SINGLET OXYGEN AND FREE-RADICAL OXIDATION OF POLYDIENES AND RELATED PROBLEMS WITH STABILIZATION: SYNERGISTIC AND ANTAGONISTIC EFFECTS[†]

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Summary

Polyisoprene is easily photo-oxidized both by a free-radical mechanism and by singlet oxygen ($^1O_2$). To stabilize this polymer towards both types of reactions different types of antioxidants, such as hindered phenols and hindered piperidines, are added. When both types of antioxidants are used together both antagonistic and synergistic effects can be observed. The mechanism of these reactions depends on the structure of the two antioxidants.

In this work we have studied the effect of a mixture of 2,6-di-*tert*-butylphenol and 2,2,6,6-tetramethylpiperidine on the photo-oxidation of rubrene which is a well-known $^1O_2$ quencher. Another aspect of this paper is to discuss the problem of the formation of $^1O_2$ in a polymer matrix. Small amounts of internal and external impurities, *e.g.* carbonyl groups, can be responsible for the generation of $^1O_2$ by an energy transfer mechanism in the polymer matrix. Benzophenone was used here to study the possibility of generating $^1O_2$ by triplet excited ketone groups. It was found that benzophenone in polyisoprene solution and in polymer film may also generate $^1O_2$ independent of the formation of ketyl radicals which are responsible for the chain scission of polyisoprene. When a hindered phenol was used as antioxidant in the presence of benzophenone, 3,5-di-*tert*-butylfuchsone was formed, which is also an effective sensitizer for the chain scission of polyisoprene.

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1. Introduction

Reaction of singlet oxygen ($^1O_2$) with polybutadiene [1 - 13] and *cis*-polyisoprene [8 - 17] yields an allylic hydroperoxide with an olefinic double bond shifted in the polymer chain. The mechanism of this ene-type oxidation for polymers has been reviewed in detail [8, 18 - 20]. How $^1O_2$ can be generated in a polymer matrix remains an open question. It is generally accepted that small amounts of internal impurities (*e.g.* carbonyl groups) or external impurities (other catalysts, sensitizers, additives etc.) present in commercially produced polymers can be responsible for the generation of $^1O_2$ by an energy transfer mechanism. The resultant hydroperoxides formed are photodecomposed and/or thermally decomposed and a subsequent chain scission of the macromolecules occurs. In practice it is impossible to separate the $^1O_2$ oxidation of polymers from the free-radical oxidation. The two parallel reactions occur simultaneously. To prevent these reactions several antioxidants are added which react with free radicals and/or decompose hydroperoxide groups. Some of these antioxidants (*e.g.* phenols, hindered amines) are considered to be effective both for the deactivation of $^1O_2$ and for decreasing the rate of free-radical oxidation. A mixture of two or more antioxidants sometimes exhibits a synergistic effect. For example, a mixture of hindered and unhindered phenols is a much more efficient antioxidant than either a hindered or an unhindered phenol alone as is seen for a mixture of 2,6-di-*tert*-butyl-4-methylphenol and *p*-methoxyphenol [21]. The reason for this synergistic behaviour of the two phenols arises from the regeneration of *p*-methoxyphenol. Mixtures of different antioxidants such as hindered phenols and hindered piperidines exhibit synergistic or antagonistic effects depending on the structure of the components [22 - 25]. Both synergistic and antagonistic effects in the antioxidant activity are known to decrease the free-radical oxidation of polymers. It is not known whether such effects exist in the quenching of $^1O_2$ by a mixture of different $^1O_2$ quenchers.

2. Experimental details

The $^1O_2$ and free-radical oxidation of *cis*-polyisoprene (EGA Chemie) (1 wt.%) was carried out in benzene (analytically pure) in the presence of air. The kinetics of the chain scission were determined from viscosimetric measurements.

Benzophenone (Merck) was additionally purified by recrystallization from CH_2Cl_2 (analytically pure) under nitrogen. 2,6-di-*tert*-butylphenol (Fluka) was purified by recrystallization from methanol (analytically pure). 2,2,6,6-tetramethylpiperidine (Aldrich) was used without additional purification. 3,5-di-*tert*-butylfuchsone was synthesized according to the literature [26].

Rubrene (Aldrich) was used without additional purification. The photo-oxidation of rubrene was monitored by changes in the light absorption at 520 nm using a Perkin–Elmer 675 UV/VI spectrometer.

The samples were irradiated with one of the following light sources: (i) a UV low pressure lamp type HPK 125 W (Philips, The Netherlands) producing 254 nm irradiation; (ii) a tungsten lamp type R63 60 W (Osram, Germany) producing visible light which was passed through a transmittance filter (Melles–Griot, The Netherlands) to cut off all light below 500 nm.

3. Results and discussion

The mechanism of generation of $^1O_2$ in polymer matrices is based on the following considerations.

(i) The donor molecule D, *i.e.* a chromophore group permanently attached to the polymer chain (*e.g.* carbonyl groups, conjugated double bonds or external impurities such as traces of catalysts, photosensitizers etc.), absorbs light and is excited to singlet (^1D) and/or triplet (^3D) states:

$$D + h\nu \longrightarrow {}^1D$$

$$^1D \longrightarrow {}^3D$$
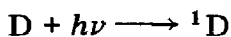
(ii) In the absence of O_2 (acceptor), donor molecules exhibit the normal luminescence properties, *i.e.* both fluorescence and phosphorescence.

(iii) In the presence of O_2 (acceptor), the phosphorescence is quenched, returning the donor to its ground state and producing $^1O_2$ via electronic energy transfer from the excited triplet state (^3D):

$$^3D + O_2 \longrightarrow D + {}^1O_2$$
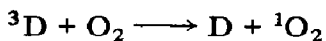
(iv) It is rather unexpected that $^1O_2$ can be formed by quenching the excited singlet state (^1D), because of its very short lifetime (about 10^{-6} - 10^{-9} s).

(v) Energy transfer processes in polymer matrices are always diffusion-controlled processes. The diffusion of O_2 in a polymer matrix is complicated by a zigzag path between the macromolecules. Collisions of an excited donor molecule (^1D and/or ^3D) with O_2 in a space densely populated with macromolecules occur only in sets because of "cage effects".

(vi) Energy transfer processes in polymer matrices also depend on the distribution and size of the chromophore groups and on the stiffness and mobility of the polymer chain [27]. The free volume available for a chemical reaction of $^1O_2$ with a polymer is also important. As the temperature is increased the amount of free volume increases. It can be seen that a polymer matrix provides a relatively continuous increase in the volume available for reactions to take place as the temperature is increased. $^1O_2$ reacts with macromolecules in the amorphous polymeric matrices but not in the crystalline domains.

Polyisoprene is oxidized by $^1O_2$ according to the ene-type mechanism during which an allylic hydroperoxide is formed with a double bond shifted in the polymer chain and/or to a side methyl group [8 - 17]:
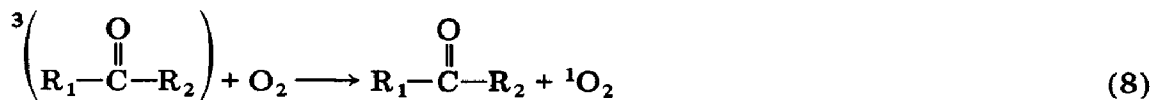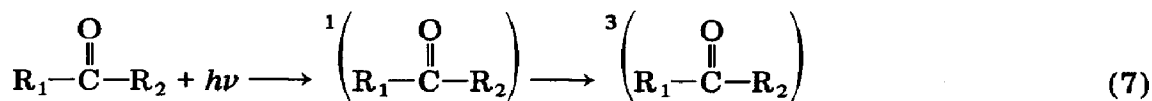
$$\ldots \xrightarrow{+ \, ^1O_2} \ldots \qquad (1)$$
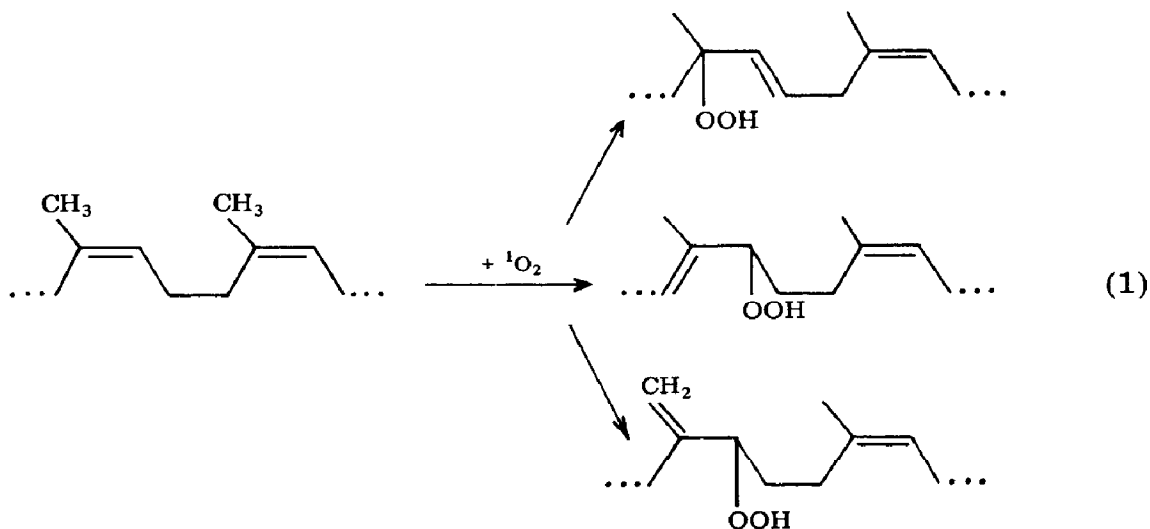
Rubrene is an orange hydrocarbon which reacts efficiently with $^1O_2$ to form a colourless photoperoxide. When a solution of rubrene is irradiated in the presence of O_2 and a $^1O_2$ quencher, the following reactions take place (Ru $\equiv$ rubrene; PIP $\equiv$ polyisoprene):

$$Ru + h\nu \longrightarrow {}^1Ru \longrightarrow {}^3Ru \qquad (2)$$

$$^3Ru + O_2 \longrightarrow Ru + {}^1O_2 \qquad (3)$$

$$Ru + {}^1O_2 \longrightarrow RuO_2 \qquad (4)$$

$$PIP + {}^1O_2 \longrightarrow PIP{-}OOH \qquad (5)$$

$$^1O_2 \longrightarrow O_2 \qquad (6)$$

Rubrene in the presence of polyisoprene in benzene solution or in a solid film of polyisoprene is much more slowly photo-oxidized than it is in pure benzene solution (Fig. 1). Some of the $^1O_2$ formed from the energy transfer reaction from photoexcited rubrene ^3Ru molecules to O_2 (reaction (3)) is further consumed by rubrene (reaction (4)) and polyisoprene (reaction (5)) molecules.

Commercial polymers always contain internal impurities in the form of carbonyl groups (chromophoric groups) [28]. Evidence has been found for the generation of $^1O_2$ from the quenching of excited states of dialkyl ketones by O_2 [29]:

$$\underset{\substack{\| \\ R_1{-}C{-}R_2}}{\overset{O}{}} + h\nu \longrightarrow {}^1\!\left(\underset{\substack{\| \\ R_1{-}C{-}R_2}}{\overset{O}{}} \right) \longrightarrow {}^3\!\left(\underset{\substack{\| \\ R_1{-}C{-}R_2}}{\overset{O}{}} \right) \qquad (7)$$

$$^3\!\left(\underset{\substack{\| \\ R_1{-}C{-}R_2}}{\overset{O}{}} \right) + O_2 \longrightarrow \underset{\substack{\| \\ R_1{-}C{-}R_2}}{\overset{O}{}} + {}^1O_2 \qquad (8)$$
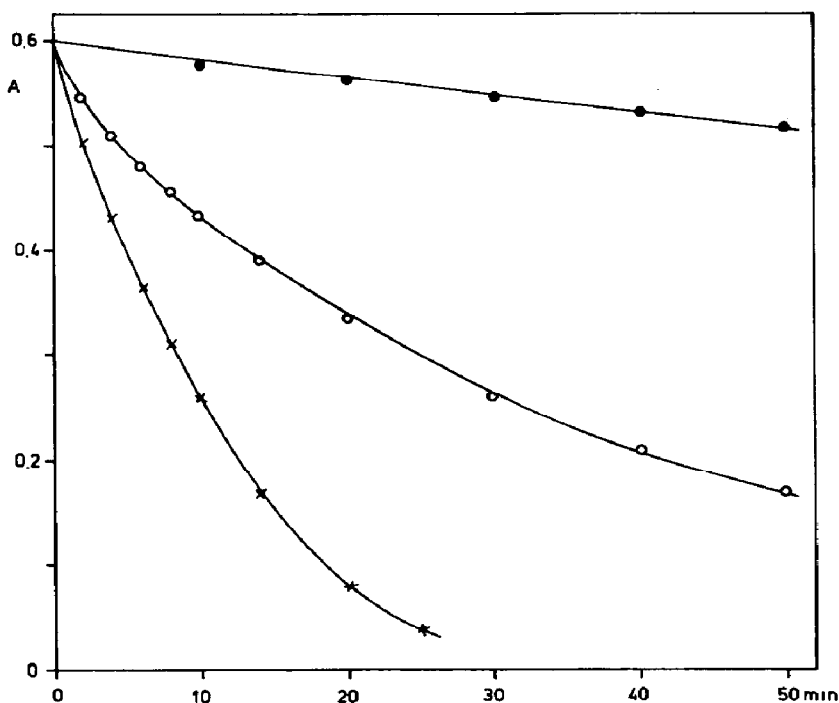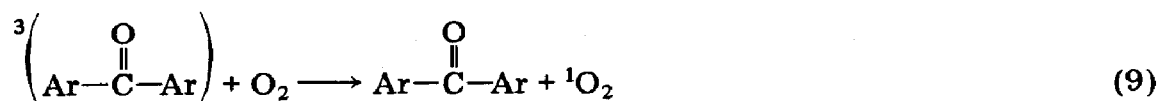
Fig. 1. Kinetics of rubrene (5×10^{-5} M) photo-oxidation (change in light absorption) vs. time of exposure to visible light ($\lambda > 500$ nm) in benzene solution ($\times$), 1wt.%polyisoprene–benzene solution (o) and solid polyisoprene film (●).

The quantum yields for generation of $^1O_2$ from 2-pentanone and 3-pentanone were 0.03 and 0.04 respectively, whereas for 2,4-dimethyl-3-pentanone the quantum yield was 0.0003 [29]. This result shows that, as long as there is no alkyl substitution at the carbon atom adjacent to the carbonyl group, the yield of $^1O_2$ is relatively independent of the chain length of the aliphatic ketone. The macrocarbonyl impurities found in polymers such as polyethylene generally belong to this class of non-substituted aliphatic ketones. Furthermore, although the yield of $^1O_2$ is small for this class of ketones (about 0.03), it is an observable and substantial quantity when the time of exposure of the polymer to the photo-oxidation reaction is taken into consideration [29].

Aryl ketones such as benzophenone have been reported to be donors from which energy would be transferred to O_2 resulting in the generation of $^1O_2$ [30]:

$$^3\left(\underset{Ar-C-Ar}{\overset{\overset{\textstyle O}{\|}}{}}\right) + O_2 \longrightarrow \underset{Ar-C-Ar}{\overset{\overset{\textstyle O}{\|}}{}} + {}^1O_2 \qquad (9)$$

Benzophenone has a strong absorption at 250 nm ($\epsilon = 18\,000$) and a weak absorption at 340 nm ($\epsilon = 120$) [31]. Excitation of the triplet state

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occurs during UV irradiation (254 nm). Under the same irradiation conditions rubrene is rapidly photo-oxidized (Figs. 2 and 3).

Benzophenone in its excited triplet state also exists as a biradical which can effectively abstract hydrogen from hydrogen donor molecules, *e.g.* alcohols, producing ketyl radicals [31 - 33]:
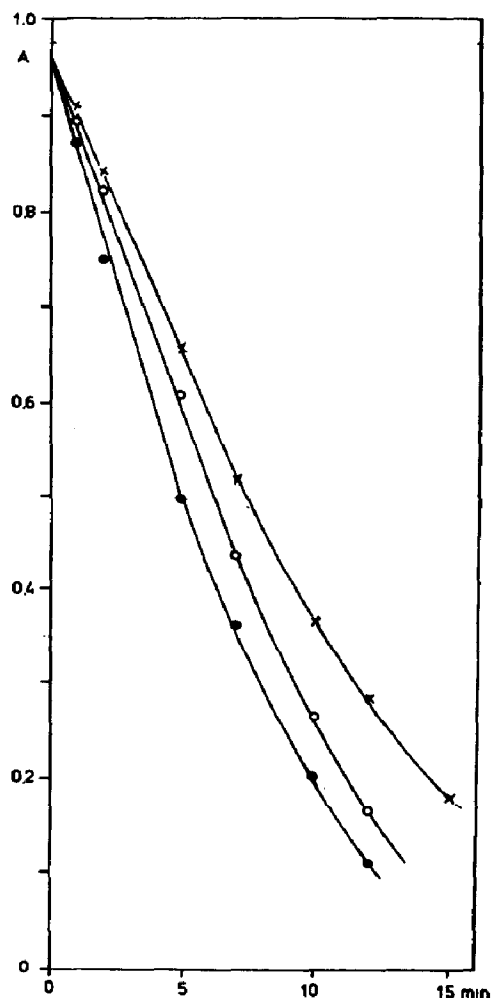
$$
{}^3\left(\underset{\dot{Ar}-\overset{\overset{\displaystyle\dot{O}}{|}}{\underset{\displaystyle}{C}}-Ar}{}\right) + \underset{R}{\overset{H}{>}}C\underset{R}{\overset{OH}{<}} \longrightarrow Ar-\overset{\overset{\displaystyle OH}{|}}{\underset{\displaystyle\dot{}}{C}}-Ar + \underset{R}{\overset{\displaystyle\dot{}}{C}}\underset{R}{\overset{OH}{<}} \tag{10}
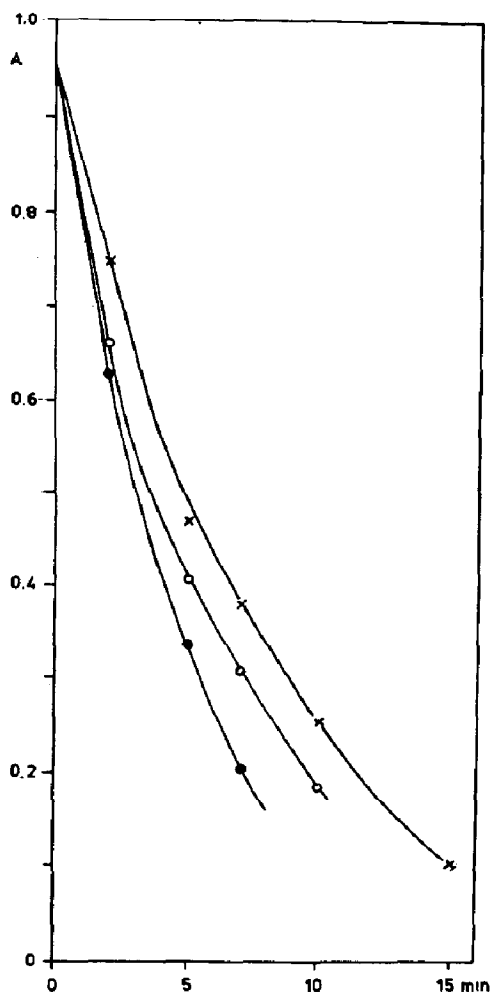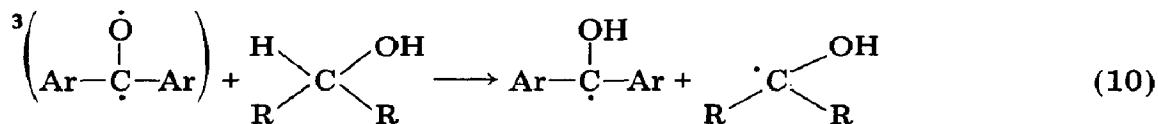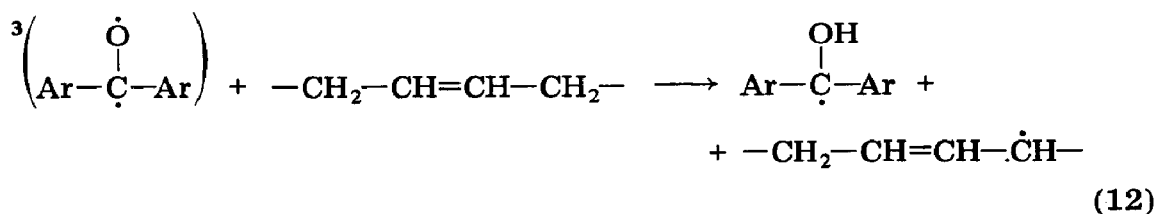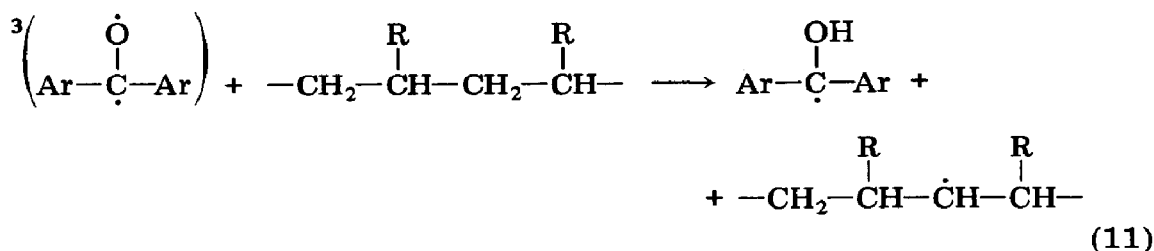$$

Fig. 2. Kinetics of rubrene (8×10^{-5} M) photo-oxidation *vs.* time of exposure to UV radiation ($\lambda = 254$ nm) in CH_2Cl_2 (X) and in CH_2Cl_2 with rubrene:benzophenone molar ratios of 1:1 (○) and 1:10 (●).

Fig. 3. Kinetics of rubrene (8×10^{-5} M) photo-oxidation *vs.* time of exposure to UV radiation ($\lambda = 254$ nm) in benzene (X) and in benzene with rubrene:benzophenone molar ratios of 1:1 (○) and 1:10 (●).

For this reason experiments were carried out in CH_2Cl_2 (Fig. 2) and in benzene (Fig. 3) to avoid reaction (10).

If benzophenone generates $^1O_2$ it should accelerate the oxidation of rubrene (reaction (4)). Rubrene is an effective $^1O_2$ quencher with a rate constant k_q for $^1O_2$ quenching of 7.3×10^7 l mol^{-1} s^{-1} [34 - 36]. Rubrene has also been widely employed in studies of rate constants for $^1O_2$ quenching by other compounds [37 - 39]. Our results show that addition of benzophenone to rubrene solution in a 1:1 molar ratio accelerates the oxidation of rubrene. When the concentration of benzophenone is increased to a benzophenone:rubrene molar ratio of 10:1 the quenching effect and self-absorption by benzophenone play evident roles (Figs. 2 and 3). These results show that benzophenone can be involved in the generation of $^1O_2$.

Benzophenone is a well-known photosensitizer for the oxidative degradation of several polymers such as polyolefins [40, 41], polydienes [42] and poly(vinyl chloride) [43]. The main reaction occurs via hydrogen abstraction by the benzophenone in its excited triplet state (biradical) from the methylene groups in the polymer molecules:

$$^3\left(\begin{array}{c} \overset{\displaystyle \overset{\bullet}{O}}{\underset{\displaystyle \underset{\bullet}{|}}{||}} \\ Ar-C-Ar \end{array}\right) + \quad -CH_2-\overset{\overset{\displaystyle R}{|}}{CH}-CH_2-\overset{\overset{\displaystyle R}{|}}{CH}- \quad \longrightarrow \quad Ar-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\bullet}{|}}{C}}-Ar \; +$$

$$+ \quad -CH_2-\overset{\overset{\displaystyle R}{|}}{CH}-\overset{\bullet}{CH}-\overset{\overset{\displaystyle R}{|}}{CH}- \tag{11}$$

$$^3\left(\begin{array}{c} \overset{\displaystyle \overset{\bullet}{O}}{\underset{\displaystyle \underset{\bullet}{|}}{||}} \\ Ar-C-Ar \end{array}\right) + \quad -CH_2-CH=CH-CH_2- \quad \longrightarrow \quad Ar-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\bullet}{|}}{C}}-Ar \; +$$

$$+ \quad -CH_2-CH=CH-\overset{\bullet}{CH}- \tag{12}$$

In solution a rapid chain scission is observed (Fig. 4) when polyisoprene is irradiated in the presence of benzophenone. Solid state cross-linking reactions of benzophenone occur instead of or as well as the chain scission. Because these reactions occur by a free-radical mechanism, the rate of reaction should decrease and the reaction should even be stopped by the addition of an antioxidant which is an effective free-radical scavenger, e.g. 2,6-di-tert-butylphenol. Experimental results show that the rate S of chain scission of polyisoprene in benzene:methanol (9:1) solution in the presence of benzophenone is influenced by the addition of 2,6-di-tert-butylphenol but the chain scission reaction cannot be stopped completely even when the 2,6-di-tert-butylphenol:benzophenone molar ratio is increased to 2:1 (Fig. 4). During this reaction a rapid yellowing of the solutions was observed (Fig. 5).
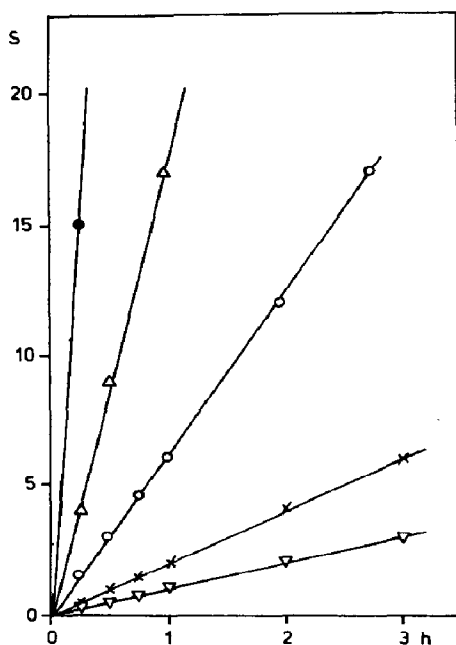
Fig. 4. Rate S of chain scission vs. time of exposure to UV radiation (λ = 254 nm) of polyisoprene (1 wt.%) in benzene:methanol (9:1) solution ($\times$) and in benzene–methanol with benzophenone (10^{-3} M) ($\bullet$), 3,5-di-tert-butylfuchsone (10^{-3} M) ($\triangle$), a mixture of benzophenone and 3,5-di-tert-butylfuchsone (both 10^{-3} M) ($\circ$) and with 2,6-di-tert-butylphenol ($\triangledown$).
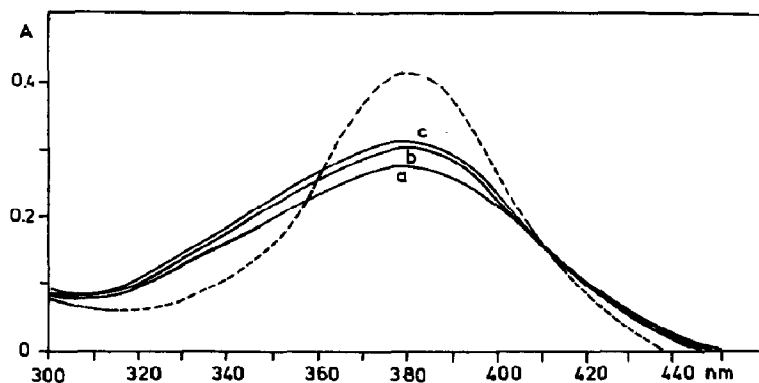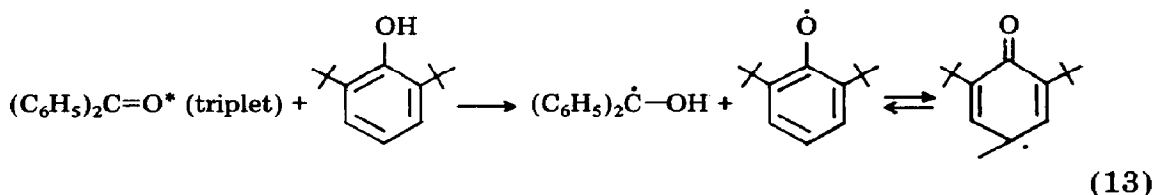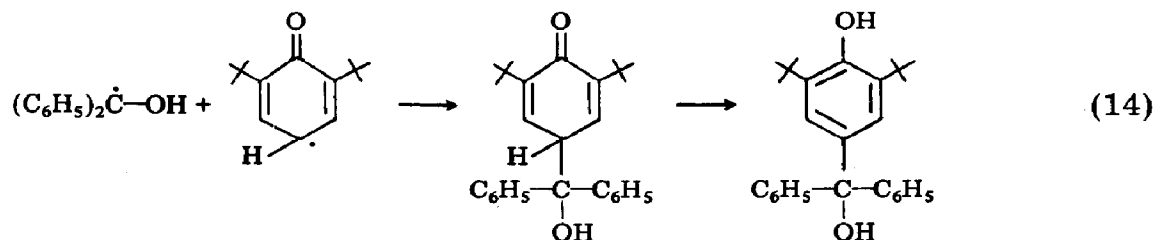

Fig. 5. Absorption spectrum of 3,5-di-tert-butylfuchsone (10^{-4} M) in benzene:methanol (9:1) solution (— — —) and changes in the absorption spectrum of polyisoprene (1 wt.%) with benzophenone (5×10^{-4} M) and 3,5-di-tert-butylphenol (5×10^{-4} M) during UV irradiation (λ = 254 nm) after 1 h (curve a), 2 h (curve b) and 3 h (curve c).

Chemical analysis indicated that 3,5-di-tert-butylfuchsone (which has a strong absorption at 380 nm) was produced. The triplet state of benzophenone reacts with 2,6-di-tert-butylphenol and abstracts hydrogen, leading to the formation of benzophenone ketyl radical and 2,6-di-tert-butylphenoxy radical [26]:
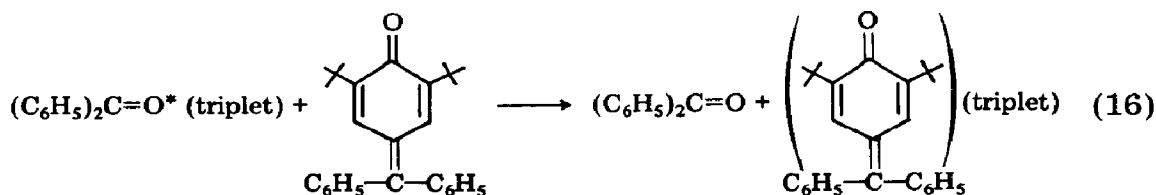
$(C_6H_5)_2C=O^*$ (triplet) + [2,6-di-tert-butylphenol] $\longrightarrow$ $(C_6H_5)_2\dot{C}-OH$ + [aryloxy radical] $\rightleftharpoons$ [cyclohexadienone radical]

$$(13)$$

This radical pair then undergoes a coupling reaction to give 4-diphenyl-carbinol-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one:

$(C_6H_5)_2\dot{C}-OH$ + [cyclohexadienone radical] $\longrightarrow$ [dienone with C_6H_5–C–C_6H_5 / OH] $\longrightarrow$ [phenol OH with C_6H_5–C–C_6H_5 / OH]
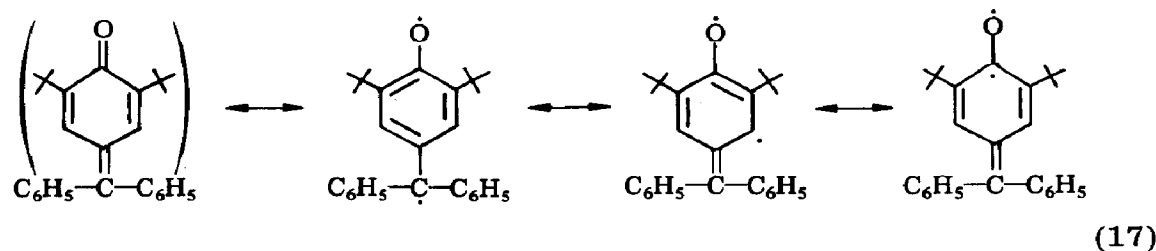
$$(14)$$

In the next step a water molecule is separated to give 3,5-di-*tert*-butylfuchsone which is a yellow compound with a maximum absorption at 380 nm (Fig. 5):
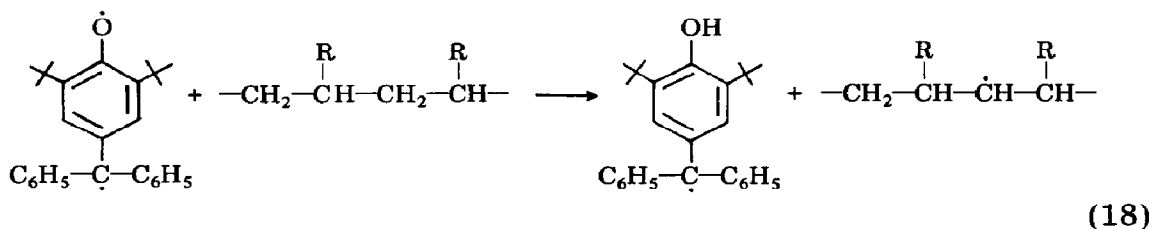
[phenol with C_6H_5–C–C_6H_5 / OH] $\longrightarrow$ [fuchsone with C_6H_5–C–C_6H_5] + H_2O

$$(15)$$
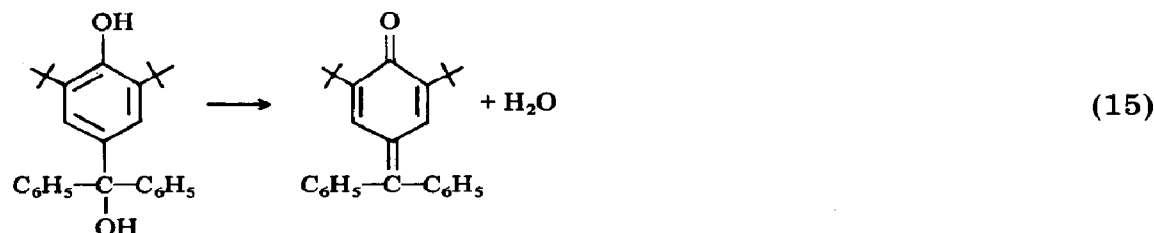
At higher concentrations of benzophenone a triplet–triplet energy transfer from benzophenone to 3,5-di-*tert*-butylfuchsone can be observed:

$(C_6H_5)_2C=O^*$ (triplet) + [fuchsone, C_6H_5–C–C_6H_5] $\longrightarrow$ $(C_6H_5)_2C=O$ + ([fuchsone, C_6H_5–C–C_6H_5]) (triplet)

$$(16)$$

The triplet state of 3,5-di-*tert*-butylfuchsone can exist as a biradical in the following resonance forms:

([fuchsone resonance form, C_6H_5–C–C_6H_5]) $\longleftrightarrow$ [resonance form, C_6H_5–$\dot{C}$–C_6H_5] $\longleftrightarrow$ [resonance form, C_6H_5–C–C_6H_5] $\longleftrightarrow$ [resonance form, C_6H_5–C–C_6H_5]

$$(17)$$

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The triplet state of 3,5-di-*tert*-butylfuchsone can also be responsible for the hydrogen abstraction from a methylene group in polymer molecules:
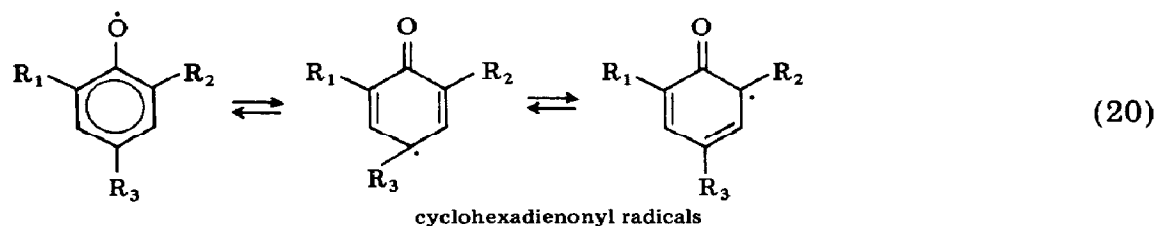
$$
\text{(structure)} + \text{—CH}_2\text{—}\overset{\text{R}}{\text{CH}}\text{—CH}_2\text{—}\overset{\text{R}}{\text{CH}}\text{—} \longrightarrow \text{(structure)} + \text{—CH}_2\text{—}\overset{\text{R}}{\text{CH}}\text{—}\overset{\cdot}{\text{CH}}\text{—}\overset{\text{R}}{\text{CH}}\text{—}
$$

(18)

In mixtures of benzophenone and 2,6-di-*tert*-butylphenol chain scission reactions can be caused by both benzophenone and 2,6-di-*tert*-butylphenol biradicals (Fig. 4).

Hindered phenols are capable both of reacting with polymer oxy and/or peroxy radicals (acting as antioxidants) and of reacting and/or quenching $^1O_2$ (acting as $^1O_2$ quenchers). The amount of antioxidant added to commercial polymers is 0.1 - 1.0 wt.% and sometimes even more. On the assumption that the presence of carbonyl group impurities in a given polymer is 1 per 1000 monomer units, the added antioxidant:carbonyl group molar ratio is 10 000:1.

The phenolic antioxidants may react with free radicals present in an oxidized polymeric system (chain breaking reaction) forming a non-radical substrate and a phenoxy radical by donating a hydrogen atom from the antioxidant to the free radical [36, 44 - 49] ($R_1 \equiv R_2 \equiv R_3 \equiv CH_3$ or $C(CH_3)_3$; POO·, peroxy radical; PO·, polymer oxy radical):

$$
\text{(structure)} + \text{POO· (PO·)} \longrightarrow \text{(structure)} + \text{POOH (POH)}
$$

(19)
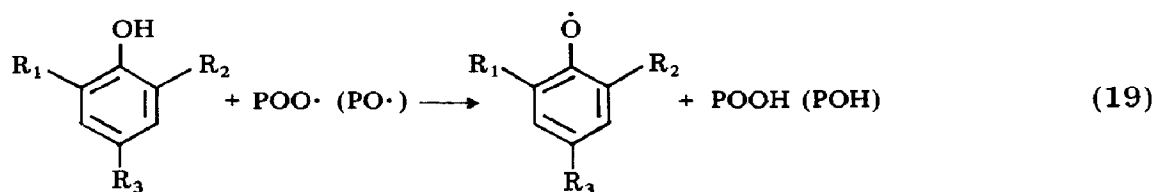
If the resulting phenoxy radical is stabilized or sterically hindered from reacting further, it will not act as an initiator of further reactions. It may, however, react with a second polymer oxy and/or peroxy radical in the system

$$
\text{(structure)} \rightleftharpoons \text{(structure)} \rightleftharpoons \text{(structure)}
$$

(20)

cyclohexadienonyl radicals

$$\text{(diagram)} + \text{POO} \cdot \text{(PO} \cdot \text{)} \longrightarrow \text{(diagram)} \quad (21)$$
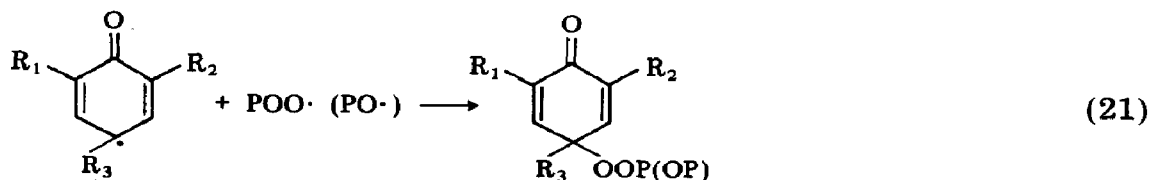
When the R_3 substituent is a hydrogen atom, a hindered quinone may also be formed:

$$\text{(diagram)} \longrightarrow \text{(diagram)} + \text{HOP} \quad (22)$$
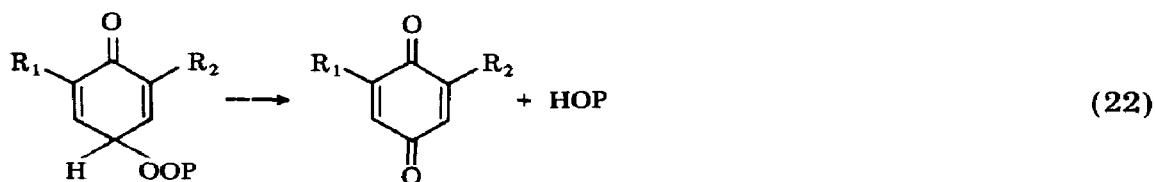
Hindered phenols are also capable of both reacting with and quenching $^1O_2$ depending on their substituents (R_1, R_2 and R_3 in *ortho* and *para* positions) and the reaction conditions [50 - 53]. On the basis of the rate effects and the detection of the phenoxy radicals the following mechanism for $^1O_2$ oxidation of hindered phenols has been proposed [51 - 56]:

$$\text{(reaction scheme 23)} \quad (23)$$
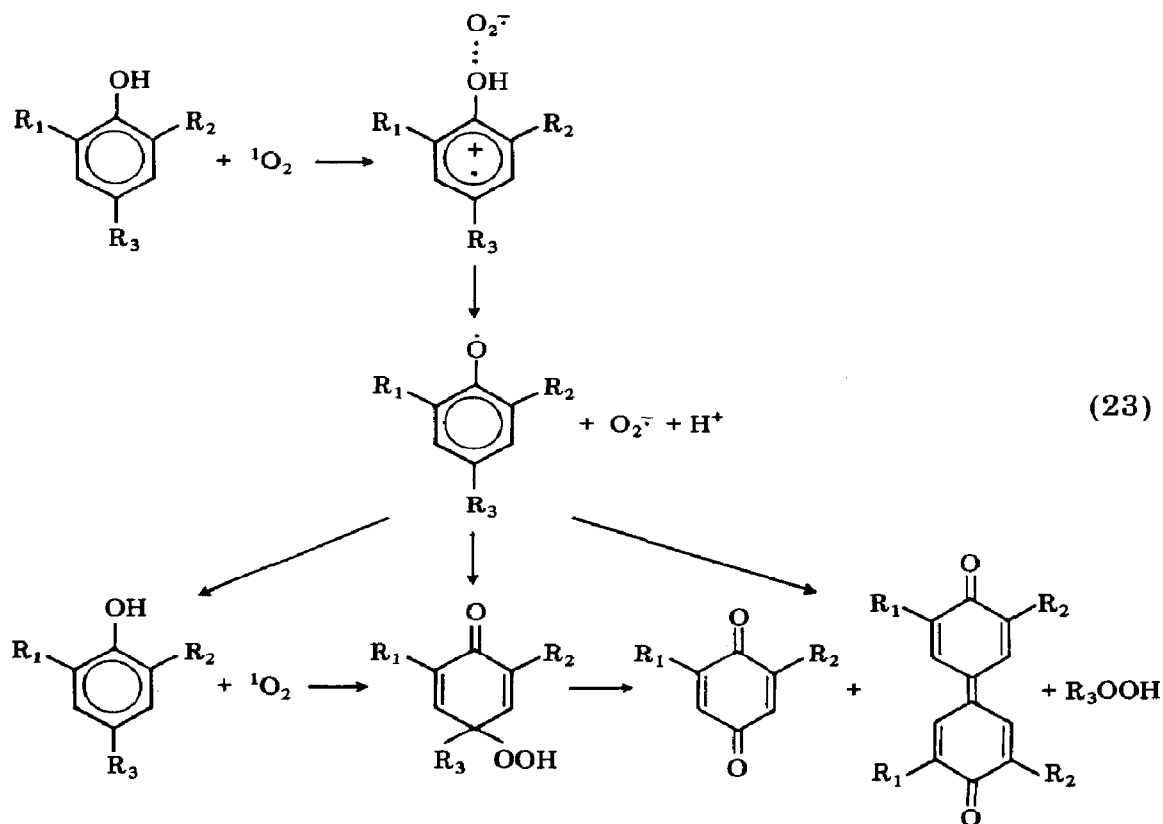
This mechanism considers some transfer of charge but not the formation of a complete electron transfer complex.

The quenching rate constant k_q has a value up to 7×10^8 l mol^{-1} s^{-1} for tocopherol in methanol [57]. It has also been found that the logarithm of the total quenching rate for $^1O_2$ is a linear function of the half-wave oxidation potential of the phenol [53]. The ratio of the quenching rate to the reaction rate (in benzene) varies from very large values with triphenylphenol to about 4 for 2,6-di-*tert*-butylphenol. The rate constant for quenching of 2,6-di-*tert*-butylphenol in methanol is 10^6 l mol^{-1} s^{-1}. This compound which is frequently used to inhibit free radicals also reacts with $^1O_2$. At concentrations below 0.01 M, its influence on the $^1O_2$ reaction is small in methanol, although it is larger for solvents in which $^1O_2$ has a longer lifetime. From our experiments with rubrene we have calculated k_q for 2,6-di-*tert*-butylphenol in CH$_2$Cl$_2$ to be 7.5×10^5 l mol^{-1} s^{-1}. Quenching measurements (Fig. 6) show that even at very high concentrations of 2,6-di-*tert*-butylphenol with 2,6-di-*tert*-butylphenol:rubrene molar ratios of 100:1, 1000:1 and 10 000:1 it is not possible to stop the $^1O_2$ oxidation of rubrene.

However, 2,6-di-*tert*-butylphenol can be used successfully as an anti-oxidant against the free-radical oxidation of polymers [22, 45]. Addition of 2,6-di-*tert*-butylphenol decreases the photo-oxidative chain scission rate of polyisoprene in benzene:methanol (9:1) solution (Fig. 4). The main disadvantage in practice is that most phenols are not very compatible with non-polar solid polymers and tend to form crystalline aggregates in the polymer matrix, leaving large volumes of unstabilized material. Since the centres for the antioxidant activity are, in general, polar groups (OH), there is a certain incompatibility between inert polymers and hindered phenols. In practice this effect can be overcome by incorporating hydrophobic groups into the phenol molecules.

The stabilizing efficiency of hindered phenols can be enhanced by coupling them with other compounds, *e.g.* with imidazolyl groups [58]. However, this procedure must be considered with caution, because in some cases, *e.g.* in coupling hindered phenols with a hindered piperidine, an antagonistic effect can be observed.

Hindered amines based on the substituted 2,2,6,6-tetramethylpiperidine are capable both of reacting directly with polymer alkyl (and/or allyl) radicals and indirectly with polymer oxy and/or peroxy radicals (acting as antioxidants) and of reacting and/or quenching $^1O_2$ (acting as $^1O_2$ quenchers). The mechanism of these reactions is much more complicated than those in hindered phenols [36, 59 - 65].

It has been postulated that the stabilizing effects of hindered piperidines depend on their ability to form stable nitroxyl radicals:
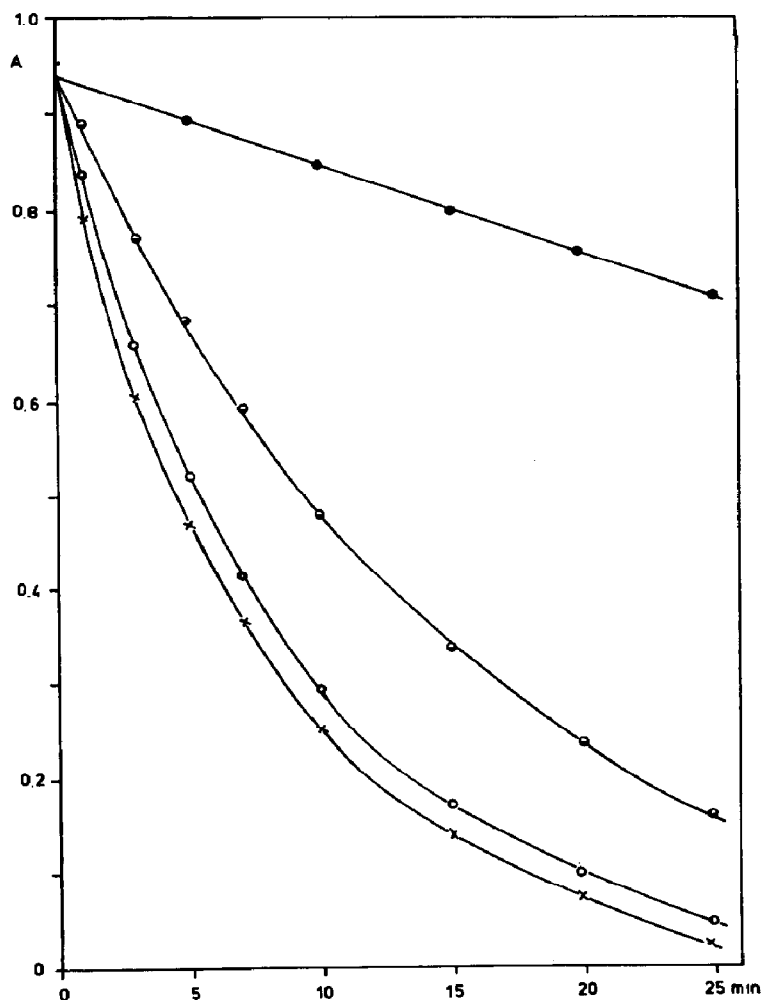

$$\text{(24)}$$

Fig. 6. Kinetics of rubrene $(8 \times 10^{-5}$ M) photo-oxidation *vs.* time of exposure to visible light $(\lambda > 500$ nm) in CH_2Cl_2 (×) and in CH_2Cl_2 with rubrene:3,5-di-*tert*-butylphenol molar ratios of 1:100 (o), 1:1000 (⊖) and 1:10 000 (●).

which may then react with polymer alkyl radicals P· formed during the free-radical oxidation of a polymer:


(25)

Nitroxyl radicals react with polymer alkyl and/or allyl radicals but do not react directly with polymer oxy and/or peroxy radicals. These last two radicals participate in the regeneration of the nitroxyl radicals according to

(26)
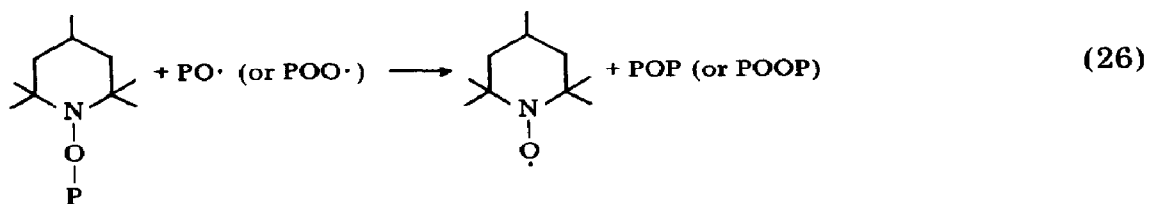
It was also suggested that hindered piperidines may decompose hydroperoxide groups formed in polymers during thermal oxidation and/or photo-oxidation, according to [64, 66 - 71]

(27)
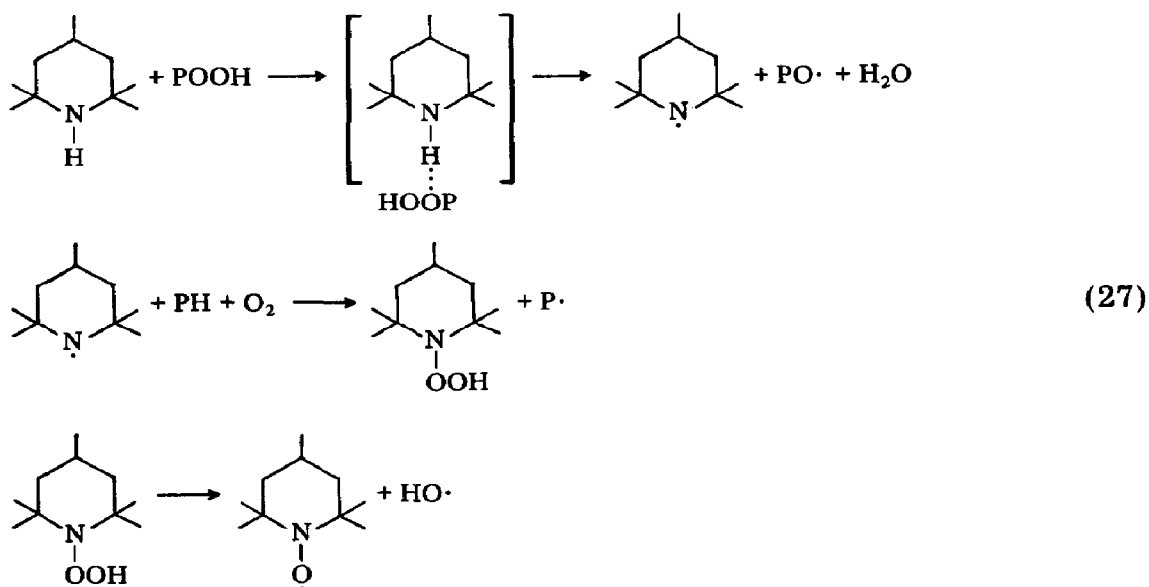
Hindered piperidines are also capable of reacting with $^1O_2$. During the reaction nitroxyl radicals are formed according to [38, 72 - 78]

(28)

charge transfer complex
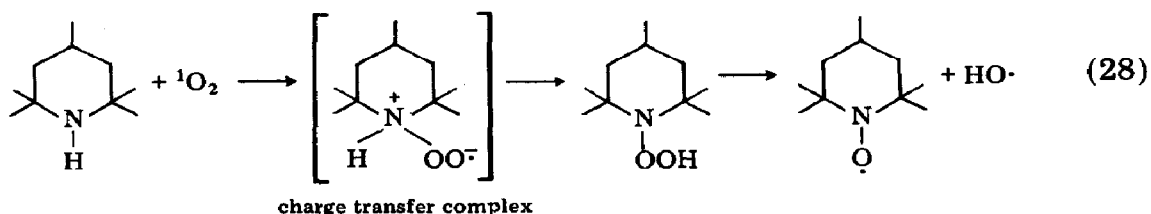
The quenching rate constants k_q determined for several hindered piperidines show that introduction of a methyl group instead of a hydrogen atom at the nitrogen atom enhances quenching [38]. From our experiments with rubrene we have determined k_q for 2,2,6,6-tetramethylpiperidine in CH_2Cl_2 to be 3.8×10^5 l mol^{-1} s^{-1}. Quenching measurements (Fig. 7) show that even at very high 2,2,6,6-tetramethylpiperidine concentrations with 2,2,6,6-tetra-
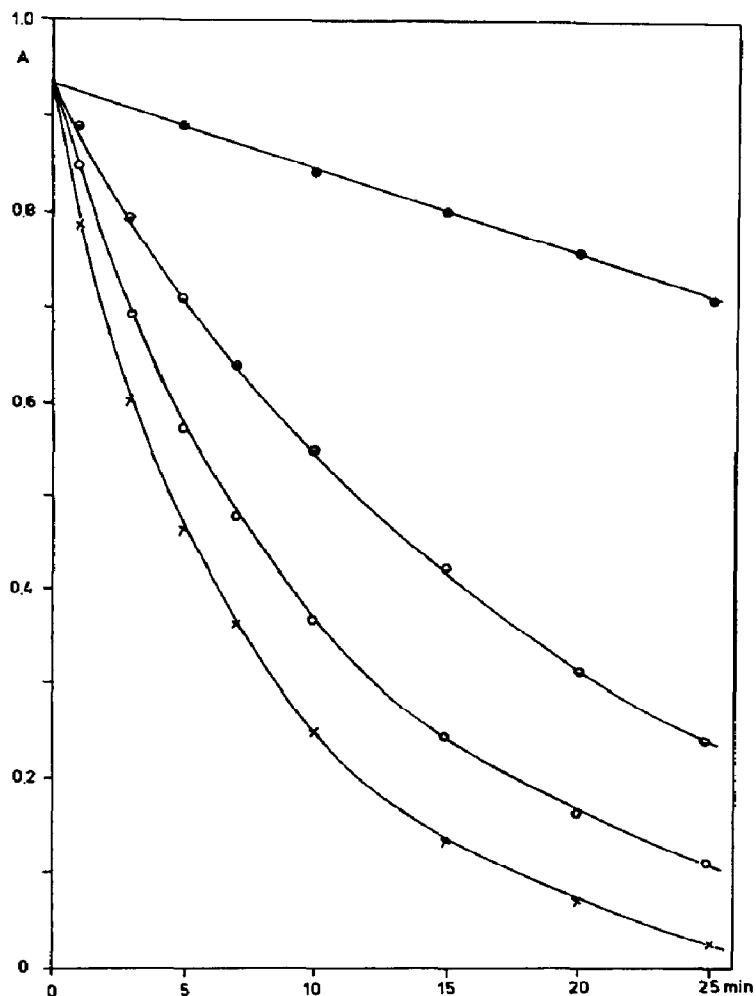
Fig. 7. Kinetics of rubrene $(8 \times 10^{-5}$ M) photo-oxidation $vs.$ time of exposure to visible light ($\lambda > 500$ nm) in CH_2Cl_2 (×) and in CH_2Cl_2 with rubrene:2,2,6,6-tetramethylpiperidine molar ratios of 1:100 (○), 1:1000 (◒) and 1:10 000 (●).

methylpiperidine:rubrene molar ratios of 100:1, 1000:1 and 10 000:1 it is not possible to stop the $^1O_2$ oxidation of rubrene.

For mixtures of hindered phenols and hindered piperidines an antagonistic effect was observed in the free-radical oxidation mechanism which can be explained as a reaction of nitroxyl radicals with hydroxyl groups in hindered phenols according to [23, 24, 79 - 81]

(29)
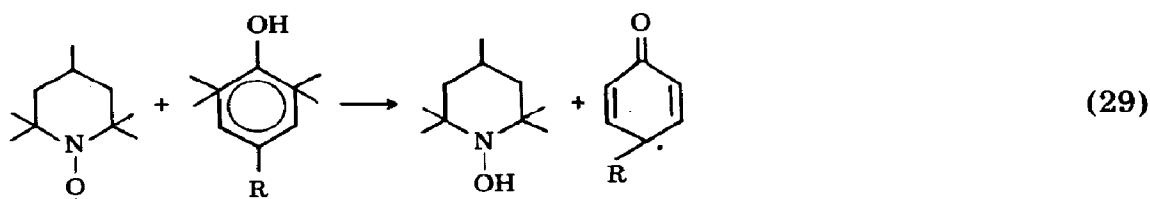
A mixture of 2,6-di-*tert*-butylphenol and 2,2,6,6-tetramethylpiperidine does not show any antagonistic or synergistic effect on quenching $^1O_2$ (Fig. 8). The observed quenching effects of piperidine and phenol are additive.

The results presented and discussed in this paper show how complicated are the reactions which are involved in the stabilization of polymers towards free-radical and $^1O_2$ oxidation. It is necessary to check carefully all additives such as photostabilizers, thermal stabilizers and antioxidants for their photo-chemical activity and to study the photoreactions which may occur between them. This research programme has been carried out in our institute during the last 5 years and research in this field will be continued.
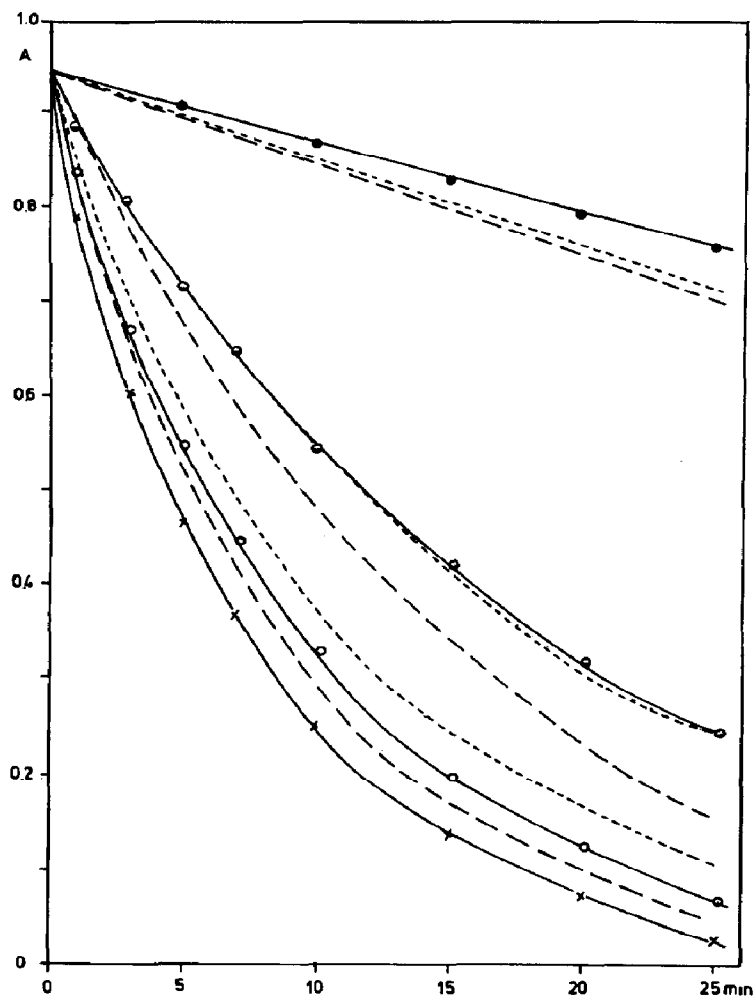

Fig. 8. Kinetics of rubrene $(8 \times 10^{-5}$ M) photo-oxidation *vs.* time of exposure to visible light $(\lambda > 500$ nm) in CH_2Cl_2 ($\times$) and in CH_2Cl_2 with rubrene:3,5-di-*tert*-butylphenol: 2,2,6,6-tetramethylpiperidine molar ratios of 1:50:50 ($\circ$), 1:500:500 ($\ominus$) and 1:5000:5000 ($\bullet$): — — —, - - - -, results from Figs. 6 and 7 respectively (used here for comparison to determine the synergistic or antagonistic effects between 3,5-di-*tert*-butylphenol and 2,2,6,6-tetramethylpiperidine).

Acknowledgment

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