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Reactions of antioxidants with molecular oxygen. Part III: Influence of phenolic stabiliser structures on their oxidation in an inert matrix

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ABSTRACT

The oxidation of five different phenolic antioxidants in inert substrates has been investigated varying the temperature and oxygen pressure conditions. The stabiliser consumption in this reaction has been quantified by steric exclusion chromatography. The tendency of the variation of the residual antioxidant concentration with exposure time in the presence of oxygen shows a simple apparent first order process in all cases. The kinetic parameters were determined applying this simple kinetic model. The influence of structural characteristics of stabilisers under study on kinetic parameters of the direct reaction with the oxygen has been analysed. On the other hand, the information obtained about reaction products generated for each antioxidant helped us to explain the results obtained.

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1. Introduction

Polymer stabilisation by hindered phenols (AH) has generated an abundant literature in the past half century [1–5]. It is well established that abstraction of the phenolic hydrogen by a peroxy radical is a key reaction:



Here, A^\bullet is a phenoxy radical unable to propagate the oxidation radical chain. Reaction (VII) competes with the propagation of polymer oxidation:



In a first approach, it can be assumed that, to be efficient, the event must have a rate r_7 of the same order of magnitude as propagation rate r_3 or higher. This condition can be described by:

$$\frac{r_7}{r_3} = \frac{k_7[\text{POO}^\bullet][\text{AH}]}{k_3[\text{POO}^\bullet][\text{PH}]} \geq 1$$

i.e.

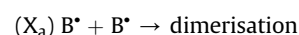
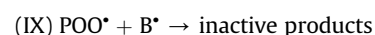
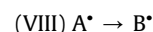
$$\frac{k_7}{k_3} \geq \frac{\text{PH}}{\text{AH}} \geq 1$$

For technical (limited solubility) as well as for economical reasons, stabilisers are used in concentrations generally lower than $10^{-2} \text{ mol l}^{-1}$. In common hydrocarbon polymers, the concentration of active hydrogen ($[\text{PH}]$) is generally higher than 10 mol l^{-1} , so that the condition for stabiliser efficiency would be, roughly:

$$\frac{k_7}{k_3} \geq 1000$$

This reasoning is, no doubt, an oversimplification as will be seen below, but it stresses the interest of a knowledge of the reactivity of these stabilisers in hydrogen abstraction reactions.

These reactions are not very easy to study in oxidizable substrates because they coexist with other reactions, especially those involving a cyclohexadienonyl radical B^\bullet resulting from isomerization of the phenoxy radical:



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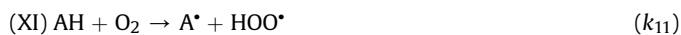
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Table 1

Code, chemical name, commercial name, molar mass and concentration used in kinetic investigation.

Code	Chemical name	Commercial name	M _w (g mol ⁻¹)	Concentration (mol l ⁻¹) × 10 ³
AO1	2,2'-Thiobis (6-tert-butyl-p-cresol)	Irganox 1081	358.5	4.75
AO2	5-Tert-butyl-4-hydroxy-2-methylphenyl sulphide	Irganox 415	358.5	8.43
AO3	4,4'-Butylidenebis (6-tert-butyl-m-cresol)		382.6	5.63
AO4	Isooctyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Irganox 1135	390.6	17.4
AO5	2,2'-Methylene-bis (4-methyl-6-tert-butylphenol)	Irganox 2246	340.5	5.99

In certain circumstances, with certain phenols [6] and probably with all phenols at high oxygen pressures [7], atmospheric oxygen is able to react by oxygen abstraction [8–10]:



In the ground state, the O₂ molecule is a biradical considerably less reactive than an alkyl peroxy radical, but presumably obeying similar structure–reactivity relationships. A kinetic study is easier for the oxygen-stabiliser reaction than for the peroxy-stabiliser reaction provided that it is studied in a non-oxidizable solvent. As a matter of fact, the oxygen concentration can be precisely known whereas the concentration of peroxy radicals in an oxidizable substrate is difficult to determine except in rare cases where it can be determined by ESR. Furthermore, in oxidizable substrates, there are other reactive species eventually able to react with stabiliser molecules, for instance alkyl radicals or hydroperoxides. These latter

species can play an important role in the case of thiobisphenols [11–14]. In the case of oxygen-stabiliser reactions in inert solvents, no sulphur–oxygen reactions are expected at moderate temperatures (≤120 °C), which is perhaps not the case at 200 °C [1,15].

It seemed to us interesting to compare the reactivities towards oxygen of five commercial phenolic stabilisers among which were two isomeric thiobisphenols, two bisphenols having a hydrocarbon bridge and one common monofunctional phenol.

2. Equipment and experimental procedure

2.1. Materials

The stabilisers under study are listed in Table 1. AO1, AO2 and AO3 were supplied by Sigma Aldrich. AO4 and AO5 were supplied by Ciba SC. The antioxidant structures are shown in Fig. 1.

The chosen inert solvents were a polydimethylsiloxane oil (silicone) having a viscosity of 50 mPa s at 25 °C (DC 200 from Sigma Aldrich) and 1,2,4-trichlorobenzene (TCB from Sigma Aldrich), having a density of 1.454 g ml⁻¹ at 25 °C. The solubility coefficient of oxygen S_{O₂} in silicone at 90 °C was 4.92 × 10⁻⁸ mol l⁻¹ Pa⁻¹ [16]. S_{O₂} was not known in the case of TCB. As Richaud [17] it will be considered that from the point of view of oxygen solubility, TCB is not very far from benzene, for which S_{O₂} = 1.06 × 10⁻⁸ mol l⁻¹ Pa⁻¹ at 90 °C. Comparison of results obtained in both solvents are thus to be cautiously interpreted, but results obtained in both solvents with AO5 will give us an interesting orientation.

2.2. Ageing conditions

AO1, AO4 and AO5 are soluble in silicone oil, which makes the analysis by the analytical techniques used easier [18,19]. However,

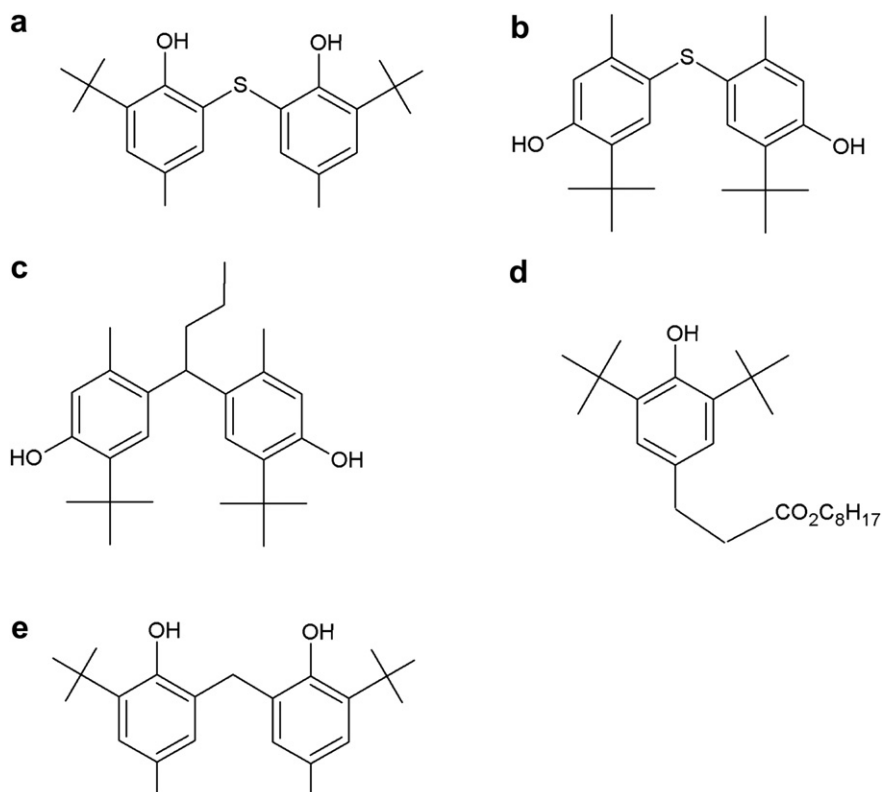


Fig. 1. Structure of stabilisers studied: (a) AO1, (b) AO2, (c) AO3, (d) AO4 and (e) AO5.

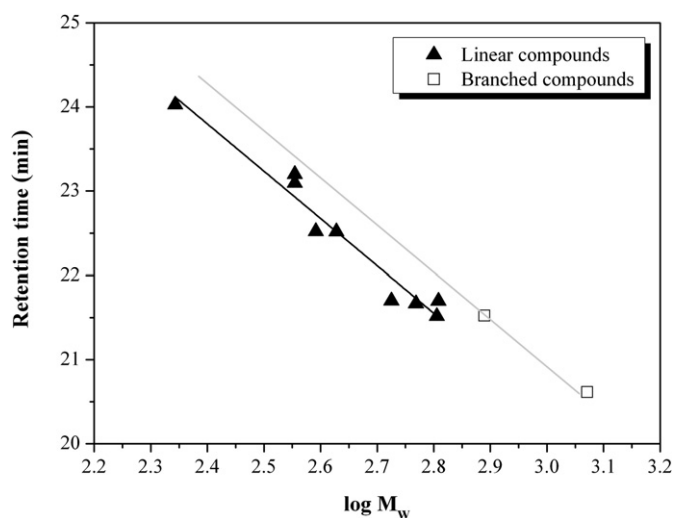


Fig. 2. Calibration curve for molar mass determination.

AO2 and AO3 antioxidants are insoluble in this substrate and, therefore, TCB was employed. The stabiliser concentrations used in ageing tests are given in Table 1. For AO1, AO4 and AO5, ageing experiments were performed at 80, 90, 100 and 110 °C under 3.0 MPa oxygen pressure. For all the stabilisers, experiments were performed at 90 °C and 3.0 MPa oxygen pressure. The effect of oxygen pressure was studied only at 120 °C for AO1, AO4 [19] and AO5 [18].

2.3. Analytical methods

Initial stabilisers and their reaction products were analysed by steric exclusion chromatography (SEC). SEC was performed using a WATERS 714 chromatograph equipped with a photodiode array detector (PDA). Two columns were placed in series, HR1 and HR4E (5 µm, 4.6 × 300 mm) and maintained at 40 °C. Tetrahydrofuran (THF) was used as mobile phase at a rate of 0.3 ml min⁻¹. Each antioxidant sample was dissolved in 2 ml of THF. In the SEC analysis of AO2 and AO3 antioxidants, where TCB was employed, the signal saturation caused by TCB from 25 min forced us to switch off SEC analysis. Therefore, it was impossible to observe the potential presence of compounds with lower molar masses than the residual stabiliser.

A calibration curve was built in order to determine the molar masses of reaction products. Various aromatic compounds (toluene

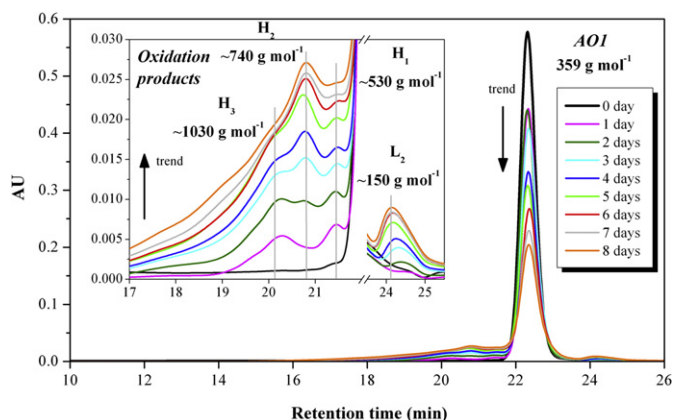


Fig. 3. SEC chromatograms of AO1 acquired at 293 nm at various exposure times at 90 °C under 3.0 MPa oxygen pressure.

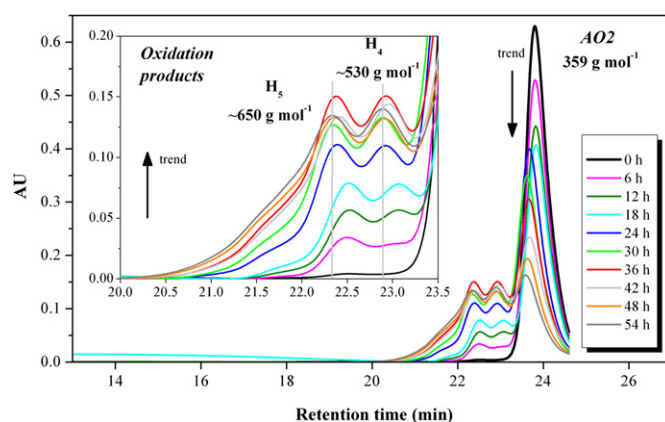


Fig. 4. SEC chromatograms of AO2 acquired at 283 nm at various exposure times at 90 °C under 3.0 MPa oxygen pressure.

and xylene), phenolic antioxidants (ionol, Irganox 1520, Irganox 1076, Irganox 245, Irganox 259, Irganox 1035, Irganox 1330 and Irganox 1010) and, indeed, the five antioxidants under study (AO1, AO2, AO3, AO4 and AO5) were used as standards. The calibration curve is shown in Fig. 2. A different behaviour can be observed for the linear and branched compounds. The slope of straight lines is the same, varying the ordinate. The approximation of calculated molar masses from calibration straight line of linear compounds was better for oxidation products of low molar mass, while a better approximation was obtained for oxidation products of high molar mass when the calibration straight line of branched compounds was applied. This method is not precise enough to determine the exact molar mass value, but it allows to clearly distinguish between monomeric starting compounds and reaction products resulting from their degradation or from their oligomerisation.

3. Results and discussion

Examples of changes of chromatograms acquired at the wavelength of the initial antioxidant peak are shown in Fig. 3 (AO1), Fig. 4 (AO2), Fig. 5 (AO3), Fig. 6 (AO4) and Fig. 7 (AO5).

In all the cases one observes the progressive disappearance of the initial antioxidant peak and the growth of various species whose molar mass has been estimated using the calibration curve. The only exception is observed in the case of AO4 (Fig. 6), where a by-product having almost the same molar mass as AO4 interferes with AO4 peak. HPLC was used to achieve the complete separation between the residual antioxidant and its by-products [19]. The

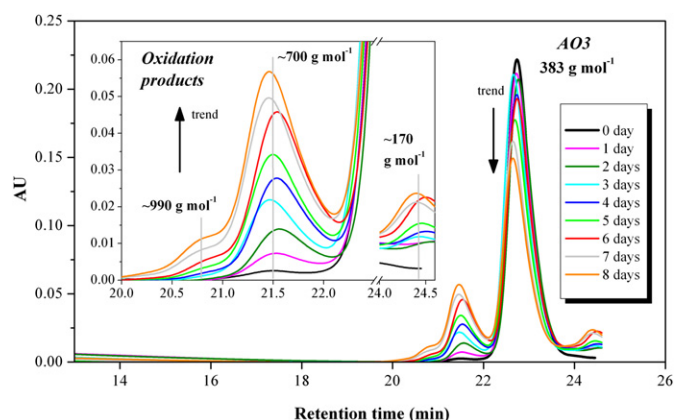


Fig. 5. SEC chromatograms of AO3 acquired at 281 nm at various exposure times at 90 °C under 3.0 MPa oxygen pressure.

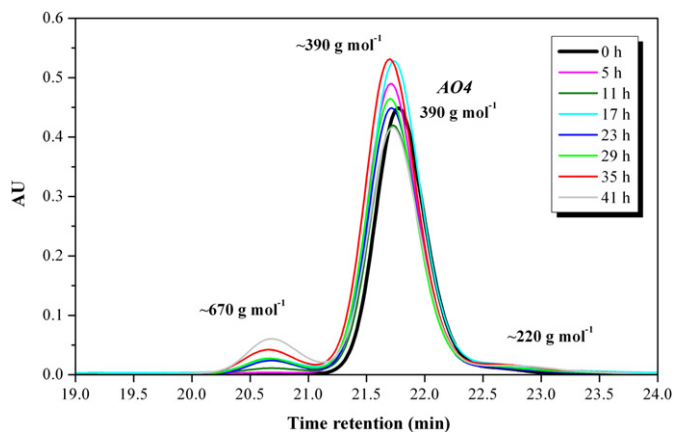


Fig. 6. SEC chromatograms of AO4 acquired at 276 nm at various exposure times at 90 °C under 3.0 MPa oxygen pressure.

molar mass data are summarized in Table 2. It was not possible to identify precisely the oxidation products owing to the scatter of calibration curve, but the uncertainty intervals are sharp enough to permit to determine the number of rings in the molecule.

For all the antioxidants under study, oxidation leads to coupling or oligomerisation products of molar mass higher than the initial stabiliser one. Pseudo dimeric species largely predominate in the case of thiobisphenol AO2 and monophenol AO4, whereas trimeric species or even larger molecules appear in the other bisphenolic antioxidants.

In many cases, reaction products of molar mass lower than the initial stabiliser one are formed. They can result from the breaking of the bisphenol bridge, for instance in the case of AO1 or from breaking of the aliphatic tail, for instance in the case of AO4. This later stabiliser has been the subject of a detailed study in the preceding part of this article [19]. It is partly transformed into cinnamate of which the molar mass (388.6 g mol^{-1}) differs only slightly from AO4 one (390.6 g mol^{-1}), but with its UV/VIS absorption band bathochromically shifted from 276 nm to 311 nm.

To clarify some eventual problems of peak overlapping in SEC chromatograms, we have recorded these latter with another detection wavelength, for instance at 418 nm for AO1 (Fig. 8) or at 398 nm for AO2 (Fig. 9). In the case of AO1, the chromatogram reveals the presence of a species of approximate molar mass $\sim 250 \text{ g mol}^{-1}$ (L_1) which is totally transparent at 293 nm wavelength. The high molar mass products (H_1 , H_2 , H_3 , etc) contain

Table 2

Summary of SEC results for the antioxidants under study.

Antioxidant	RT in SEC (min)	M_w (g mol^{-1})	M_w/M_w AO	Possible attribution
AO1	20.3	$\sim 1030-1080$	2.9–3.0	“Trimer” [13,21]
	20.8	$\sim 740-790$	2.1–2.2	“Dimer” [13,21]
	21.4	$\sim 530-560$	1.5–1.6	Triphenolic structures [22]
	22.3	358.5	1	AO1
	22.7	$\sim 250-330$	0.7–0.9	Sulphonic acid derivative [13]
AO2	24.1	$\sim 150-190$	0.4–0.5	6-tert-butyl-4-methyl-1,2-benzoquinone [13]
	22.0	$\sim 650-770$	1.8–2.1	“Dimer”
	22.5	$\sim 510-640$	1.4–1.7	Triphenolic structures [22]
	23.3	358.5	1	AO2
AO3	23.6	$\sim 330-420$	0.9–1.2	Sulphoxide, sulphone [13]
	20.8	$\sim 990-1090$	2.6–2.9	Oligomeric product
	21.5	$\sim 700-810$	1.8–2.1	Oligomeric product
	22.7	382.6	1	AO3
AO4	24.4	$\sim 170-240$	0.4–0.6	Chain-breaking product
	20.6	$\sim 670-820$	1.7–2.1	“Dimer” [19]
	21.7	~ 400	1.0	AO4, cinnamate [19]
	22.9	$\sim 220-320$	0.6–0.8	Benzoquinone, quinone methide [19]
AO5	23.5	$\sim 170-250$	0.4–0.6	Chain-breaking product [19]
	19.8	$\sim 1230-1310$	3.6–3.9	“Tetramer” [18]
	20.3	$\sim 950-1080$	2.8–3.2	“Trimer” [18]
	20.9	$\sim 670-820$	2.0–2.4	“Dimer” [18]
	22.5	340.5	1	AO5

apparently the chromophore of L_1 and the chromophore of the initial molecule since they are detected at 293 nm as well as at 418 nm. Compared to the presumed “dimer” (H_2) and “trimer” (H_3), the species having an approximate molar mass of $\sim 530 \text{ g mol}^{-1}$ (H_1) absorbs less at 293 nm and more at 418 nm. There is a wide consensus on the attribution of the absorption at $\sim 400 \text{ nm}$ to a quinone structure [20]. The fact that high molar mass species, i.e. mainly oligomers, contain both phenolic and quinone chromophores agrees with various literature proposals (Scheme 1) [13,21].

Such oligomeric species would be formed independently of the nature of the bisphenol bridge: sulphur (AO1) or methylene (AO5).

The only reasonable assignment for the species having an approximate molar mass of $\sim 530 \text{ g mol}^{-1}$ (H_1) seems to be a triaromatic compound resulting from first the rupture of the sulphur bridge in a thiobisphenol molecule (or one of its transformation products preserving the diaromatic character). Second the grafting of one monoaromatic compound resulting from this rupture to a thiobisphenol molecule (or to one of its transformation products

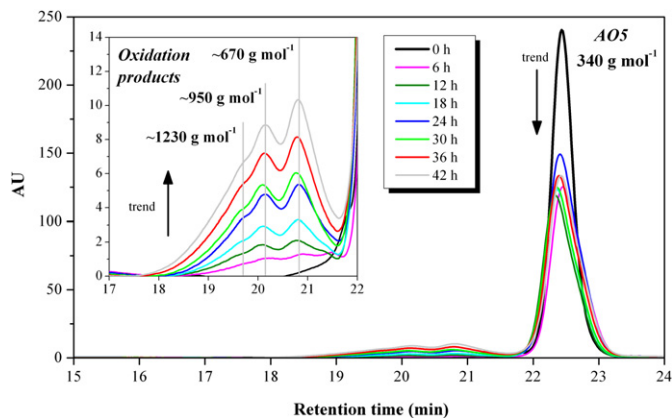


Fig. 7. SEC chromatograms of AO5 acquired at 280 nm at various exposure times at 90 °C under 3.0 MPa oxygen pressure.

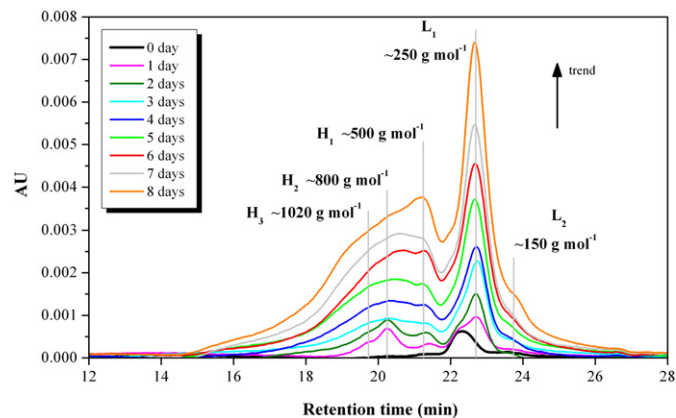


Fig. 8. SEC chromatograms of AO1 acquired at 418 nm at various exposure times at 90 °C under 3.0 MPa oxygen pressure.

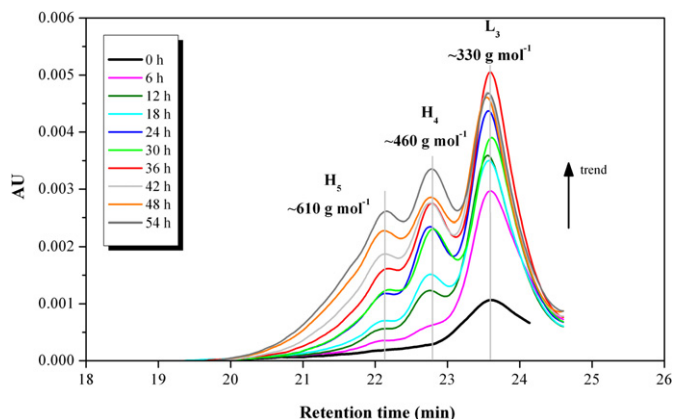


Fig. 9. SEC chromatograms of AO2 acquired at 398 nm at various exposure times at 90 °C under 3.0 MPa oxygen pressure.

in which the diaromatic character has been preserved). According to UV data, this species would be more conjugated than “dimer” and “trimer” ones.

Such species were previously found by Uhniat et al. [22] which proposed a triphenolic structure (Scheme 2).

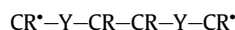
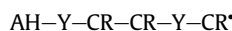
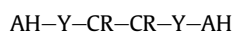
It is noteworthy that the formation of such molecules needs a complex set of splitting/recombination events. A comparison of AO1 chromatograms obtained at 293 nm (Fig. 3) and 418 nm (Fig. 8), clearly shows that the species of molar mass c.a. 530 g mol⁻¹ contain the quinone chromophore, that disagrees with the structures of Scheme 2. These latter seem to result exclusively from a process in which the primary event would be the scission of the sulphur-carbon bond although we are not able to imagine a recombination process preserving the phenolic character of the molecule. Here, it seems reasonable to suppose that the primary event is exclusively, in all cases, the abstraction of the phenolic hydrogen by oxygen. In thiobisphenols, the resulting radicals would presumably rearrange (among other secondary processes), by splitting of the sulphur-carbon bond and formation of reactive fragments able to recombine with the starting antioxidant or one of its quinone derivatives. The product of molar mass c.a. 250 g mol⁻¹ is presumably the mononuclear sulphonic acid derivative [13], that confirms the hypothesis of sulphur-carbon bond splitting.

In the case of AO2, the comparison of chromatograms acquired at 283 nm (Fig. 4) and 398 nm (Fig. 9) reveal the growth of a species having almost the same molar mass as the starting stabiliser, but almost transparent at its peak wavelength (283 nm). The distribution of high molar mass species differs significantly from AO1. The yield in molecules of high molar mass (>700 g mol⁻¹) is considerably lower for AO2 than for AO1. But the main difference concerns low molar mass fraction. The molar mass of the main

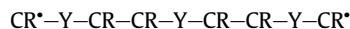
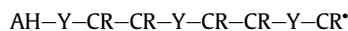
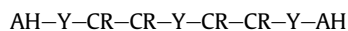
oxidation product is significantly higher for AO2 (~330 g mol⁻¹) than for AO1 (~250 g mol⁻¹) and the species of lowest molar mass eluted for AO1 (~150 g mol⁻¹) does not appear for AO2.

All the observations made are summarized in Table 2, in which “dimer”, “trimer”, etc mean molecules having about same molar mass as true dimers, trimers, etc. In fact this distinction can be justified as follows for bisphenols. There is a wide consensus in the literature to assume that the primary chemical act is always the abstraction of the phenolic hydrogen to give a phenoxy radical (AR*) which isomerises easily into cyclohexadienonyl radical CR* (Scheme 3).

The cyclohexadienonyl radical CR* can eventually evolve into another unspecified conjugated species but we will consider here, in the sake of simplicity, that the chemical evolution of a single phenolic group stops at CR* level. For a bisphenol having the bridge Y, we can thus imagine three main types of diaromatic species: unreacted (AH-Y-AH); monoreacted (AH-Y-CR*) and direacted (CR*-Y-CR*). Supposing that the unreacted bisphenol is not directly reactive in coupling and oligomerisation processes, one can imagine the following combination for “dimers”:

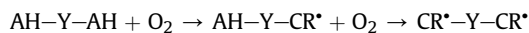


And for “trimers”:

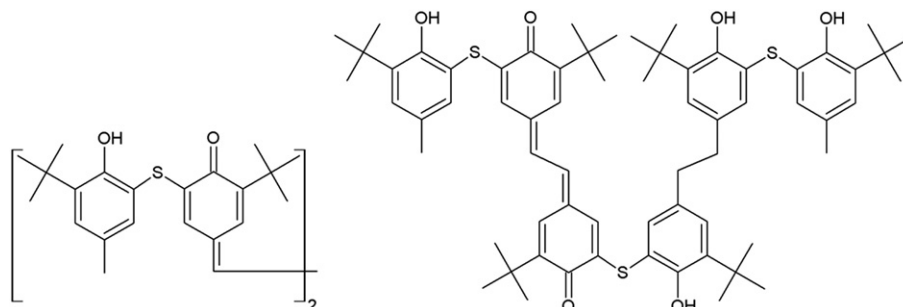


One can see that unreacted and reacted phenol moieties can coexist in “dimer” and “trimer” mixtures, that explains why these species absorb at both wavelengths characterizing respectively the initial stabiliser and its conjugated reaction product. These observations agree with previously found or hypothesized product structures. The main references for possible peak assignments are given in Table 2.

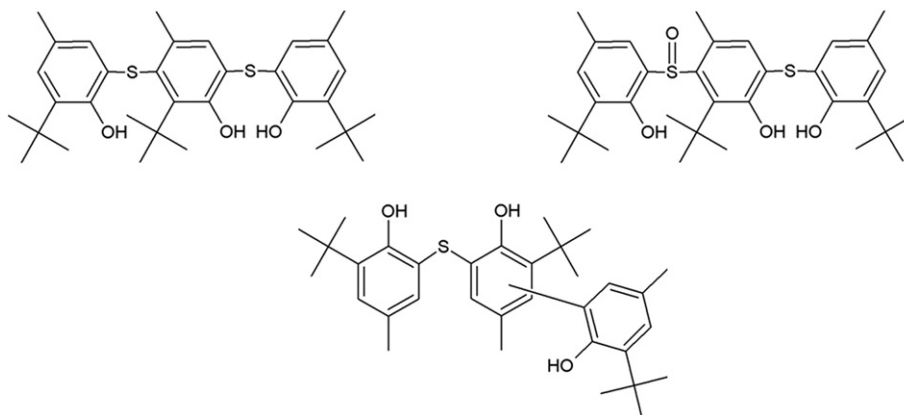
Let us now consider kinetic aspects. The rate of phenolic group consumption can be determined from the decrease of the stabiliser peak intensity assuming that at the beginning of exposure (at low conversion), the decrease of this peak is only due to the reaction:



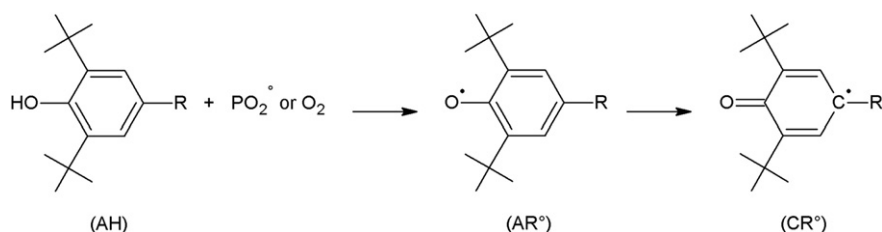
That is kinetically equivalent to:



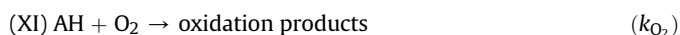
Scheme 1. Oligomeric species proposed by the literature [13,21].



Scheme 2. Triphenolic structures proposed by Uhnai et al. [22].



Scheme 3. Classical mechanism of the abstraction of the phenolic hydrogen.



The reaction is expected to be second order:

$$\frac{d[AH]}{dt} = -f_{AH}k_{O_2}[AH][O_2]$$

being f_{AH} the phenol functionality, k_{O_2} the true second order rate constant, $[O_2]$ the oxygen concentration in the solution and $[AH]$ the residual stabiliser concentration. However, since in principle, the oxygen concentration is maintained constant, it can be assimilated to a first order process:

$$\frac{d[AH]}{dt} = -K[AH]$$

with $K = f_{AH} k_{O_2} [O_2]$, i.e. $\ln [AH] = \ln [AH]_0 - Kt$.

The intensity of the chromatographic peak of the initial stabiliser decreases in an apparent first order process (Fig. 10), that seems to agree with our hypothesis. Second order rate constants k_{O_2} have been determined in various conditions. They are listed in Table 3 for all the antioxidants and ageing conditions under study. The oxygen concentrations were determined or estimated from the data reported in section 2.1, considering that oxygen concentration is the result of multiply the oxygen solubility by the oxygen pressure.

These results call for the following comments:

- Concerning first the temperature effect: k_{O_2} increases with temperature. Its apparent activation energy is of the order of 100 kJ mol^{-1} and seems to display only a second order influence of structure.
- Concerning the data relative to silicone oil, the hierarchy of k_{O_2} values is, at all temperatures:



The difference between AO5 and AO1, which differ only by the bisphenol bridge, is relatively subtle. AO4 is significantly more reactive than the bisphenols, that could seem surprising since, in this case, the phenolic function is partly regenerated through the formation of a cinnamic derivative [19].

- Concerning the data relative to trichlorobenzene, the hierarchy of k_{O_2} values (at 90°C) is:



Here, the thiobisphenol, of which the isomer AO1 was the less reactive in silicone oil, is the most reactive in trichlorobenzene.

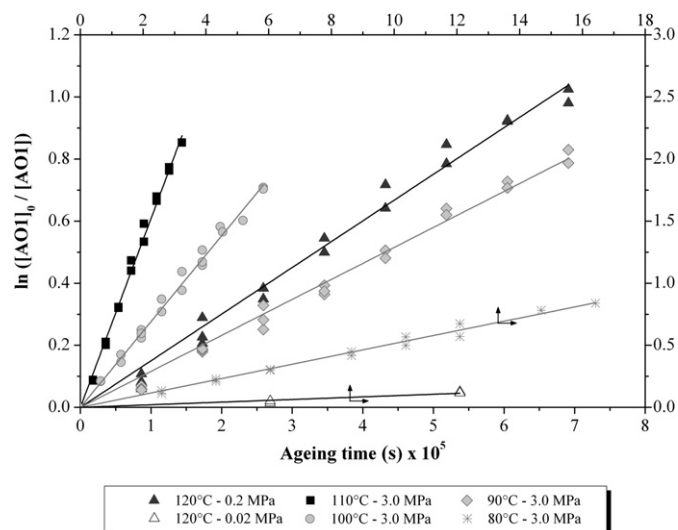


Fig. 10. First order plot for AO1 consumption at different experimental conditions.

Table 3

Kinetic parameters of the antioxidant reaction with oxygen.

Antioxidant	Matrix	E_{act} (kJ mol ⁻¹)	SO_2 at 90 °C (mol l ⁻¹ Pa ⁻¹) × 10 ⁸	k_{O_2} (l mol ⁻¹ s ⁻¹) × 10 ⁵			
				80 °C	90 °C	100 °C	110 °C
				3.0 MPa	3.0 MPa	3.0 MPa	3.0 MPa
AO1	Silicone oil	103	4.92	0.17	0.39	0.94	2.09
AO2	1,2,4-Trichlorobenzene	–	1.06	–	7.78	–	–
AO3	1,2,4-Trichlorobenzene	–	1.06	–	1.09	–	–
AO4	Silicone oil	98	4.92	0.94	1.04	3.50	7.79
AO5	Silicone oil	112	4.92	0.38	0.50	1.16	2.97
	1,2,4-Trichlorobenzene	–	1.06		3.73		

d) Assuming that the hierarchy of reactivities is the same in silicone oil and trichlorobenzene, it comes:

AO2 > AO5 > AO1

The difference between AO2 and AO5 is presumably linked, at least partly, to the fact that OH group is less hindered in AO2 than in AO5. The small difference between AO5 and AO1 can be attributed to a small difference between inductive effects of methylene and sulphur bridges.

e) AO5 appears more reactive than AO3, probably because its OH group is less hindered. It is tempting to conclude that the replacement of the methylene bridge by a propyl group one does not modify strongly the phenol reactivity.

Concerning now the practical aspects of this work, it can be first observed that the rate constant of the hindered phenol–oxygen reaction is more than one million times lower than the rate constant for the phenol–peroxy reaction [7]. Phenol–oxygen reactions will thus be negligible in many cases of thermal oxidation in air at atmospheric pressure (0.02 MPa) but they will significantly contribute to antioxidant consumption at high oxygen pressures where they cannot be ignored in kinetic modelling.

Despite the difference of reactivity between PO₂^{*} radicals and O₂ (biradical), one can suppose that there are some similarities in their structure–reactivity relationships. It will be tried, in the future, to check these similarities.

4. Conclusions

Five hindered phenols used as polymer antioxidants have been exposed to molecular oxygen in inert solvents at temperatures ranging from 80 to 110 °C under 3.0 MPa oxygen pressure. The structural transformations have been monitored by steric exclusion chromatography using various UV wavelengths for detection.

Silicone oil appears as the ideal matrix for such studies, owing to its very low UV absorption. However, certain antioxidants are almost insoluble in this medium, which led us to make certain experiments with trichlorobenzene with the inconvenience of its absorption in short-medium UV range.

All the stabilisers under study are destroyed by reaction with oxygen in a pseudo first order process corresponding to a true second order process of which the rate constant is of the order of 10⁻⁵ l mol⁻¹ s⁻¹ at 90 °C.

The observed differences in reactivity are relatively small. However, they put in evidence a clear influence of steric hindrance. The reactivity of a 2,2'-thiobisphenol is almost the same as the one of the corresponding 2,2'-methylenebisphenol. For all the antioxidants, SEC measurements reveal the formation of oligomeric species containing both phenolic and quinone

chromophores. Whereas thiobisphenols differ from alkylidene bisphenols by the fact that their oxidation leads to products containing three aromatic (or quinone) nuclei not seen in the case of alkylidene bisphenols or simple alkyl substituted monophenols. Some practical consequences of these results have been briefly discussed.

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