Free radicals from biogenic volatile organic compounds (VOCs): an electron spin resonance investigation

Andrew Hudson,[a] **Daniel Waterman**[a] **and Angelo Alberti**[b]
[a] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ*
[b] *I.Co.C.E.A.-CNR, Area della Ricerca, Via P. Gobetti 101, I-40129 Bologna, Italy*

Electron spin resonance has been used to characterise free radicals formed by the reactions of photochemically generated *tert*-butoxyl radicals with α-pinene, β-pinene, α-terpinene, γ-terpinene, car-2-ene, car-3-ene and limonene. The spectra have been interpreted using computer analysis and simulation and assigned to substituted cyclohexenyl or cyclohexadienyl radicals formed by abstraction of a hydrogen atom from the parent terpene.

Introduction

Much interest has been shown in the role of anthropogenic and natural biogenic hydrocarbons in tropospheric chemistry. A great deal of literature exists reporting the reaction of terpenes in simulated atmospheres (for an overview see ref. 1). Formation of aerosols and ground-level ozone is of particular environmental concern, and terpenes have been shown to contribute, along with other volatile organic compounds (VOCs), in the conversion of NO into NO_2.[2–4] Details of the reactions of terpenes with ozone, hydroxyl radicals and nitrate radicals have been reported, and rate constants for such processes have been measured and estimated.[5–7] The various carbonyl products of atmospheric oxidation of terpenes have also been well documented.[8] Most tropospheric chemistry involves free-radical processes and, for a detailed understanding of the mechanisms of atmospheric reactions, the free-radical initiation processes must be elucidated. Little work has been carried out in this area and this paper reports the results of an investigation of abstraction of hydrogen from various terpenes by photochemically generated *tert*-butoxyl radicals.

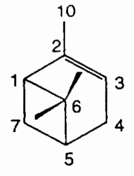
It has been the aim of these investigations to determine the primary step in terpene oxidation. In order to characterise the radicals using electron spin resonance (ESR), it is necessary to work in the liquid phase. The terpenes have therefore been studied in conditions closer to those experienced in aerosol droplets than in the atmosphere. The ESR spectra of radicals derived from these unsymmetrical molecules will be complicated and an initial objective was to see whether useful information could be obtained. A number of numerical methods have been developed in recent years to assist in the analysis of weak and complicated ESR spectra.[9]

In a pioneering study Hammond and co-workers[10] showed that whereas hydroxyl radicals add to propene, *tert*-butoxyl radicals abstract hydrogen to give the allyl radical. Although there are many potentially abstractable hydrogen atoms in a terpene, we might therefore anticipate that the formation of substituted allyl or pentadienyl systems would be preferred. Although this reduces the number of radicals, overlapping spectra from two or more species might still be observed. In practice we have found that a single species usually dominates.

Experimental

Materials

α-Pinene, β-pinene, α-terpinine, γ-terpinene, car-2-ene, car-3-ene and limonene **1**–**7** were obtained from Aldrich in 97–99% purity. Many terpenes autoxidise so it is important to use high-purity samples. Di-*tert*-butyl peroxide and *tert*-butylbenzene were also purchased from Aldrich.



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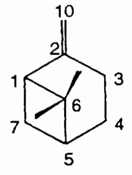

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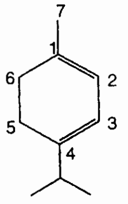

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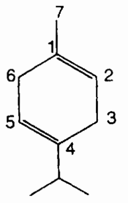

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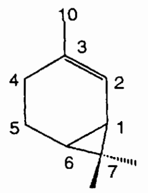

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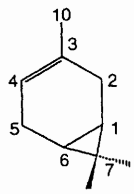

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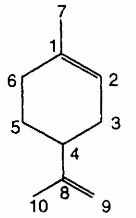

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ESR experiments

The spectra were recorded on Bruker ER-200D and Varian E104 spectrometers using previously described procedures.[11] The terpenes were mixed with di-*tert*-butyl peroxide in a 1:3 volume ratio, in quartz ESR tubes. Oxygen was removed by purging the solutions with nitrogen for between 5 and 20 min and the solutions were then cooled to −45/−50 °C. The solutions were photolysed *in situ* by focusing UV light from a 1 kW high-pressure mercury–xenon lamp into the cavity. IR radiation was removed by passing the light through a water-filled quartz window.

The ESR spectrometers were coupled to computers and the results were digitised and recorded using a spectral manipulation program. This allowed the spectra to be Fourier filtered and smoothed, if necessary, before interpretations were carried out.

Results and discussion

The hyperfine coupling constants for all of the radicals for which a satisfactory analysis of the ESR spectrum has been possible are summarised in Table 1. We shall discuss the results for each radical in turn.

Abstraction of hydrogen from either the 4-methylene or the

Table 1 Hyperfine coupling constants

Compound	Hfs constants (G)
α-Pinene **1**	16.5 (3 H), 13.4 (1 H), 3.1 (1 H), 1.5 (1 H), 0.5 (2 H)
β-Pinene **2**	23.5 (2 H), 16.0 (1 H), 13.5 (1 H), 12.5 (1 H), 0.6 (3 H)
α-Terpinene **3**	44.6 (2 H), 12.9 (1 H), 8.7 (1 H), 4.3 (1 H), 2.2 (3 H), 1.8 (1 H)
γ-Terpinene **4**	44.9 (2 H), 12.9 (1 H), 8.7 (1 H), 4.3 (1 H), 2.2 (3 H), 1.8 (1 H)
Car-3-ene **6**	16.7 (3 H), 13.5 (1 H), 10.2 (1 H), 23.5 (2 H), 3.7 (1 H)

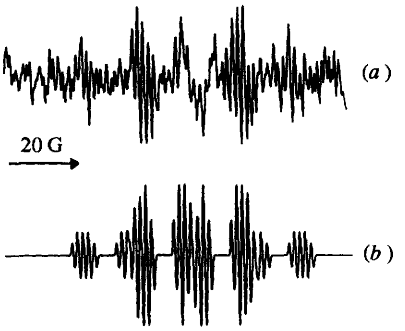
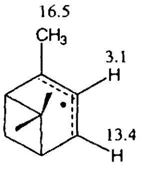
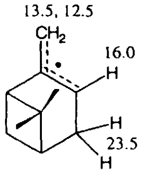


Fig. 1 Experimental (*a*) and computer-simulated (*b*) ESR spectra from α-pinene **1** at −40 °C recorded at high modulation amplitude. A secondary signal has been removed from the centre of the experimental spectra using Fourier filtering.

10-methyl group in α-pinene can create stabilised allyl radicals. The ESR spectrum and the corresponding simulation, Fig. 1, show the presence of a substantial methyl splitting (Table 1), clearly demonstrating that abstraction occurs from position 4 to give the radical (**A**) and not from the methyl group.



(A)



(B)

Indeed the methyl splitting of 16.5 and the two hydrogen splittings of 3.1 and 13.4 G are typical of an allyl radical.[12] The small 1.5 G doublet and 0.5 G triplet have not been assigned but must arise from long-range coupling to the hydrogens in positions 1, 5 and 7.

The central portions of many of the experimental spectra obtained in this work were distorted by the presence of an unidentified broad signal. In the case of α-pinene this was removed by a Fourier filter prior to correlation analysis. The apparent lack of intensity in the central part of the experimental spectrum shown in Fig. 1 is a consequence of the filtering procedure.

β-Pinene **2** has only one position (carbon 3) from which abstraction of hydrogen will lead to the allyl radical (**B**). Fig. 2 shows the spectrum and the best-fit simulation. Of the splittings in Table 1 the large coupling from two hydrogens reflects the conformationally averaged interaction of the methylene hydrogens in position 4. The hydrogen in position 3 gives a splitting of 16 G which is acceptable for an α-hydrogen in an allyl group.[12] The remaining splittings are from the two α-hydrogens attached to carbon 10. The absence of fast rotation about the partial double bond makes the protons magnetically non-equivalent and thus results in slightly different hyperfine coupling constants. Under conditions of low modulation amplitude a further small quartet splitting of 0.6 G is resolvable. This can be attributed to long-range coupling from three of the four protons in positions 1, 5 and 7.

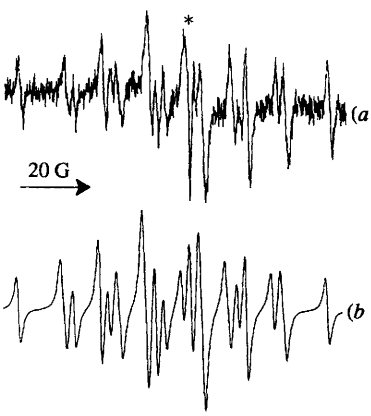
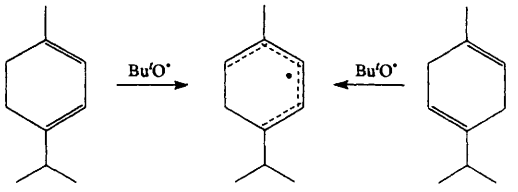


Fig. 2 Experimental (*a*) and computer-simulated (*b*) ESR spectra from β-pinene **2** at −50 °C recorded at high modulation amplitude. The marked line * is due to an impurity in the quartz sample tube.

The terpinenes give essentially identical ESR spectra (Fig. 3) which are attributed to the same radical. This is explained by considering the possibilities for abstraction of hydrogen. Compound **3** has abstractable hydrogens in position 5 and 6, and compound **4** in positions 3 and 6. In fact in both cases hydrogen abstraction must occur preferentially from position 6, since the same cyclohexadienyl radical is observed in each case. The important feature is the small methyl splitting which indicates that the electron density is low on carbon 1 adjacent to the methyl group.



3 **4**

This abstraction puts electron density either side of the remaining methylene group and produces a large triplet of 44.5 G. Griller *et al.*[13] reported hyperfine splittings, similar in magnitude to those reported here, for several substituted cyclohexadienyl radicals. In the absence of a substituent a proton coupling of ~8 G is observed from the 4-position. A molecular-mechanics study of this system using the MM+ option in 'HyperChem' indicates that, in the minimum-energy configuration, the β-hydrogen of the isopropyl group lies close to the plane of the conjugated system, in accord with the small observed hyperfine splitting.

The preference for abstraction from position 6 need not be very great. It is possible to make an estimate of the coupling constants for the alternative radicals; for example, the species formed from compound **3** by abstraction from the 5-position would have a methyl coupling of about 11 G. The ESR spectrum would have its intensity dispersed over more lines and have greater width. We have simulated the spectra expected for mixtures of the two radicals and, with the existing signal-to-noise ratio, estimate that it would be difficult to see the second species until it comprised about 40% of the radical mixture.

Car-3-ene **6** has three positions for abstraction to produce an allylic system, two in the ring (positions 2 and 5) and one methyl. We have found no evidence for abstraction from a methyl group in other terpenes. If abstraction occurs from position 2, the radical would be identical to that formed by

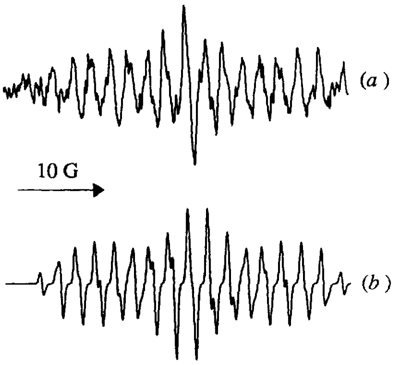


Fig. 3 The high-field section (40 G) of the spectra obtained from γ-terpinene **4**, experimental (*a*) and the computer simulation (*b*), at −45 °C

abstraction from position 4 in car-2-ene. The spectra obtained for this system were difficult to analyse, but from the tentative splittings in Table 1 it is clear that abstraction occurs from position 5 and not position 2. The 16.7 G methyl splitting and the 13.5 and 3.66 G doublets are typical of a 1-methyl-substituted allyl system, and the 23.5 triplet is consistent with conformationally averaged β-protons. It has proved difficult to obtain a reliable value for the remaining splitting, but a reasonable fit is obtained if a 10.2 G doublet is assigned to the β-proton in position 6. A molecular-mechanics calculation on this radical using MM+ in HyperChem suggests that the ring system is essentially planar and that the two protons in position 2 have almost equal out-of-plane angles.

Car-2-ene **5** has two positions from which hydrogen abstraction would form an allylic system. Results from the previous terpenes would suggest that abstraction from the methyl group is unlikely and therefore only position 4 is left. However, surprisingly, we have so far been unable to obtain a satisfactory ESR spectrum for analysis. It is possible that opening of the cyclopropyl ring in the carenes is leading to a variety of radical species.

Limonene **7** has five positions from which abstraction of hydrogen would produce an allylic system. It proved difficult to obtain a good ESR spectrum because of the rapid growth of a broad underlying signal. However, on the basis of the results obtained from the other terpenes, we would anticipate abstraction from position 6 to give a 4-substituted cyclohexenyl radical. The overall width and appearance of the observed spectrum are well accounted for by a simulation performed using the hyperfine parameters reported for the cyclohexenyl radical by de Tannoux and Pratt.[14] The line-broadening due to ring inversion observed in the parent radical would be prevented in the limonene-derived system by the presence of the bulky isopropenyl substituent in the 4-position.

Conclusions

We have shown that it is possible to observe and analyse ESR spectra from primary radicals formed by abstraction of hydrogen from a series of monoterpenes. In each case, the single species observed is stabilised by electron delocalisation and corresponds to either a substituted cyclohexenyl or a substituted cyclohexadienyl radical. In future work we intend to extend this study to include radical-addition reactions and to investigate other radical initiators including OH and NO_3.

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