to be of less importance [2].

GLC analyses of the photoreaction of **1** in the presence of a biphenyl compound, bicreosol (2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl) **9**, showed that the substrate was completely stable but that **9** was consumed rather fast (Fig. 10). The biphenyl structures seem to be of negligible importance in light-induced oxygenation of other phenols although they are not photochemically stable themselves.

In conclusion, it can be said that of the chromophoric structural units found in lignin the aromatic α carbonyl compounds are of the greatest significance. These structures have the strongest sensitizing ability and are not consumed during irradiation as long as there are compounds with free
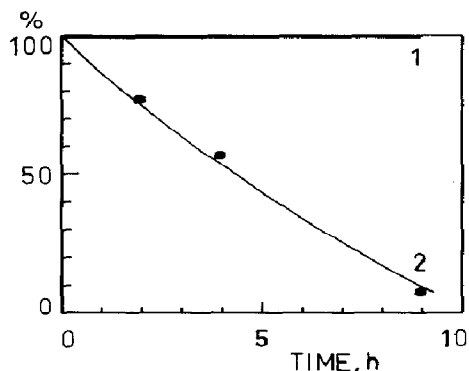
Fig. 10. Rate of disappearance of 1 $(10^{-2}$ M$)$ (curve 1) and of 9 $(10^{-2}$ M$)$ (curve 2) during irradiation in aerated dimethoxyethane.

phenolic groups left. Aromatic compounds with ring-conjugated double bonds are somewhat weaker sensitizers and are consumed at a high rate during irradiation and their effect decreases gradually. In contrast, carbonyl structures arise via double-bond cleavage and double-bond structures can thus react via an indirect pathway.

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