EXPERIMENTAL AND COMPUTER MODELLING STUDY OF THE PHOTOCHEMICAL REACTION OF *tert*-BUTYLGUAIACYLCARBINOL SENSITIZED BY *p*-METHOXYPROPIOPHENONE IN OXYGEN-FREE DIMETHOXYETHANE

INGEGERD FORSSKÅHL and HENRIK TYLLI

Department of Chemistry, University of Helsinki, E. Hesperiankatu 4, SF-00100 Helsinki 10 (Finland)

Summary

The photochemical reaction of *tert*-butylguaiacylcarbinol sensitized by *p*-methoxypropiophenone in an oxygen-free solution was studied experimentally and by computer modelling. The simulation of the reactions of these lignin model compounds was done in two steps. In the first step the reaction of the sensitizer was followed using a reaction set consisting of 15 reactions. With this set the reaction could be followed for 5 h with good agreement with the experimental results. In the second step the simulation of the photochemical reaction of the phenol in the presence of sensitizer was attempted, using a reaction set consisting of 33 reactions. For the phenol good agreement with experiment was obtained for reaction times of up to 5 h. However, the reaction of the sensitizer could be modelled with reasonable agreement with the experiment for only up to 2 h. For longer reaction times an increasing deviation between the experimental and the calculated reaction rates was observed with the present set. The reason for the discrepancy is discussed.

1. Introduction

The photochemical yellowing of wood and high yield pulps is a complicated process with important practical consequences. It is clear that the process is a light-induced oxidation of lignin influenced by atmospheric oxygen and that aromatic compounds with an α carbonyl group play an active role as photosensitizers [1 - 6]. In a number of studies [5, 7 - 9] with phenolic lignin model compounds it has been demonstrated that the phenol is consumed in the photochemical reaction in the presence of aromatic α carbonyl compounds, leading to colour generation and a variety of products. The formation of radical intermediates has been proved directly with electron spin resonance measurements of the reaction mixtures both in the presence and in the absence of oxygen [3, 10] and also indirectly from the

structures of isolated reaction products [4, 5, 11]. Recent results by Das *et al.* [12] indicate that the quenching of the aromatic carbonyl triplets in the presence of phenolic compounds is complicated. In the absence of oxygen the carbonyl triplet abstracts hydrogen, generating intermediate radicals. Intermediate ketyl and phenoxy radicals have indeed been detected with UV absorption spectroscopy [12, 13] and with the chemically induced dynamic nuclear polarization technique [14]. However, the detailed mechanism of the light-induced reaction of lignin still remains to be clarified.

In the present study we have employed computer modelling to elucidate the mechanism of the solution state photochemical reaction of a phenolic lignin model compound (*tert*-butylguaiacylcarbinol) in the presence of a second lignin model compound with an α carbonyl group (*p*-methoxypropiophenone). Because the introduction of oxygen leads to a substantial complication of the system, we decided to begin with the mechanism in the absence of oxygen, but we hope to return to the system including oxygen in a separate study.

2. Methods

2.1. Experimental details

Dimethoxyethane (Fluka) was purified by distillation, dried over sodium wire and redistilled immediately before use. Dodecane and *p*-cymene (Fluka) were analytical grade and used as such. *p*-Methoxypropiophenone was prepared according to ref. 15 and purified by vacuum distillation three times (boiling point, 152 °C at 18 mmHg). The sample was found to be gas chromatographically pure to 99%. *tert*-Butylguaiacylcarbinol was synthesized according to ref. 16 and was purified by column chromatography (Silica gel 60; 70 - 230 mesh; Merck) using a 1:2 mixture of (ethyl acetate): cyclohexane as eluent. The product was recrystallized from (diethyl ether)–ligroin (boiling point, 60 - 80 °C) and melted at 73 - 74 °C.

The UV–visible absorption spectrum of *p*-methoxypropiophenone was measured in dimethoxyethane using a Shimadzu UV-240 spectrometer. The spectrum consists of two main absorption bands at 216 nm (log ϵ = 4.02) and 264 nm (log ϵ = 4.23). The band centred at 264 nm is asymmetric and displays a shoulder which results because the carbonyl chromophore extends to about 350 nm (log $\epsilon_{320\,nm}$ = 2.08).

The irradiation experiments were performed in 15 ml Pyrex test-tubes (diameter, 15 mm) provided with a reflux condenser in a Rayonet photochemical reactor RPR-208 fitted with eight UV lamps, yielding light of wavelengths 305 - 420 nm with the maximum centred at 350 nm. The concentrations of the substrate, the sensitizer and the internal standard were 10^{-2} mol l^{-1} in dimethoxyethane. The reaction mixture (10 ml) was stirred with a stream of oxygen-free (10% pyrogallol in 2 M NaOH) dried nitrogen and small samples were withdrawn at different time intervals for subsequent gas–liquid chromatography (GLC) analysis. In the absence of

sensitizer *tert*-butylguaiacylcarbinol was not consumed under otherwise identical irradiation conditions. This implies that the irradiation transmitted by the Pyrex vessels (cut-off at about 300 nm) is not absorbed by the substrate.

The GLC analyses were performed with a Perkin–Elmer 990 gas chromatograph and recorder 159, equipped with flame ionization detectors and two 2 m (diameter, 3 mm) packed columns (5% SE-30 on Varaport 30; 80 - 100 mesh), and a Hewlett–Packard 3373 B integrator. *p*-Cymene and dodecane were used as internal standards. The error limits in the experimental results are estimated to be ±10%.

2.2. Computational simulations

The simulations were carried out using the program system HAVCHM, described by Stabler and Chesick [17], adapted to the Burroughs 7800 computer at the University of Helsinki Computing Centre. The performance of the system on the Burroughs installation was checked against the results of several published modelling studies [18 - 21].

3. Formulation of the reaction set

The general principles to be considered in connection with the formulation of reaction sets for modelling studies have been discussed by several researchers [22 - 24]. We have restricted our attention to a number of elementary processes, all of which are well documented in the literature.

TABLE 1

Reaction set used in the modelling of the photochemical reaction of *p*-methoxypropiophenone in oxygen-free dimethoxyethane

Set number	Reaction	k
1	HSENS → (^{1}(HSENS)*) → ^{3}(HSENS)*	1.0×10^{-3} s^{-1}
2	^{3}(HSENS)* → HSENS	1.0×10^5 s^{-1}
3	^{3}(HSENS)* + HSENS → ·$C_{10}H_{13}O_2$ + SENS·	1.0×10^6 M^{-1} s^{-1}
4	·$C_{10}H_{13}O_2$ + SENS· → HSENS + HSENS	1.0×10^4 M^{-1} s^{-1}
5	^{3}(HSENS)* + ^{3}(HSENS)* → HSENS + HSENS	5.0×10^9 M^{-1} s^{-1}
6	^{3}(HSENS)* + HSENS → HSENS + HSENS	1.0×10^8 M^{-1} s^{-1}
7	·$C_{10}H_{13}O_2$ + SENS· → $C_{20}H_{24}O_4$	1.0×10^9 M^{-1} s^{-1}
8	SENS· + SENS· → $C_{20}H_{22}O_4$	1.0×10^9 M^{-1} s^{-1}
9	·$C_{10}H_{13}O_2$ + ·$C_{10}H_{13}O_2$ → $C_{20}H_{26}O_4$	1.0×10^9 M^{-1} s^{-1}
10	·$C_{10}H_{13}O_2$ + HSENS → HSENS + ·$C_{10}H_{13}O_2$	8.0×10^7 M^{-1} s^{-1}
11	^{3}(HSENS)* + SENS· → ·$C_{20}H_{23}O_4$	1.0×10^1 M^{-1} s^{-1}
12	·$C_{10}H_{13}O_2$ + HSENS → $C_{10}H_{14}O_2$ + SENS·	1.0×10^6 M^{-1} s^{-1}
13	^{3}(HSENS)* + $C_{10}H_{14}$ → ·$C_{10}H_{13}O_2$ + ·$C_{10}H_{13}$	1.0×10^5 M^{-1} s^{-1}
14	^{3}(HSENS)* + $C_{10}H_{14}$ → HSENS + $C_{10}H_{14}$	2.8×10^6 M^{-1} s^{-1}
15	^{3}(HSENS)* + ·$C_{10}H_{13}O_2$ → ·$C_{20}H_{25}O_4$	1.0×10^1 M^{-1} s^{-1}

88

The elementary processes included in our study are as follows: excitation of the sensitizer followed by intersystem crossing giving the sensitizer in an excited triplet state; hydrogen transfer; physical and chemical quenching of the carbonyl triplet; radical coupling; energy and electron transfer.

The reaction schemes are shown in Figs. 1 and 2 and the reaction sets are shown in Tables 1 and 2. To maintain the problem at a manageable size some restrictions had to be made. Dimeric reaction products were not re-entered in the reaction set, but were considered as non-reactive end products. However, dimers were allowed to take part in the physical quenching. Radical disproportionation and the possible involvement of the solvent were omitted from the reaction scheme as being of minor significance in this system.

3.1. Evaluation of rate constants for the reaction of the sensitizer (see Table 1)

(1) The constant k_1 is not a rate parameter in the usual sense but rather a parameter which is used to describe the excitation process in this
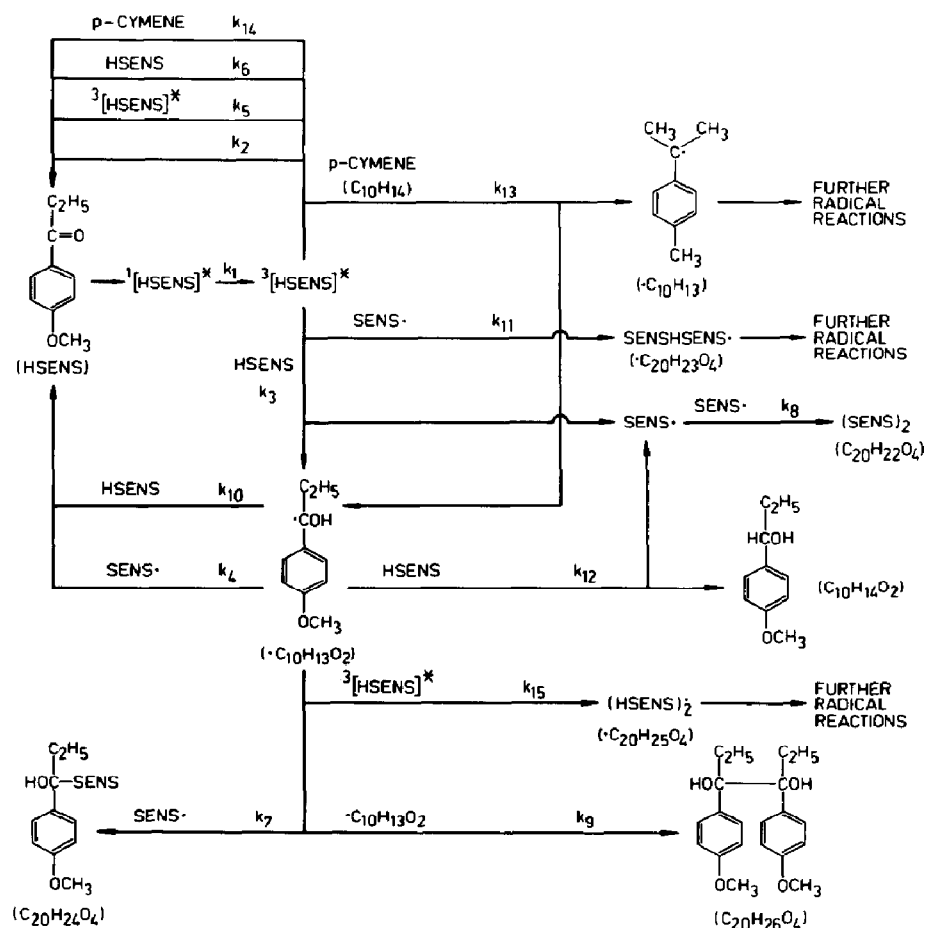
Fig. 1. Reaction scheme for the photochemical reaction of p-methoxypropiophenone in oxygen-free dimethoxyethane.
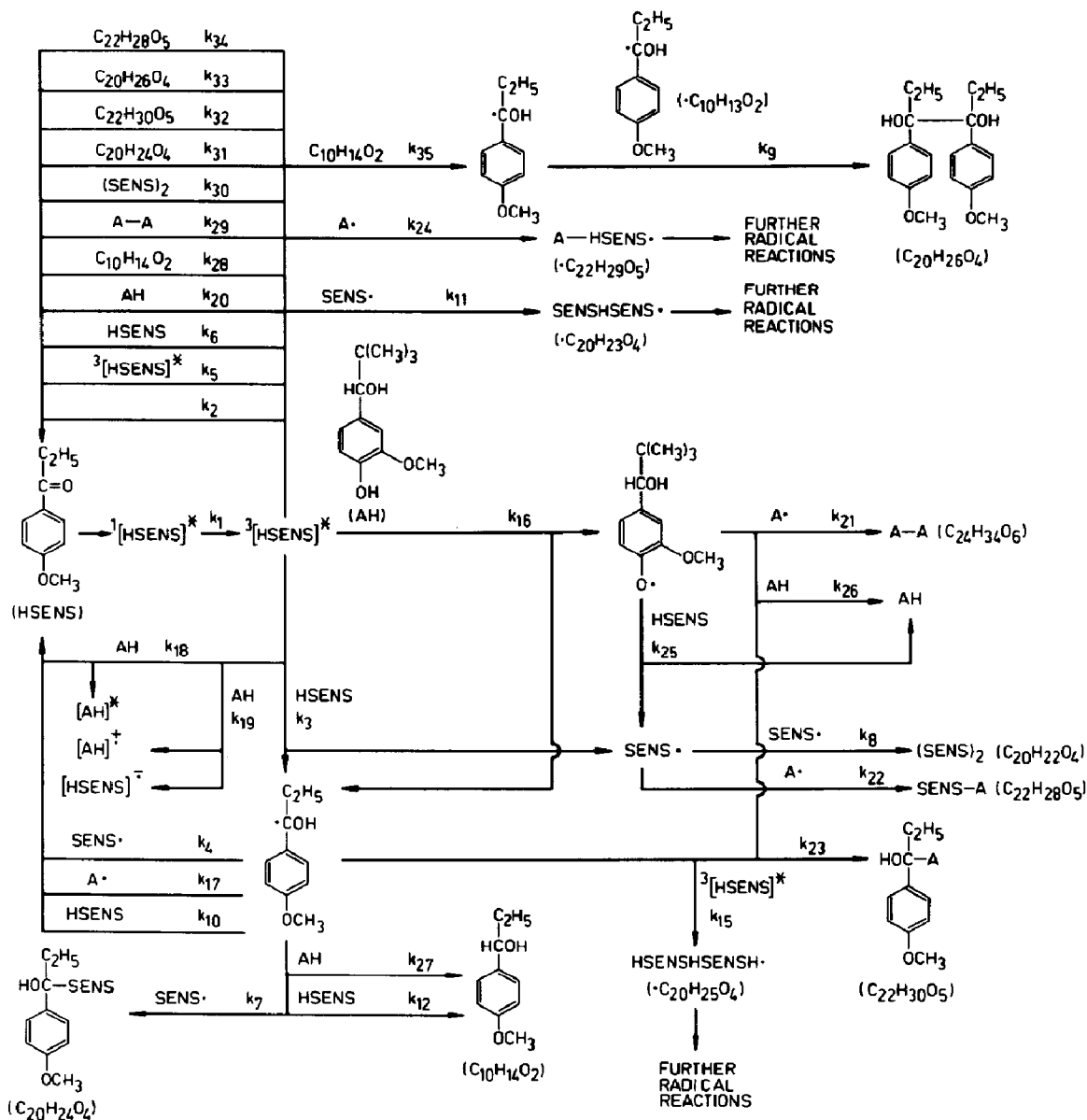
Fig. 2. Reaction scheme for the photochemical reaction of *tert*-butylguaiacylcarbinol sensitized by *p*-methoxypropiophenone in oxygen-free dimethoxyethane.

experimental set-up. Because a theoretical evaluation of the parameter is complicated [25] an empirical approach was used. The rate constant for excitation of an aromatic α carbonyl group is of the order of 10^{10} s^{-1} [26]. In modelling the experimental set-up the fact to consider is that only molecules in a thin outer layer of the solution in the test-tube absorb the light and undergo further reactions resulting ultimately in product formation. Stirring the reaction solution by nitrogen bubbling keeps the molecules of the solution uniformly distributed with new carbonyl groups entering the absorbing area continuously. The small fraction of molecules actually taking

TABLE 2

Reaction set used in the modelling of the photochemical reaction of *tert*-butylguaiacyl-carbinol sensitized by *p*-methoxypropiophenone in oxygen-free dimethoxyethane

Set number	Reaction	k
1	HSENS $\to$ (^{1}(HSENS)*) $\to$ ^{3}(HSENS)*	1.0×10^{-3} s^{-1}
2	^{3}(HSENS)* $\to$ HSENS	1.0×10^5 s^{-1}
3	^{3}(HSENS)* + HSENS $\to$ $\cdot C_{10}H_{13}O_2$ + SENS$\cdot$	1.0×10^6 M^{-1} s^{-1}
4	$\cdot C_{10}H_{13}O_2$ + SENS$\cdot$ $\to$ HSENS + HSENS	1.0×10^4 M^{-1} s^{-1}
5	^{3}(HSENS)* + ^{3}(HSENS)* $\to$ HSENS + HSENS	5.0×10^9 M^{-1} s^{-1}
6	^{3}(HSENS)* + HSENS $\to$ HSENS + HSENS	1.0×10^8 M^{-1} s^{-1}
7	SENS$\cdot$ + $\cdot C_{10}H_{13}O_2$ $\to$ $C_{20}H_{24}O_4$	1.0×10^9 M^{-1} s^{-1}
8	SENS$\cdot$ + SENS$\cdot$ $\to$ (SENS)$_2$	1.0×10^9 M^{-1} s^{-1}
9	$\cdot C_{10}H_{13}O_2$ + $\cdot C_{10}H_{13}O_2$ $\to$ $C_{20}H_{26}O_4$	1.0×10^9 M^{-1} s^{-1}
10	$\cdot C_{10}H_{13}O_2$ + HSENS $\to$ HSENS + $\cdot C_{10}H_{13}O_2$	8.0×10^7 M^{-1} s^{-1}
11	SENS$\cdot$ + ^{3}(HSENS)* $\to$ $\cdot C_{20}H_{23}O_4$	1.0×10^1 M^{-1} s^{-1}
12	$\cdot C_{10}H_{13}O_2$ + HSENS $\to$ $C_{10}H_{14}O_2$ + SENS$\cdot$	1.0×10^6 M^{-1} s^{-1}
15	^{3}(HSENS)* + $\cdot C_{10}H_{13}O_2$ $\to$ $\cdot C_{20}H_{25}O_4$	1.0×10^1 M^{-1} s^{-1}
16	^{3}(HSENS)* + AH $\to$ $\cdot C_{10}H_{13}O_2$ + A$\cdot$	1.4×10^8 M^{-1} s^{-1}
17	$\cdot C_{10}H_{13}O_2$ + A$\cdot$ $\to$ HSENS + AH	1.0×10^6 M^{-1} s^{-1}
18	^{3}(HSENS)* + AH $\to$ HSENS + (AH)*	1.0×10^1 M^{-1} s^{-1}
19	^{3}(HSENS)* + AH $\to$ (HSENS)$^-$ + (AH)$^+$	1.0×10^1 M^{-1} s^{-1}
20	^{3}(HSENS)* + AH $\to$ HSENS + AH	6.0×10^8 M^{-1} s^{-1}
21	A$\cdot$ + A$\cdot$ $\to$ A $-$ A	1.0×10^9 M^{-1} s^{-1}
22	A$\cdot$ + SENS$\cdot$ $\to$ A $-$ SENS	1.0×10^9 M^{-1} s^{-1}
23	A$\cdot$ + $\cdot C_{10}H_{13}O_2$ $\to$ $C_{22}H_{30}O_5$	1.0×10^9 M^{-1} s^{-1}
24	A$\cdot$ + ^{3}(HSENS)* $\to$ $\cdot C_{22}H_{29}O_5$	1.0×10^1 M^{-1} s^{-1}
25	A$\cdot$ + HSENS $\to$ AH + SENS$\cdot$	1.0×10^3 M^{-1} s^{-1}
26	A$\cdot$ + AH $\to$ AH + A$\cdot$	1.0×10^6 M^{-1} s^{-1}
27	$\cdot C_{10}H_{13}O_2$ + AH $\to$ $C_{10}H_{14}O_2$ + A$\cdot$	7.0×10^5 M^{-1} s^{-1}
28	^{3}(HSENS)* + $C_{10}H_{14}O_2$ $\to$ HSENS + $C_{10}H_{14}O_2$	4.0×10^9 M^{-1} s^{-1}
29	^{3}(HSENS)* + $C_{24}H_{34}O_6$ $\to$ HSENS + $C_{24}H_{34}O_6$	4.0×10^9 M^{-1} s^{-1}
30	^{3}(HSENS)* + $C_{20}H_{22}O_4$ $\to$ HSENS + $C_{20}H_{22}O_4$	4.0×10^9 M^{-1} s^{-1}
31	^{3}(HSENS)* + $C_{20}H_{24}O_4$ $\to$ HSENS + $C_{20}H_{24}O_4$	4.0×10^9 M^{-1} s^{-1}
32	^{3}(HSENS)* + $C_{22}H_{30}O_5$ $\to$ HSENS + $C_{22}H_{30}O_5$	4.0×10^9 M^{-1} s^{-1}
33	^{3}(HSENS)* + $C_{20}H_{26}O_4$ $\to$ HSENS + $C_{20}H_{26}O_4$	4.0×10^9 M^{-1} s^{-1}
34	^{3}(HSENS)* + $C_{22}H_{28}O_5$ $\to$ HSENS + $C_{22}H_{28}O_5$	4.0×10^9 M^{-1} s^{-1}
35	^{3}(HSENS)* + $C_{10}H_{14}O_2$ $\to$ $\cdot C_{10}H_{13}O_2$ + $\cdot C_{10}H_{13}O_2$	1.0×10^7 M^{-1} s^{-1}

part in the absorbing event is accounted for with the very small value of k_1. This rate constant must be adjusted to the experimental conditions when, for example, devices with different geometries are used, and it can thus be regarded as a parameter used to reproduce the experimental results. The intersystem crossing from the sensitizer excited singlet to the triplet state of carbonyl compounds of this type is 100% efficient [26, 27].

(2) k_2 was evaluated from the corresponding reaction of benzophenone in benzene ((5 - 3.3) $\times 10^5$ s^{-1} [28], 1.5 $\times 10^5$ s^{-1} [29]) and of acetophenone in benzene (1.86 (± 0.6) $\times 10^5$ s^{-1} [30], 2.5 $\times 10^5$ s^{-1} [29]). The phosphorescence lifetime for the following carbonyl compounds decreases in

the order p-methoxyacetophenone > propiophenone > acetophenone [31], placing the non-examined p-methoxypropiophenone at the beginning of this series. The chosen value for k_2 is thus assumed to be smaller than the deactivation rate constant for triplet acetophenone.

(3) The triplets of p-methoxyacetophenone and p-methoxypropiophenone react similarly in hydrogen abstraction reactions [32]. The quenching rate constants are generally at least 50 times smaller in the presence of methoxybenzenes than in the presence of free phenols, for which rate constants of $(5 - 7) \times 10^9$ M^{-1} s^{-1} have been obtained in non-polar solvents [12]. The rate constant for the total quenching of the triplet p-methoxypropiophenone by methoxybenzenes in benzene solution has been reported to be about 10^6 M^{-1} s^{-1} [12]. The sensitizer has different sites for hydrogen abstraction: the methoxy group, the aromatic ring or the alkyl side-chain, the order of the rate constants being presumably $k(\text{ring hydrogen}) < k(\text{OCH}_3) < k(\text{alkyl chain})$. The rate constant for hydrogen abstraction from p-methoxypropiophenone is chosen to be 10^6 M^{-1} s^{-1}.

(4) The "reverse" of reaction (3), leading to the sensitizer in the ground state, is thought to be of minor importance and the simulation is not sensitive to the value chosen.

(5) This reaction is generally considered to be a pseudobimolecular process. The rate constants for triplet–triplet annihilation are generally high and close to the diffusion limit. A rate constant of 5×10^9 M^{-1} s^{-1} for triplet–triplet annihilation has been obtained for triplet benzophenone [33] and this value was used for k_5.

(6) According to Scaiano and Selwyn [34] the triplet self-quenching of phenyl alkyl ketones is considerable in micellar solutions. Chapman and Wampler [35] obtained a value of 9×10^7 M^{-1} s^{-1} for the rate constant k_{sq} for self-quenching for p-methoxyacetophenone, whereas Das et $al.$ [12] found a value of 5.9×10^8 M^{-1} s^{-1} for p-hydroxypropiophenone in benzene. For the p-methoxysubstituted analogue we used a smaller value.

(7) The rate constant for the coupling reaction of these two different radicals is considered to be rather high (order of magnitude, about 10^9 M^{-1} s^{-1}) as are the rate constants for the coupling of carbon radicals in general. Coupling is thought not to proceed inside the solvent cage (see reaction (3)), because of the slow spin inversion of the radicals compared with their diffusion rate out of the cage [36]. Few quantitative rate constants are available and little is known about the coupling of radicals of this type in dimethoxyethane.

(8) The rate constant k_8 for dimerization of the sensitizer radical was chosen as in reaction (7).

(9) Experimental proof of the importance of this dimerization reaction (see reaction (7)) leading to substituted pinacols can be obtained from product studies in photoreduction experiments, $e.g.$ acetone and benzophenone in the presence of hydrogen donors [26, 36]. Irradiation of acetophenone in alcohol solution yields acetophenone pinacol [37] and, in the presence of catalytic amounts of phenol, the same product is obtained in addition to

1,2-dibenzoylethane [11]. Photoreduction of 4-methylacetophenone, 3,4-dimethylacetophenone and propiophenone also yields the corresponding pinacols [11].

(10) The hydrogen transfer from an acetophenone ketyl radical to an aromatic α carbonyl was found experimentally to take place with a rate constant of 8×10^7 M^{-1} s^{-1} [38], a value which is adopted here for the hydrogen abstraction from a similar ketyl radical. However, this parameter is not significant because there is no net result of the reaction.

(11) The reaction between the triplet carbonyl and a radical is thought to be unimportant in this system, because of energy and spin restrictions.

(12) Hydrogen abstraction from the sensitizer by the ketyl radical is chosen to be of the same magnitude as that by the triplet carbonyl group ($k_3 = 10^6$ M^{-1} s^{-1}). The reaction product is a benzyl alcohol compound which also may be formed via other routes, e.g. by disproportionation which has been omitted from the present reaction scheme. Therefore, the rate constant used in the simulation may be too high. Although ketyl radicals are thought to be reducing agents the conversion of the ketyl radical to a benzyl alcohol has been shown to occur [37]. This type of reaction has also been proposed by Lin and Kringstad [4].

(13) The hydrogen abstraction rate constant k_{13} was evaluated from the corresponding value of the rate constant in the reaction of triplet benzophenone and cumene. The measured relative rates were 1.5 [39] and 0.71 [40] (mean value, 1.1) for cumene and 4.4 [39] for 2-propanol in relation to cyclohexane. The absolute rate constants for hydrogen abstraction from 2-propanol, determined in different experiments, vary from 1.1×10^6 to 1.8×10^6 M^{-1} s^{-1} [27], giving a value for k_H(cumene) ranging from 0.2×10^6 to 0.5×10^6 M^{-1} s^{-1}. The total quenching rate constant for cumene has been found to be greater than that for p-cymene [41] and the same ratio is thought to be valid for the hydrogen abstraction rate constants also. Consequently k_{13} was given a slightly smaller value, namely 1.0×10^5 M^{-1} s^{-1}.

(14) Recent experimental results by Olea et al. [41] demonstrate that the total quenching rate constant k_q^{tot} for a triplet carbonyl (benzophenone) by p-cymene is 2.90×10^6 M^{-1} s^{-1}. Subtraction of the hydrogen abstraction rate constant, 1.0×10^5 M^{-1} s^{-1}, given in reaction (13), from k_q^{tot} gives 2.8×10^6 M^{-1} s^{-1} for the physical quenching by p-cymene. This value is used for k_{14}. The mechanism by which the quenching of an aromatic carbonyl triplet by an alkyl aromate takes place appears to be a question of great uncertainty. The coupling ratios of different radicals formed in the photoreduction of acetophenone by alkylbenzenes [42] have been used to propose the formation of exciplexes. In our simplified reaction set these reactions have been ignored.

(15) This reaction is of little importance (see reaction (11)).

3.2. Evaluation of rate constants for the reaction of the phenol and the sensitizer (see Table 2)

The rate constants for reactions (1) - (15) have already been discussed in connection with Table 1.

(16) The behaviour of *tert*-butoxy radicals has been found to parallel that of radical-like ketone triplets in hydrogen abstractions. However, the observed rate constants for hydrogen abstractions are generally higher for the carbonyl triplets than for the alkoxy radicals [28], for which the only mode of reaction is considered to be a hydrogen transfer. For aromatic carbonyl triplets additional interactions are also possible, leading to higher values for the observed rate constants [12, 41]. The experimentally found rate constant for the hydrogen abstraction by the *tert*-butoxy radical from *o*-methoxyphenol ($k = 1.7 \times 10^8$ M^{-1} s^{-1}) is about one-tenth of the corresponding value for abstraction from *p*-methoxyphenol ($k = 1.8 \times 10^9$ M^{-1} s^{-1}) [41] in benzene. An explanation of this may be the intramolecular hydrogen bond present in *ortho*-substituted phenols. This is supported by the observation that the decrease in the quenching rate constant for carbonyl triplets has been found to correlate with the strength of the hydrogen bond between the phenol quencher and the solvent [32]. Thus the rate constant k_{16} is thought to be of the order of 10^8 M^{-1} s^{-1} because the substrate is an *o*-methoxyphenol. Solvent effects are difficult to estimate, but the quenching rate constants usually decrease on going from a non-polar to a polar solvent [12]. In the simulations k_{16} was used as a fine tuning parameter and was allowed to vary between the limits of 1×10^8 and 2×10^8 M^{-1} s^{-1}.

(17) The "reverse" of reaction (16), leading to the sensitizer in the ground state and the phenol, is of minor importance. The simulation was not sensitive to the value chosen.

(18) Energy transfer from triplet *p*-methoxypropiophenone ($E \approx 301$ kJ mol^{-1}) to the phenol is considered to be extremely unlikely because the lowest triplet state of phenols is usually considerably higher in energy. The large isotope effect found for the quenching of triplet *p*-methoxypropiophenone in the presence of phenols further indicates that the main quenching event goes via hydrogen abstraction and not via energy transfer [12]. Consequently k_{18} was kept very small (1.0×10^1 M^{-1} s^{-1}).

(19) As for k_{18} the electron transfer, *i.e.* k_{19}, is also considered to be very inefficient and the same value was given to this rate constant. Electron transfer may be significant in special solvents with carbonyl and phenolic compounds containing activating substituents, which our compounds probably lack. Nevertheless, the simulation was not sensitive to variations in this rate constant in the interval 10^1 - 10^6 M^{-1} s^{-1}.

(20) The approximate value of the rate constant for the physical quenching of the carbonyl triplet by the phenol is calculated as the difference between the observed quenching constant for triplet *p*-methoxypropiophenone by *p*-methoxyphenol (6.7×10^9 M^{-1} s^{-1}) [12], reduced by one power of ten because of the guaiacyl structure, and the observed value for the quenching of *tert*-butoxy radicals by *o*-methoxyphenol (1.7×10^8 M^{-1} s^{-1}). This gives a value of 5×10^8 M^{-1} s^{-1}. The simulation was quite sensitive to k_{20} and better agreement with the experiments was found with a slightly higher value of k_{20}, *i.e.* 6×10^8 M^{-1} s^{-1}.

(21), (22), (23) The rate constants for the radical reactions k_{21}, k_{22} and k_{23} were all set equal (see Table 1, k_7).

(24) For k_{24} (see Table 1, k_{11}).

(25) The rate constant for the abstraction of hydrogen from the sensitizer by a phenoxy radical is considered to be small. Nevertheless, such a reaction appears to be a pathway of significance. The simulation was quite sensitive to changes in this rate constant. This reaction seems to provide a way to restore the substrate and to obtain a proper balance between substrate and sensitizer concentrations at the beginning of the simulation. k_{25} was used as a fitting parameter to match the initial rate of the reaction to the experimental result.

(26) The hydrogen transfer to a phenoxy radical from the corresponding phenol is assumed to be more probable than reaction (25) and consequently k_{26} was given a higher value (1.0×10^6 M^{-1} s^{-1}). However, the chosen value is not significant because there is no net effect of the reaction.

(27) The simulation was very sensitive to variations in k_{27}. Using k_{27} as a fitting parameter we arrived at the value 7×10^5 M^{-1} s^{-1}.

(28), (29), (30), (31), (32), (33), (34) All the reactions (28) - (34) involve physical quenching of the excited sensitizer. The chosen value is high (see Section 4).

(35) One of the products, $C_{10}H_{14}O_2$ (ethyl(p-methoxyphenyl)carbinol), is of particular interest because reaction with a triplet carbonyl results in the formation of the ketyl radical $\cdot C_{10}H_{13}O_2$ which is of great importance in the reaction scheme. Therefore reaction (35) was introduced as the only further reaction of a product with the exception of the physical quenching reactions. The value of k_{35} is expected to lie between those of k_3 and k_{16} because of the carbinol group. Consequently, an intermediate value of $k_{35} = 1.0 \times 10^7$ M^{-1} s^{-1} was chosen. It is not known whether the hydrogen is abstracted from the OH of the benzyl alcohol or from the α CH, because the results of Wagner and Puchalski [43] indicate that both bonds may be active in the quenching process. They also suggest that a rapid hydrogen exchange occurs, resulting in the formation of the ketyl radical as the only species present in sufficient concentration to give coupling products. The abstraction from the OH has thus been omitted.

4. Results and discussion

4.1. Reactions of the sensitizer

The rate of consumption of the sensitizer was simulated using the reaction set shown in Fig. 1 and Table 1. The experimental rate of consumption of p-methoxypropiophenone is shown in Fig. 3 together with the results of the simulation. The agreement between the experimental and the calculated results is good. The key reactions are reactions (1) - (3) in Table 1. The rate constant k_1 was adjusted to obtain agreement between
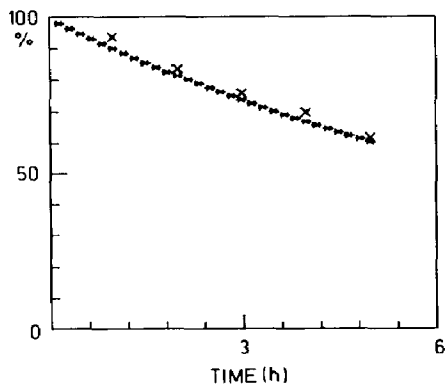
Fig. 3. Experimental (×) and calculated (✳) reaction rates of the photochemical reaction of p-methoxypropiophenone in oxygen-free dimethoxyethane.

the experimental and the calculated initial reaction rates. It should be emphasized that this parameter is valid only for our experimental set-up. The rate constants k_2 and k_3 are based on literature values. The computed response regarding variations in k_4 was low. Variation between the limits 10^{-3} and 10^5 gave negligible changes in the computed rate of disappearance. The rate constants k_7, k_8 and k_9 for the coupling reactions are all given the same value which should be of the correct order of magnitude. Additional experimental work is needed to determine the rate constants for reactions of radicals formed from lignin model compounds in organic solvents before a distinction between the reactivity of the different radicals can be made. Reaction (11) represents a bimolecular reaction between two reaction products from the key reactions (1) and (3) and is therefore included in the reaction set. Little is known about the magnitude of k_{11}. This reaction channel becomes effective with a rate constant value near 10^5 M^{-1} s^{-1}. This value is likely to be too high for the present reaction. Because the internal standard, p-cymene, may participate in the reaction, the elementary reactions (13) and (14) were included in the reaction set. The rate constants are evaluated from literature values. With these reactions included, a better agreement between the experimental and the calculated rate of disappearance could be obtained for longer reaction times. The consumption of p-cymene obtained from the simulation amounted to only a few per cent after 5 h, which is well under the error limit for the experimental work. This does not influence the ability of p-cymene to function as an internal standard of GLC under the present conditions, even if it apparently participates to a small degree in the reaction. Reaction (15) is analogous to reaction (11) and is therefore included in the reaction set (k_{15} should be compared with k_{11} (Table 1)).

4.2. Reactions of tert-butylguaiacylcarbinol and the sensitizer

The rates of consumption of $tert$-butylguaiacylcarbinol and the sensitizer were simulated with the reaction set shown in Fig. 2 and Table 2. The experimental rates of consumption of $tert$-butylguaiacylcarbinol and the
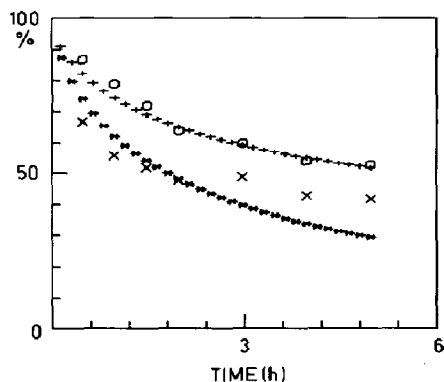
Fig. 4. Experimental and calculated reaction rates of the photochemical reaction of *tert*-butylguaiacylcarbinol (O, experimental; +, calculated) sensitized by *p*-methoxypropiophenone (×, experimental; ✳, calculated) in oxygen-free dimethoxyethane.

sensitizer are shown in Fig. 4 together with the results of the simulation. The key reactions (1) - (3) are the same as in the presence of the sensitizer alone. Reaction (16), which produces phenoxy radicals and ketyl radicals, is a further key reaction. With the present reaction set reactions (12), (16), (25) and (27) were of crucial importance and the results of the simulation were quite sensitive to variations in these rate constants. It was also observed that these reactions were coupled in a way that allowed a small increase in one of the rate constants if a change in another of the rate constants was performed simultaneously, without any significant change in the result of the simulation. The dependence was not straightforward but indicated that the present reaction set is not exclusive and that another set of rate constants may be found giving comparable results at least within some limits of the chosen rate constants. Nevertheless, we feel that these limits are not very large and that the present simulation reflects the very essence of the reaction mechanism, at least for reaction times of less than 3 h. The elementary reactions for the sensitizer are the same as in the previous case except for reactions (13) and (14) which refer to the reactions of the internal standard *p*-cymene, which was replaced by dodecane. Dodecane which is a better internal standard than *p*-cymene was excluded from the reaction set because the rate constant for hydrogen abstraction from dodecane is much lower [44]. Further, according to GLC no consumption of dodecane was detected during the irradiation. When the rate constant for the elementary reaction (16), a key reaction, was varied, drastic effects on the result of the simulation were observed resulting in a distorted balance in the consumption of the sensitizer and the phenol. The system containing oxygen behaves differently [7, 45]. In this case the triplet carbonyl compound acts as a true sensitizer because its concentration remains constant throughout the reaction. This could also be taken as proof of non-involvement of the solvent with the excited carbonyl.

The rate constants for physical quenching of the triplet carbonyl by the phenol and the sensitizer are different. The higher value of the rate

constant for the phenol may be interpreted in terms of intermolecular and intramolecular hydrogen bonding. Reactions (28) - (34) involve the physical quenching of the triplet carbonyl and such types of reaction become more significant with prolonged reaction times, when the pool of ultimate or relatively stable products is built up. The physical quenching is thought to be efficient but the value, 4×10^9 M^{-1} s^{-1}, used near the diffusion limit is considered to be too high, but chosen to give the best fit. Nevertheless, exact agreement with the experiment could not be accomplished for the sensitizer, a fact which indicates that the reaction process becomes much more complicated with prolonged irradiations when products and intermediates may participate both in the photochemical event and in further reactions. The high values for k_{28} - k_{34} thus compensate for some of the reactions not included in the reaction set, $i.e.$ reactions which consume the carbonyl triplet and restore the concentration of the sensitizer.

The agreement between the experimental and the calculated results for the phenol is good for up to 5 h. For the sensitizer an increasing deviation between the experimental and the calculated curves is observed after 2 h. Despite considerable efforts the agreement could not be improved with the present reaction set. The reason for the discrepancy may be twofold. Firstly, the reaction scheme may be too restricted. The dimer reaction products were not re-entered in the reaction scheme, a fact which particularly might affect the calculated results for longer reaction times. Some of the reactions, thought to be elementary reactions (Table 2), may be too simplified, implying that they may contain several elementary steps. Secondly, at least part of the discrepancy may be due to the light absorption of the reaction products. This may influence the parameter k_1, introducing a time dependence in the excitation of the sensitizer not accounted for in the present simulation.

5. Conclusions

The present investigation may be regarded as an initial attempt towards the clarification of the mechanism of the photochemical reactions of phenolic lignin model compounds sensitized by aromatic α carbonyl groups. The reaction sets formulated in the present work may not be exclusive for the two reaction systems. However, it is evident from the results that the mechanisms proposed reflect the main features of the reactions. Several items require further studies.

Some of the rate constants given are order-of-magnitude estimates. To increase the reliability of the simulation these unknown constants should be determined. Solvent dependence of the rate constants should also be investigated.

It is evident that the reaction set is too restricted to simulate the reaction for longer reaction times, $i.e.$ the reactions of the dimer products should be included.

98

Isolation and identification of intermediates and reaction products may provide a further clue to the mechanism.

The elementary reactions should be critically examined.

It is desirable to introduce a time dependence for the parameter k_1.

References

1 G. J. Leary, *Tappi, 51* (1968) 257.
2 S. Y. Lin and K. P. Kringstad, *Tappi, 53* (1970) 658.
3 K. P. Kringstad and S. Y. Lin, *Tappi, 53* (1970) 2296.
4 S. Y. Lin and K. P. Kringstad, *Nor. Skogind., 25* (1971) 252.
5 G. Brunow and B. Eriksson, *Acta Chem. Scand., 25* (1971) 2779.
6 J. Gierer and S. Y. Lin, *Sven. Papperstidn., 75* (1972) 233.
7 G. Brunow and M. Sivonen, *Pap. Puu, 57* (1975) 215.
8 G. Gellerstedt and E.-L. Pettersson, *Sven. Papperstidn., 80* (1977) 15.
9 G. Brunow, I. Forsskåhl, A. C. Grönlund, G. Lindström and K. Nyberg, in B. Rånby and J. F. Rabek (eds.), *Singlet Oxygen — Reactions with Organic Compounds and Polymers*, Wiley, London, 1978, pp. 311 - 315.
10 T. N. Kleinert, *Papier (Darmstadt), 24* (1970) 563.
11 H.-D. Becker, *J. Org. Chem., 32* (1967) 2115, 2124, 2131, 2136, 2140.
12 P. K. Das, M. V. Encinas and J. C. Scaiano, *J. Am. Chem. Soc., 103* (1981) 4154.
13 P. K. Das and S. N. Bhattacharyya, *J. Phys. Chem., 85* (1981) 1391.
14 M. L. M. Schilling, *J. Am. Chem. Soc., 103* (1981) 3077.
15 *Organikum, Organisch-Chemisches Grundpraktikum,* VEB Deutscher Verlag der Wissenschaften, Berlin, 1970, p. 354.
16 P. C. Roberti, R. F. York and W. S. MacGregor, *J. Am. Chem. Soc., 72* (1950) 5760.
17 R. N. Stabler and J. P. Chesick, *Int. J. Chem. Kinet., 10* (1978) 461.
18 L. A. Farrow and D. Edelson, *Int. J. Chem. Kinet., 6* (1974) 787.
19 D. Edelson, *J. Chem. Educ., 52* (1975) 642.
20 D. Edelson, R. J. Field and R. M. Noyes, *Int. J. Chem. Kinet., 7* (1975) 417.
21 D. L. Allara and D. Edelson, *Int. J. Chem. Kinet., 7* (1975) 479.
22 R. M. Noyes, *J. Phys. Chem., 81* (1977) 2315.
23 V. S. Engelman, *J. Phys. Chem., 81* (1977) 2320.
24 R. G. Pearson, *J. Phys. Chem., 81* (1977) 2323.
25 J. S. Chang, A. C. Hindmarsh and N. K. Madsen, in R. A. Willoughby (ed.), *Simulation of Chemical Kinetics in the Stratosphere*, Plenum, New York, 1974.
26 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin–Cummings, Menlo Park, CA, 1978.
27 S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973.
28 M. V. Encinas and J. C. Scaiano, *J. Am. Chem. Soc., 103* (1981) 6393.
29 A. J. G. Barwise, A. A. Gorman, R. L. Leyland, P. G. Smith and M. A. J. Rodgers, *J. Am. Chem. Soc., 100* (1978) 1814.
30 T. Wilson and A. M. Halpern, *J. Am. Chem. Soc., 102* (1980) 7272.
31 D. R. Arnold, *Adv. Photochem., 6* (1968) 301.
32 K. Bobrowski and P. K. Das, *Chem. Phys. Lett., 80* (1981) 371.
33 D.-J. Lougnot and P. Jacques and J.-P. Fouassier, *J. Photochem., 19* (1982) 59.
34 J. C. Scaiano and J. C. Selwyn, *Can. J. Chem., 59* (1981) 2368.
35 O. L. Chapman and G. Wampler, *J. Am. Chem. Soc., 91* (1969) 5390.
36 D. J. Schuster and P. B. Karp, *J. Photochem., 12* (1980) 333.
37 S. G. Cohen, D. A. Laufer and W. V. Sherman, *J. Am. Chem. Soc., 86* (1964) 3060.
38 J. C. Scaiano, *J. Phys. Chem., 85* (1981) 2851.
39 C. Walling and M. J. Gibian, *J. Am. Chem. Soc., 87* (1965) 3361.

40 A. Padwa, *Tetrahedron Lett.*, (1964) 3465.
41 A. F. Olea, M. V. Encinas and E. A. Lissi, *Macromolecules, 15* (1982) 1111.
42 P. J. Wagner and A. E. Puchalski, *J. Am. Chem. Soc., 102* (1980) 6177.
43 P. J. Wagner and A. E. Puchalski, *J. Am. Chem. Soc., 102* (1980) 7138.
44 L. Giering, M. Berger and C. Steel, *J. Am. Chem. Soc., 96* (1974) 953.
45 I. Forsskåhl, *Proc. Conf. on Singlet Molecular Oxygen, Clearwater Beach, FL, January 4 - 7, 1984,* in *J. Photochem., 25* (1984) 197.