

Electronic supplementary information

Reaction of benzoxanthene lignans with peroxy radicals in polar and non polar media: cooperative behaviour of OH groups

Carmela Spatafora, Carmelo Daquino, Corrado Tringali, Riccardo Amorati

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Materials

Solvents (Benzene, MeCN, PhCl, H₂O, D₂O, CH₃OH, CD₃OD) were of the highest grade commercially available (Aldrich–Fluka) and were used as received. 2,6-Di-*tert*-butyl-4-methylphenol (BHT) was recrystallized from hexane. Caffeic acid, Caffeic Acid Phenethyl Ester (CAPE, ≥97%) and 2,2,5,7,8-pentamethyl-6-chromanol (PMHC) (≥97%) were from Aldrich and were used as received. Compound **4** was synthesized as previously described.¹ 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored at -20 °C. Cumene and styrene (Aldrich) were percolated twice through silica and alumina prior to use. Solutions were prepared immediately prior to use.

Determination of the BDE(OH)

Spectra were recorded in quartz tubes at 293 K on a Bruker Elexsys 500 X-band spectrometer equipped with a Bruker VT-1000 variable temperature unit. Spectral analysis was optimized by means of computer simulations and subjected to a least-squares fitting procedure based on the systematic application of the Monte Carlo method, available in WinESR Commander V.1.0 software, developed by Prof. Marco Lucarini (University of Bologna). Spectra were recorded in deoxygenated benzene solutions by irradiating the samples with a 500 W high-pressure Hg lamp and using calibrated metal sectors to modulate the intensity of irradiation. Experiments were performed at three different [BHT] / [**4**] ratios.

Autoxidation experiments

Autoxidation experiments were performed in a two-channel oxygen-uptake apparatus, based on a Validyne DP 15 differential pressure transducer and built in our laboratory. In a typical experiment, an air-saturated chlorobenzene (or acetonitrile) solution of styrene or cumene containing AIBN (0.05 M) was equilibrated with an identical reference solution containing also an excess of 2,2,5,7,8-pentamethyl-6-chromanol (PMHC) (0.1-1 mM) in the same solvent at 30 °C. When a constant oxygen consumption was observed, a concentrated solution of the antioxidant was injected into the sample flask, and the oxygen consumption was measured, after calibration of the apparatus, from the differential pressure recorded with time between the two channels (see Figure 1S).

PMHC was also used as reference antioxidant to measure the rate of initiation R_i , see eq. 1S, where τ is the duration (in seconds) of the inhibition period (Fig. S1).

$$R_i = \frac{2[PMHC]}{\tau} \quad (1S)$$

The study of cumene autoxidation is preferred in the case of weak inhibitors (i.e. $k_{\text{inh}} < 10^5 \text{ M}^{-1}\text{s}^{-1}$), which are not able to retard the autoxidation of styrene. On the other hand, cumene has a propagation constant (k_p) too low to measure k_{inh} values in the case of antioxidants having k_{inh} values larger than approx. $10^5 \text{ M}^{-1}\text{s}^{-1}$.

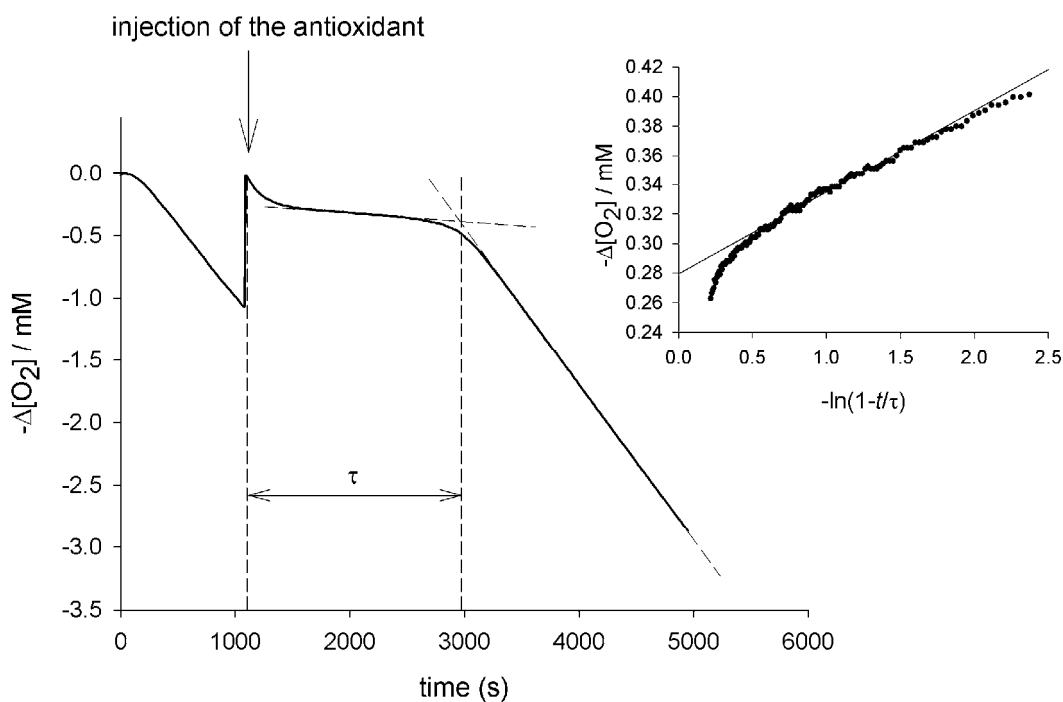
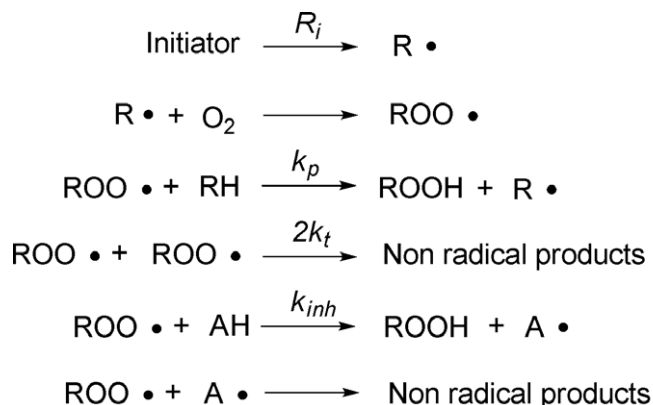


Figure 1S. Oxygen consumption measured during the autoxidation of styrene (4.3 M) in PhCl initiated by AIBN (0.05 M) at 303 K inhibited by PMHC (6.3 μM). In the inset, the kinetic treatment of equation 2S is shown.

The deuterium kinetic isotope effect (DKIE) was measured by adding 1% of CD_3OD or D_2O to PhCl and MeCN respectively and the k_{inh} measured in these conditions was compared to that obtained by using non-deuterated solvents (CH_3OH and H_2O).

Kinetic treatment

The reactions involved in the autoxidation of a generic organic substrate (RH) and in the action of a phenolic antioxidant (AH) are summarized in Scheme 1S.



Scheme 1S. The autoxidation reaction

When an evident inhibition period was observed, see for instance Fig. 1S, oxygen consumption traces were analyzed by eq. 2S, where $\Delta[\text{O}_2]_t$ is the concentration of O_2 consumed at time t , taking as $t=0$ the injection of the antioxidant.² The advantage of this equation, based on the assumption that all $\text{ROO}\cdot$ radicals disappear by reacting with the antioxidant, is that it keeps into account that the antioxidant is consumed during the course of the inhibition period.

$$\Delta[\text{O}_2]_t = (k_p[\text{RH}] / k_{inh}) \ln(1-t/\tau) \quad (2S)$$

When the antioxidant provided only a reduced O_2 consumption without a clear inhibition, equation 3S was used, where R_{ox} and $R_{\text{ox},0}$ are respectively the slopes of the O_2 consumption measured at the beginning of the reaction in the presence and in the absence of the antioxidant (AH).³

$$\frac{R_{\text{ox},0}}{R_{\text{ox}}} - \frac{R_{\text{ox}}}{R_{\text{ox},0}} = \frac{nk_{inh}[\text{AH}]_0}{(R_i 2k_t)^{1/2}} \quad (3S)$$

Equations 2S and 3S require the knowledge of the propagation (k_p) and self-termination ($2kt$) rate constants for the organic substrate RH at the temperature of the experiment. For cumene and styrene, these are available in literature and are reported in Table 1S.

Table 1S. Rate constants at 303 K for the autoxidation of styrene and cumene.

	k_p	$2k_t$	reference
styrene	41	4.2×10^7	3
cumene	0.32	4.6×10^4	4

It should be pointed out that, with styrene, the propagation step consists of the addition of peroxy radicals to styrene to give polyperoxystyryl radicals.³

References

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