Absolute rate constants and transient intermediates in the free-radical-induced peroxidation of γ-terpinene, an unusual hydrocarbon antioxidant†

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Received (in Montpellier, France) 20th May 2003, Accepted 27th June 2003
First published as an Advance Article on the web 2nd September 2003

The peroxidation of γ-terpinene (TH) initiated by *tert*-butoxyl radicals has been investigated by means of nanosecond laser flash photolysis techniques in acetonitrile at room temperature. The absolute rate constants for the reactions implicated in the peroxidation process have been determined and the main short-lived intermediates, terpenyl and terpenylperoxyl radicals, have been detected. The rate constant for H-atom abstraction from TH by *tert*-butoxyl radicals, k_3, has been found to be 1.4×10^8 M^{-1} s^{-1} while the values for the self-quenching of $T^•$ radicals, $2k_4$, and the addition of O_2 to $T^•$, k_9, are, respectively, 1.2×10^{10} M^{-1} s^{-1} and 1.3×10^9 M^{-1} s^{-1}. The overall results strongly substantiate the peroxidation mechanism recently proposed by Foti and Ingold, *J. Agric. Food Chem.*, 2003, **51**, 2758, and provide a solid basis for a better understanding of the unusual antioxidant activity exhibited by this hydrocarbon.

Introduction

γ-Terpinene (TH) is a monoterpene hydrocarbon present in variable amounts in the essential oils[1] (EOs) of many medicinal and aromatic plants[2,3] which has recently come to the limelight because of its unexpected antioxidant properties.[4] A recent investigation,[5] in fact, demonstrated that the antioxidant activity of EOs[6] is due not only to their contents of phenols[1] (which are well-known inhibitors of lipid peroxidation[7]) but, *surprisingly*, also to the activity of simple hydrocarbons like γ-terpinene. EOs are also known to have antibacterial and antimycotic activities[8] which, together with the antioxidant properties, make them appealing candidates as preservatives for food and cosmetics, at least where "their use is not in contrast with their aroma".[5]

These unexpected properties of TH spurred some of us to investigate the kinetics of its autoxidation and the mechanism by which it retarded the thermal peroxidation of linoleic acid (LH).[4] The main results of this study are therefore briefly summarized below for sake of clarity.

γ-Terpinene in the presence of free radicals[9] and molecular oxygen yields *p*-cymene (Cy) as the only organic product (Scheme 1) in a radical-chain reaction. This reaction resembles the peroxidation of 1,4-cyclohexadiene which yields benzene in a chain reaction having $HOO^•$ as the chain-carrying species.[10] It is safe, therefore, to assume that the peroxidation of TH involves similar steps and has the same chain carrier (see Scheme 2).

The hydroperoxyl radical, $HOO^•$, plays a key role in the antioxidant activity of TH because, on mechanistic grounds,[4] it has been suggested that the cross-termination between $HOO^•$ and $LOO^•$ (the chain carrier for the peroxidation of LH) might be some 2–3 orders of magnitude faster than the self-termination of two $LOO^•$'s. Therefore, in the presence of TH, the steady-state concentration of $LOO^•$ is lower and (consequently) the rate of peroxidation of LH decreases.

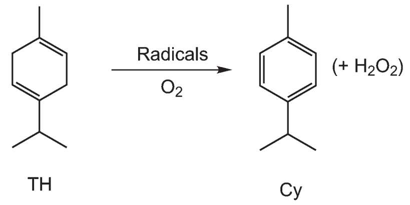
This scenario is quite unusual because: 1) only very rarely have peroxidizable hydrocarbons such as triphenylmethane,[11] β-carotene[12] and tetralin[13] been shown to have antioxidant activities; 2) the observed antioxidant mechanism for TH is completely different from the usual mechanism of action of phenols, such as vitamin E.[7a]

The present contribution aims to provide an insight into the free-radical induced peroxidation of TH by means of laser flash photolysis (LFP) techniques. The detection of some short-lived intermediates appearing in Scheme 2 and the determination of a few relevant absolute rate constants can indeed substantiate the mechanism and provide a solid basis for a better understanding of the unusual antioxidant activity exhibited by this hydrocarbon.

Experimental section

Chemicals

γ-Terpinene (>99%) was purchased from Fluka and used as received. Diphenylmethanol and di-*tert*-butyl peroxide were purchased from Aldrich and this latter was passed through alumina before use. Acetonitrile was of spectrophotometric grade.



Scheme 1

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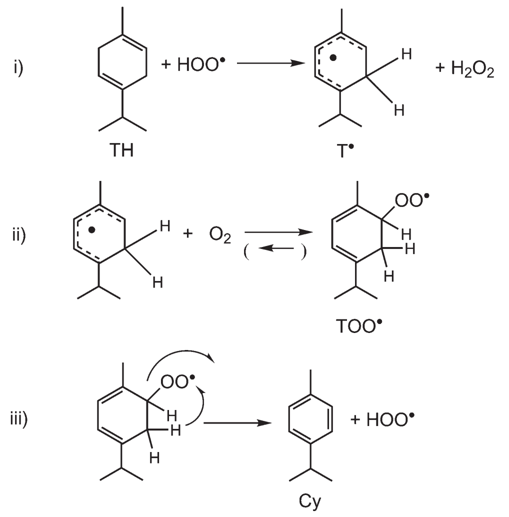
† Dedicated to Professor Giuseppe Condorelli on the occasion of his 73rd birthday.



Scheme 2

Nanosecond laser flash photolysis setup

The samples were excited with either the fourth or the third harmonic of a Nd-YAG. Continuum Surelite II-10 laser system (pulse width 6 ns FWHM) and the excited solution were analyzed at a right angle geometry using a mini mLFP-111 apparatus developed by Luzchem Research. The monitoring beam was supplied by a ceramic xenon lamp and delivered through quartz fiber optical cables. The laser pulse was probed by a fiber that synchronized the mLFP system with a Tektronix TDS 3032 digitizer operating in the pre-trigger mode. The signals from a compact Hamamatsu photomultiplier were initially captured by the digitizer and then transferred to a personal computer that controlled the experiments with a Luzchem software developed, in the LabView 5.1 environment, from National Instruments. The energy of laser pulse was measured at each laser shot by a SPHD25 Scientech pyroelectric energy monitor. Acetonitrile solutions for the experiments in the absence of oxygen were deoxygenated by bubbling with a vigorous and constant flux of pure argon (previously saturated with acetonitrile). The experiments at variable oxygen concentration were carried out by using mixtures of oxygen and nitrogen prepared with a flow gas controller-mixer system (accuracy, ±0.1%). In all the experiments the solutions were renewed (in a flow cell of 1 cm optical path) after each laser shot. The sample temperature was 295 ± 2 K.

GC-MS analyses were done on a Hewlett-Packard 5890 interfaced to a Hewlett-Packard 5971A Mass Selective Detector (DB-5 capillary columns. 30 m × 0.25 mm, film thickness 0.25 µm).

Results and discussion

The peroxidation of TH was studied in acetonitrile at room temperature and initiated by *tert*-butoxyl radicals generated *in situ* by fast photolysis of di-*tert*-butyl peroxide[14]

$$t-\mathrm{BuOOBu}-t \xrightarrow{h\nu} 2t-\mathrm{BuO}^{\bullet} \tag{1}$$

Unless otherwise stated, the fourth harmonic of a Nd-YAG laser ($\lambda = 266$ nm, ~5 mJ) was used as excitation wavelength. At this wavelength, TH did not show any significant absorption (at the concentrations used in the experiments). This offered the advantage of requiring a relatively low concentration of di-*tert*-butyl peroxide ($A_{266} \sim 0.5$) which allowed exploring the UV-spectral changes down to *ca.* 270 nm (otherwise precluded by its absorption).

LFP experiments in the absence of oxygen

The photogenerated *t*-butoxyl radicals, *t*-BuO$^\bullet$, were expected both to react with TH (by H-atom abstraction) and decay with first (β-cleavage) or pseudo-first order (reaction with the solvent) processes, eqn. 2.[15] The experiments were therefore carried out at relatively high concentrations of TH (0.02 M) so that the loss of *t*-BuO$^\bullet$ was minimized. Under such conditions, most *t*-BuO$^\bullet$ radicals abstracted a hydrogen atom from TH and produced the corresponding terpenyl radicals, T$^\bullet$, eqn. 3 (*vide infra*).

$$t-\mathrm{BuO}^{\bullet} \xrightarrow{k_2} \mathrm{decay} \tag{2}$$

$$t-\mathrm{BuO}^{\bullet} + \mathrm{TH} \xrightarrow{k_3} \mathrm{T}^{\bullet} + t-\mathrm{BuOH} \tag{3}$$

Fig. 1 shows the transient absorption spectrum taken 2 µs after the laser pulse. The spectrum is characterized by a maximum in the 315–325 nm region and by a clear drop of the absorption at around 350 nm. Apart from a small red shift, this spectrum is very similar to the reported spectra of cyclohexadienyl and methylcyclohexadienyl radicals.[16,17] Therefore, we could safely attribute the transient spectrum of Fig. 1 to the terpenyl radical, T$^\bullet$, generated by eqn. 3.

Consistent with eqns. 1–3, we observed that the growth traces (following excitation) of T$^\bullet$ radicals followed pseudo-first order kinetics, see Fig. 2A. Furthermore, the decay of T$^\bullet$ radicals followed remarkably clean second-order kinetics, in the whole spectral range explored, in agreement with the self-quenching 4 (see Fig. 2B). No new transient species was detected as T$^\bullet$ decayed.

$$\mathrm{T}^{\bullet} + \mathrm{T}^{\bullet} \xrightarrow{k_4} \text{non radical products} \tag{4}$$

The second-order fit of the trace reported in Fig. 2B gave a value of $2k_4/\varepsilon = 2.9 \times 10^6$ cm s^{-1}. In view of the similarities of the terpenyl and cyclohexadienyl radicals, we may use the value of $\varepsilon_{\max} = 4400$ M^{-1} cm^{-1} for cyclohexadienyl radical[18] to estimate a value of $2k_4 \sim 1.2 \times 10^{10}$ M^{-1} s^{-1} for the self-termination of T$^\bullet$ radicals. Since this rate constant is close to the diffusion-limit, we can therefore assert that the alkyl substituents do not significantly hinder eqn. 4.

In order to determine the absolute rate constant k_3 we used a low laser pulse energy generating therefore low initial concentrations of *t*-BuO$^\bullet$ radicals. Under such conditions, the loss of radicals by the reverse of reaction 1 was negligible and the observed rate constant, k_{obs}, for the growth of T$^\bullet$ was thereby related to the concentration of TH *via* the simple linear eqn. 5:

$$k_{\mathrm{obs}} = k_2 + k_3[\mathrm{TH}] \tag{5}$$

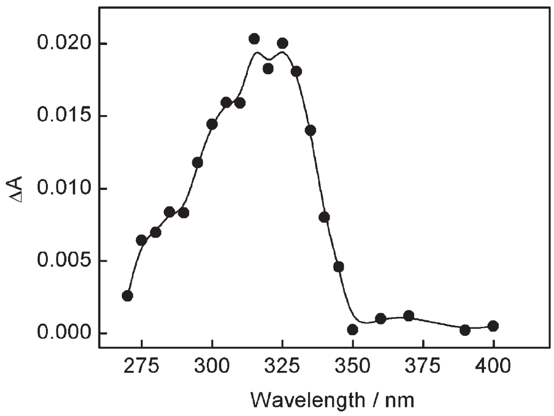


Fig. 1 Transient absorption spectrum taken 2 µs after a 266 nm laser excitation of an Ar-saturated solution of di-*tert*-butyl peroxide in acetonitrile containing 0.02 M TH.

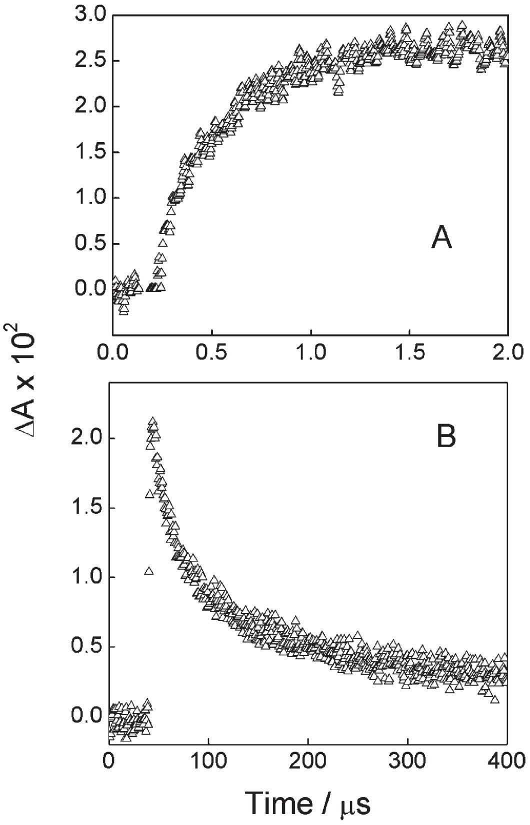


Fig. 2 Representative experimental traces showing (A) the buildup and (B) the decay of the terpenyl radical monitored at 320 nm. They were monitored at different time-scales after a 266 nm laser excitation of an Ar-saturated solution of di-*tert*-butyl peroxide in acetonitrile containing 0.02 M TH.

Fig. 3 reports a typical plot k_{obs} *versus* [TH] which is in excellent agreement with eqn. 5. The slope of the straight-line yields a value of $k_3 = 1.4 \times 10^8$ M^{-1} s^{-1}.

The value so obtained for k_3 has also been confirmed with an alternative kinetic approach which makes use of diphenylmethanol (Ph_2CHOH). This method was introduced for the first time by Scaiano in the late seventies and it has been proved to give good results for a large variety of substrates, especially for those which do not produce easily detectable radicals.[14,19] *tert*-Butoxyl radicals quickly abstract the H-atom from $Ph_2C\boldsymbol{H}OH$ and produce the resonance-stabilized ketyl radical,[20] eqn. 6, which can easily be detected at 545 nm due to its typical and intense absorption.[21]

$$t-\mathrm{BuO}^{\bullet} + \mathrm{Ph_2CHOH} \xrightarrow{k_6} t-\mathrm{BuOH} + \mathrm{Ph_2\dot{C}OH} \quad (6)$$

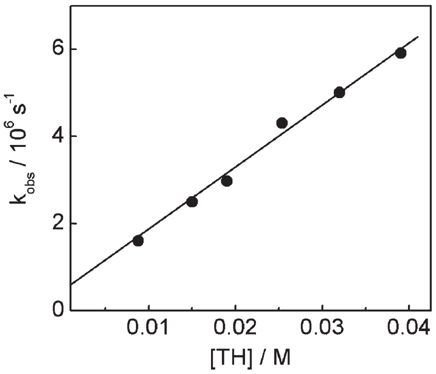


Fig. 3 Plot of the experimental pseudo-first order rate constant for the formation of T$^•$ as a function of the concentration of TH. Each point was obtained by signal average of 15 traces.

In the presence of a second substrate (in our case, TH) which reacts in competition for t-BuO$^•$ radicals, the signal of the ketyl radical becomes weaker but its growth faster. At constant Ph_2CHOH concentration, the observed rate constant for the growth of the ketyl radical is therefore expected to be dependent upon [TH], eqn. 7. Except for the intercept, $k_0 = k_2 + k_6[Ph_2CHOH]$, this equation is formally identical to eqn. 5, (see eqn. 8).

$$k_{obs} = k_2 + k_6[\mathrm{Ph_2CHOH}] + k_3[\mathrm{TH}] \quad (7)$$

$$k_{obs} = k_0 + k_3[\mathrm{TH}] \quad (8)$$

Because of the strong absorption of Ph_2CHOH at 266 nm, this time we used the third harmonic of a Nd-YAG laser (λ = 355 nm, ~5 mJ, absorbance of di-*tert*-butyl peroxide at 355 *ca.* 0.5) as excitation light source. The results of these experiments are shown in Fig. 4 for two different concentrations of Ph_2CHOH. As expected, the two straight lines are parallel (within the [TH] explored) and afford a value of $k_3 = 1.1 \times 10^8$ M^{-1} s^{-1} in excellent agreement with that obtained by a direct detection of the terpenyl radical.

It is worth observing that the value of k_3 is *ca.* 2-fold larger than the corresponding value reported for the H-atom abstraction from 1,4-cyclohexadiene by t-BuO$^•$ radicals.[22] This ratio is in pretty good agreement with the previously reported ratio for the H-atom abstraction from TH and 1,4-cyclohexadiene by linoleoylperoxyl radicals, LOO$^•$.[4] This greater hydrogen donating ability of TH was proposed to be at the basis of its better antioxidant activity in comparison with that of 1,4-cyclohexadiene.[4] That the order of reactivity of these two hydrocarbons is independent of the abstracting radical is further proof that it can only be attributed to a better stabilization of the terpenyl radical by the two alkyl substituents, *i.e.* the C–H bond dissociation enthalpy for the ring methylene groups is slightly lower in TH than in 1,4-cyclohexadiene.

LFP experiments in the presence of oxygen

In the presence of oxygen, the radical T$^•$ is quickly oxidized to the corresponding peroxyl radicals (*vide infra*):

$$\mathrm{T}^{\bullet} + \mathrm{O_2} \xrightarrow{k_9} \mathrm{TOO}^{\bullet} \quad (9)$$

The decay of T$^•$ at variable concentrations of oxygen afforded the value k_9. We used a relatively high concentration of TH (0.06 M) at which the generation of T$^•$ occurred in *ca.* 100 ns (~$1/k_3$[TH]) and relatively low O_2 concentrations (≤1.8

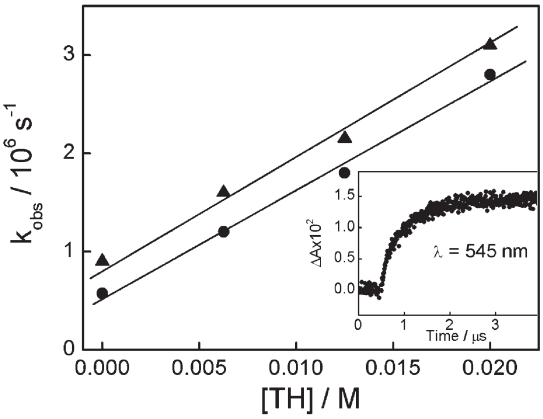


Fig. 4 Observed pseudo-first-order rate constants for the buildup of the ketyl radical as a function of the concentration of TH for two different concentrations of diphenylmethanol: (●) 0.1 M; (▲) 0.2 M. Each point was obtained by signal average of 15 traces. The inset shows the buildup of the ketyl radical at 545 nm observed after 355 nm laser excitation of an Ar-saturated solution of di-*tert*-butyl peroxide in acetonitrile containing 0.2 M diphenylmethanol.

mM) at which the lifetime of T$^\bullet$ was substantially longer than 100 ns (*ca.* 1 μs). Nevertheless, the quantity of oxygen in solution was always sufficient to "capture" all the T$^\bullet$ radicals (eqn. 9). In other words, under our experimental conditions, the loss of T$^\bullet$ by eqn. 4 was negligible. Consequently, the decay of T$^\bullet$ radicals can simply be described by the following equation:

$$k_{obs} = k'_0 + k_9[O_2] \qquad (10)$$

Fig. 5 shows a typical plot of k_{obs} *vs.* [O$_2$] together with a representative trace for the decay of T$^\bullet$ radicals (see inset). The slope of the straight-line yields a value of $k_9 = 1.3 \times 10^9$ M^{-1} s^{-1} in excellent agreement with the expected rate constants for the addition of oxygen to carbon-centered radicals.[23]

The low value of the intercept of the plot in Fig. 5 demonstrates that apart from the reaction with oxygen, all the other possible first-order processes,[23b] *e.g.* the reverse of eqn. 9 (see Scheme 2 step ii), are (at room temperature) relatively unimportant.

We went further and investigated the spectral evolution of eqn. 9. Fig. 6 shows, for instance, the time evolution of the transient absorbance observed after 266 nm laser excitation of di-*tert*-butyl peroxide in the presence of TH in air-equilibrated solution. It can easily be noted that a new absorption which extends to below the 270 nm cut off appears after the decay of the T$^\bullet$ radicals.

As shown in the inset of Fig. 6, the decay of T$^\bullet$ monitored at 320 nm matches well the growth of the new transient monitored at 270 nm. This clearly indicates that the decaying transient, T$^\bullet$, is the precursor of the grow-in. On this basis it is quite reasonable to assign this new transient absorption to the peroxyl radicals TOO$^\bullet$ generated *via* eqn. 9. The similar absorption spectrum exhibited by peroxyl radicals produced upon pulse radiolysis of 1,4-cyclohexadiene[24] validates further our assignment.

The formation of very unstable peroxyl radicals, TOO$^\bullet$, which rapidly eliminate hydroperoxyl radicals, HOO$^\bullet$ (see Scheme 2 step iii) is the keystone of the antioxidant mechanism of TH.[4] Since *t*-BuO$^\bullet$ radicals can abstract an H-atom from both the ring methylene groups with formation of two distinct T$^\bullet$ radicals, the addition of oxygen could lead (in principle) to all the peroxyl radicals **1**–**6** shown in Scheme 3.

Although all these radicals might potentially be responsible for the transient absorption observed (see Fig. 6), we believe that **2** and **5** (in roughly 1 : 1 ratio) are the most likely candidates, as discussed below.

Ingold[10a] first and von Sonntag[24] later proposed and demonstrated, respectively, that in the peroxidation of 1,4-cyclohexadiene,[23] only the peroxyl radical with conjugated double bonds (corresponding in our case to **1**, **2**, **4**, **5**) could abstract the adjacent H-atom and eliminate HOO$^\bullet$ to yield benzene (in our case, Cy, see Scheme 2 step iii). On the contrary, the peroxyl radical with *non*-conjugated double bonds (**3** and **6** in our case) led to *oxygenated* products.[24–27] With TH, the GC-MS analysis of a photolyzed solution did not reveal any significant presence of oxygenated products, under the peroxidation conditions employed, and Cy was the only detected organic product.[27] In addition, Porter and co-workers[28–30] have recently shown that peroxyl radicals with non-conjugated diene moieties, like **3** and **6**, undergo extremely rapid reversion to their carbon-centered radicals (in our case T$^\bullet$) and O$_2$ (eqn. 9). For all these reasons, we exclude, therefore, the existence of the radicals **3** and **6**.

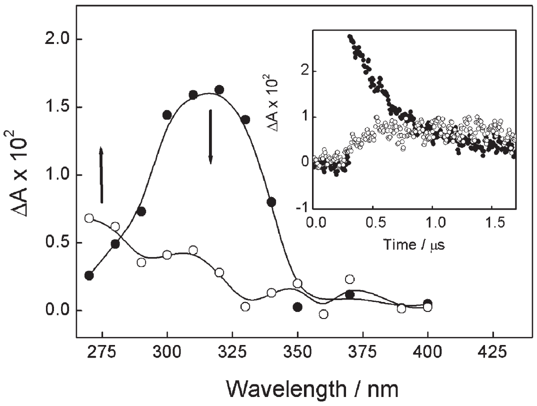


Fig. 6 Transient absorption spectra taken (●) 0.1 μs and (○) 1 μs after 266 nm laser excitation of an air-equilibrated CH$_3$CN solution of di-*tert*-butyl peroxide in the presence of 0.06 M TH. The inset shows (●) the decay and (○) the buildup observed at 320 and 270 nm, respectively.

As shown in Fig. 7, the decay of TOO$^\bullet$ monitored at 270 nm followed quite a clean first order kinetics with a rate constant $k \sim 5 \times 10^4$ s^{-1}. This value is considerably smaller than that reported by von Sonntag and coworkers for the elimination of HOO$^\bullet$ radicals from cyclohexadienylperoxyl radical in water ($k \geq 8 \times 10^5$ s^{-1}).[24] Apart from possible solvent effects on these reactions, another explanation for this discrepancy might be found by taking into account the structures of the peroxyl radicals involved. Actually, the radicals **1** and **4** do not show any significant difference with respect to cyclohexadienylperoxyl radical and, therefore, the intramolecular H-atom abstraction is expected to occur much at the same rate. On the other hand, the radicals **2** and **5** are *tertiary* alkylperoxyl radicals whereas the cyclohexadienylperoxyl radical (as

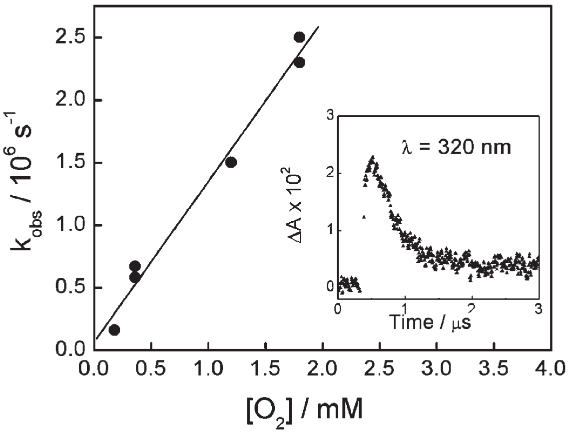
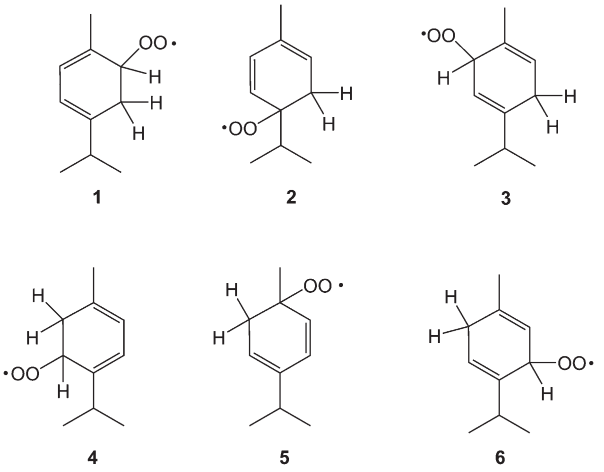


Fig. 5 Determination of the rate constant for oxygen addition to T$^\bullet$ radical, reaction 9, according to eqn. 10 ([TH] = 0.06 M). Each point was obtained by signal average of 15 traces. The inset shows a representative decay trace of T$^\bullet$ for [O$_2$] = 1.8 mM.



Scheme 3

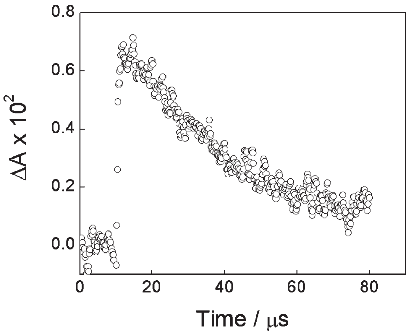


Fig. 7 Decay trace observed at 270 nm after 266 nm laser excitation of an air-equilibrated solution of di-*tert*-butyl peroxide in CH_3CN containing 0.06 M TH.

well as **1** and **4**) is a *sec*-alkylperoxyl radical. It has been demonstrated that *tert*-alkylperoxyls are roughly one order of magnitude less reactive than *sec*-alkylperoxyls in intermolecular hydrogen atom abstraction from organic substrates.[31] We therefore attribute the absorption at 270 nm and its slower decay to the radicals **2** and **5** which eliminate the $HOO^•$ radical to a comparatively slower rate than **1** and **4**. This assumption does not exclude, in fact, the co-formation of the radicals **1** and **4**. Their decay, according to ref. 24, would be as fast as their formation preventing therefore their spectral detection.

Conclusions

The present investigation has provided a direct spectroscopic evidence for the formation of the main transient intermediates, terpenyl and terpenylperoxyl radicals, involved in the free-radical induced peroxidation of γ-terpinene in acetonitrile at room temperature. From a comparison with 1,4-cyclohexadiene, it emerges that the alkyl groups in γ-terpinene seem to have an opposite effect in the initial and final steps of the peroxidation route. Indeed, the *intermolecular* H-atom abstraction by *tert*-butoxy radicals (or $HOO^•$ radicals) from the methylene groups of γ-terpinene occurs *ca.* 2-fold as fast as that in 1,4-cyclohexadiene because of the greater stabilization, due to the alkyl groups, of the terpenyl radical. On the other hand, the *intramolecular* H-atom abstraction by the terpenylperoxyl radical with elimination of $HOO^•$ radicals seems to occur more than one order of magnitude slower than in the corresponding cyclohexadienylperoxyl radical. Such a difference is in agreement with the lower reactivity of *tert*-alkyl peroxyls relative to *sec*-alkyl peroxyls in intermolecular H-atom abstraction. The overall kinetic and spectroscopic results presented herein provide a strong support to the antioxidant mechanism recently proposed for TH. This mechanism is unusual because involves the $HOO^•$ species (formed by elimination from the $TOO^•$ radicals) which is typically, from a biological standpoint, a harmful radical species (it is able to initiate a peroxidation process).

The use of vitamin E and other phenolic antioxidants as food preservatives may be limited by the *pro-oxidant* effect that, under particular conditions, these compounds may exert.[32] In this context, TH might instead provide an alternative or supplementary strategy since this hydrocarbon does not present any *pro-oxidant* effect.

Acknowledgements

Financial supports from MIUR "Cofinanziamento di Programmi di Ricerca di Rilevante Interesse Nazionale" and INCA (Consorzio Interuniversitario per la Chimica dell' Ambiente) are gratefully acknowledged. The authors also gratefully acknowledge Dr. Keith Ingold (National Research Council, Ottawa, Canada) for his helpful suggestions.

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