MASS SPECTROMETRIC AND ELECTRON SPIN RESONANCE STUDY OF ALLYLIC PEROXYL RADICALS IN THE GAS-PHASE REACTION BETWEEN ALLYLIC RADICALS AND DIOXYGEN

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Mass spectrometric measurement of the pyrolyzed (790—1 030 K) mixture of 1,5-hexadiene or 2,5-dimethyl-1,5-hexadiene with dioxygen afforded no evidence for the presence of allylic peroxyl radicals or aldehydes in the gas phase though the allylic radicals were readily detected at low ionisation potentials. On the other side, the electron spin resonance measurement revealed that the allylic radicals were converted quantitatively to allylic peroxyl radicals during condensation of pyrolytic mixtures at 77 K, and acrolein and methacrolein were found mass spectrometrically after thawing of the condensed pyrolytic material as stable products of the allylperoxyl and 2-methylallylperoxyl radical, respectively. These results are compatible with the temperature dependent dissociation equilibrium of the allylic peroxyl radicals. The allylic peroxyl radicals were trapped at 77 K using co-condensation with adamantane from the gas phase in yields as high as 30—50% of the radicals produced in pyrolysis. The electron spin resonance spectra showed partial motional freedom of the peroxyl radicals when they were trapped in the low--contaminated adamantane matrix at 77 K, but in matrices highly contaminated with the biallyl hydrocarbon and products of pyrolysis the ESR spectra indicated rigidly trapped peroxyl radicals. Free rotation of the allylic peroxyl radicals in both types of matrices occurred at 110 K.

Organic peroxyl radicals participate in the gas-phase oxidation of hydrocarbons[1], combustion[2] and air-pollution chemistry[3]. A considerable attention has been paid to the allylperoxyl radicals because of their assumed participation in the industrially important gas-phase oxidation of olefins over solid metal oxide catalysts[4], and because differing results were obtained by various methods used for their detection[1,5-9]. The allylperoxyl radicals were observed by the electron spin resonance (ESR) after being trapped in various matrices at 77 K (refs[1,5]), but they were not detected in the gas phase by mass spectrometry (MS) (refs[6,7]) or by photoelectron spectroscopy[8]. The information on the behaviour of allylperoxyl radicals in the gas phase was obtained indirectly by the MS and UV measurement of the allyl radical decay in the presence of dioxygen under the flow conditions[6,9]. These measurements revealed that the

$$C_3H_5^\bullet + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_3H_5OO^\bullet \qquad (A)$$
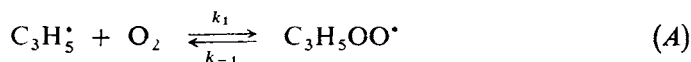
equilibrium (A) between allyl and allylperoxyl radicals is strongly temperature-
-dependent. At high temperatures $(573 - 673 \text{ K})$ the equilibrium (A) $(c_{C_3H_5}\cdot = 3$.
. 10^{14} cm^{-3}; $p_{O_2} = 332 \text{ Pa})$ was completely on the left side, the allyl radicals decaying
purely by recombination as in the absence of dioxygen. At lower concentrations of the
allyl radical, when the radical decay by recombination could be neglected, the
Arrhenius dependence of $K = k_1/k_{-1}$ showed a sudden drop at temperatures above
440 K. This drop was tentatively explained by the occurrence of the reaction (B)
yielding allene and the hydroperoxyl radical[9].

$$C_3H_5^\cdot + O_2 \quad \rightarrow \quad CH_2{=}C{=}CH_2 + HO_2^\cdot \qquad (B)$$
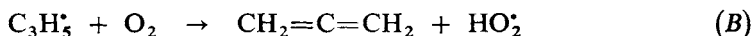
This is in accordance with the commonly assumed view that the role of alkylperoxyl
radicals in the oxidation processes at temperatures when they become unstable, is
transferred to the hydroperoxyl radical formed by the hydrogen abstraction from
hydrocarbon or the alkyl radical[10]. The mechanisms of the oxidation reactions at
high temperatures are, however, little known since many intermediates, which are
often more reactive than the starting compounds ($e.g.$, ROOH, H_2O_2), are probably
involved in the reaction chain.

We therefore found interesting to study the interaction of pyrolytically formed
allylic radicals[11] with dioxygen at $790 - 1\,030 \text{ K}$ after a short reaction time (ms)
by MS detection and, after cooling to 77 K, by ESR and MS. The aim of this work
is obtaining information on the efficiency of reactions of allylic radicals with dioxygen
under various conditions, detection of paramagnetic and diamagnetic products of
these reactions, and a study of motional behaviour of peroxyl radicals in the adam-
antane matrix condensed from the gas phase.

EXPERIMENTAL

Chemicals. 1,5-Hexadiene (*I*) and 2,5-dimethyl-1,5-hexadiene (*II*) (Fluka) were distilled *in vacuo*
and degassed by repeated thawing under pumping. Adamantane (Koch–Light) was sublimed
in vacuo and degassed. Technical oxygen ($\geqq 98\%$ according to MS analysis) was used without
purification.

Generation and detection of radicals. Mixtures of the hydrocarbon *I* or *II* with dioxygen were
pyrolyzed at temperatures $790 - 1\,030$ K and the pyrolytic products were measured by mass
spectrometry and ESR spectroscopy. The pyrolysers and devices for detection of radicals were
the same as described previously[7,11]. The pyrolyser was attached either directly to the ionisation
chamber of a mass spectrometer or to the Dewar vessel for trapping radicals on a cooled finger[11].
In the experiments monitored by ESR, the partial pressures of hydrocarbons (p_I, p_{II}) ranged
between $0\cdot1 - 0\cdot3$ Pa and the molar ratio dioxygen : hydrocarbon changed from 10 to 10^{-3}.
In the mass spectrometric measurements, the partial pressure of a hydrocarbon varied within
$0\cdot01 - 0\cdot1$ Pa and the ratio $p_{O_2} : p_I$ (or p_{II}) was equal to 10. The device for the ESR detection
was characterized by the flow rate c. 1 μmol h^{-1} and by the residence time about 10^2 ms; the
same parameters for the pyrolyser coupled with the ionisation chamber were in the range of

mmol h^{-1} and ms. In the experiments using the adamantane matrix for trapping radicals, gaseous adamantane was admitted from an entry placed close to the end of pyrolyser[11]; the partial pressure of adamantane was kept constant at 9 Pa. This high partial pressure of adamantane resulted in a partial backward motion of the gaseous mixture into the pyrolyser and therefore no attempt was made to introduce dioxygen separately into the space between pyrolyser and trap. In blank experiments, using pure dioxygen instead of its mixture with the allylic hydrocarbon, the peroxyl radicals generated from the adamantane oxidation were detected by ESR only at temperatures above 1 030 K. In experiments proving the extent of radical decay in the gas phase, the distance between pyrolyser and trap was enlarged 3-times by inserting a glass tube loop.

Measurements. Direct mass spectrometric measurement of pyrolytic products in the gas phase was carried out on a MI 1305 spectrometer (modified as described previously[7]) applying ionisation energies 11—80 eV. The temperature of ionisation chamber was influenced by the temperature of the pyrolyser and reached maximum c. 470 K.

The pyrolytic products were also trapped at 77 K in the absence of adamantane, using the same Dewar vessel as used for the ESR measurements; the condensed material was warmed up to room temperature and distilled at low pressure into the reservoir of a Jeol MS D 100 mass spectrometer. The main components of the final products of pyrolysis were identified by their MS spectra and the elemental composition of ions.

The ESR spectra of the pyrolytic products condensed at 77 K on the inner finger of the Dewar vessel were measured on an ERS-220 spectrometer (German Academy of Sciences, Berlin, G.D.R.) in the X-band. For the measurements at temperatures above 77 K, the liquid nitrogen in the Dewar vessel was replaced by cooled gaseous nitrogen generated in a variable temperature unit STT-3. Quantitative evaluation of the radical yields (number of radicals trapped during 1 h) was carried out by comparing areas of the absorption ESR spectra with those of the standard DPPH solution. The correction was taken for different populations of the spin states at 77 K and 293 K. The amounts of allyl radicals and allylperoxyl radicals in a mixture were determined by subtracting the area of the upper-field half of the allyl radical spectrum multiplied by 2 from the overall area of the absorption ESR spectrum; the peroxyl radical spectrum does not interfere with the upper-field half of the allyl radical spectrum as it is shown in Fig. 1.

RESULTS AND DISCUSSION

Mass Spectrometric Investigation of the Interaction of Allylic Radicals with Dioxygen

Direct mass spectrometric measurement of the pyrolysis of *I* or *II* in the presence of dioxygen revealed no products of oxidation, *e.g.* the allylic peroxyl radicals or aldehydes. The intensities of mass peaks of allylic radicals, measured at 11 eV under molecular flow conditions[11], decreased slightly in the presence of dioxygen (c. 10%), presumably as a result of the changed inlet rate of reactants into the ionisation chamber. Insertion of a quartz wool plug into the outlet of pyrolyser resulted in an increased extent of the hydrocarbon decomposition and in occurrence of stable products of pyrolysis. Under such conditions, allene and propene were detected as the products of *I*, and allene and 3-methyl-1-butene as the products of *II*. It is remarkable that these products were formed both in the presence as well as in absence

of dioxygen. The composition of these products indicates that they arise from a non--radical dissociation of biallyl hydrocarbons (Eq. (C)), possibly catalyzed by glass
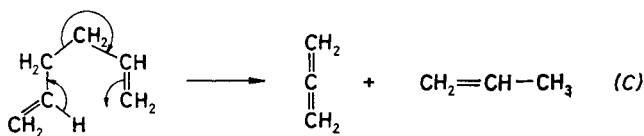
or quartz surfaces. Since the relative abundances of both pairs of disproportionation products were not markedly influenced by the presence of dioxygen, the formation of allene at high temperatures, which affected the UV measurement of the allyl radical concentration[9] at 223 nm, took origin in the above-mentioned dissociation of biallyl hydrocarbons rather than in the hydrogen abstraction from the allyl radical by dioxygen (B).

Only trace amounts of CO_2 were detected in the presence of dioxygen, indicating the deep oxidation process, while the corresponding amount of water could not be distinguished from the spectrometer background. The absence of acrolein and methacrolein, respectively, was surprising because benzaldehyde was found to be the only product of the reaction of benzyl radicals with O_2 at 800 K under conditions, and with the apparatus, used in this work[7].

On the other hand, when the pyrolytic products were trapped on a cooled finger at 77 K and then annealed at room temperature, the mass spectrometric analysis
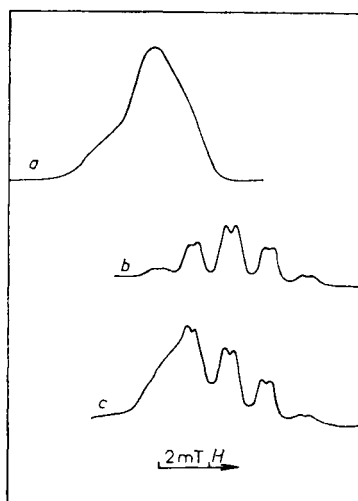

FIG. 1

Integrated records of ESR spectra of radicals in the adamantane matrix at 77 K. a Allylperoxyl radical, b allyl radical, c mixture of allylperoxyl radical (43.5%) and allyl radical (56.5%); temperature of pyrolysis 910 K, $p_I = 0.1$ Pa; a $p_{O_2} : p_I = 10$; b $p_{O_2} = 0$; c $p_{O_2} : p_I = 0.02$

revealed acrolein and methacrolein to be the main oxidation products of *I* and *II*, respectively. Their formation under these conditions indicates that they mainly arose from the low-temperature $(160 - 293$ K$)$ reactions of the allylic peroxyl radicals which were trapped in a high yield at 77 K. Allene and the olefins were also found in the final pyrolytic products, regardless of the dioxygen presence in the pyrolyses.

All the above observations are compatible with the properties of equilibrium (A) as described elsewhere[6,9]. Since the pyrolyses were carried out under similar dioxygen pressure and at much higher temperatures than used for measurement of the equilibrium constant of (A), no allylperoxyl radicals should have been expected at the outlet of the pyrolyser. The conditions for formation of the peroxyl radicals remain unfavourable also in the ionisation chamber since its temperature is well above 400 K and the pressure of both reactants is by one order lower than in the pyrolyser.

Nevertheless, the present results of the direct MS analysis of the pyrolyzed gaseous biallyl–O_2 mixtures cannot be considered a proof for the absence of allylperoxyl radicals because nothing is known about the process of ionisation of allylperoxyl radicals upon electron impact. Also, the absence of unsaturated aldehydes in the gas phase, as found by direct MS measurement, may be brought about by a low rate of the peroxyl radical-to-aldehyde transformation. The role of possibly formed hydroperoxyl radicals in the described high-temperature oxidative pyrolyses could not be specified but the interpretation of ESR spectra shows that the radicals trapped at 77 K are the allylic peroxyl radicals (see below).

Trapping of Allylic Peroxyl Radicals at 77 K

The ESR spectra of pyrolytic products trapped at 77 K on the cooled finger have shown that allylic peroxyl radicals were easily formed in the presence of dioxygen *cf*. Fig. 1). The pyrolytic products were trapped either in the matrix of the unde-composed biallyl hydrocarbon or in the adamantane matrix. The latter exerted excellent capability for radical trapping and a specific property allowing, *e.g.*, free rotation of the allylic radicals at 77 K (ref.[11]). The dependencies of the peroxyl radical yields on pressure of the biallyl hydrocarbon and on the pyrolytic tempera-ture have shown that considerably higher radical yields were obtained and a better reproducibility was achieved with the adamantane matrix. Since the motional behaviour of peroxyl radicals in the adamantane matrix is also a topic of interest, we refer only to results obtained with this matrix.

The comparison of yields of allylperoxyl radical with the yields of the allyl radical obtained in the absence of dioxygen[11] surprisingly showed that both yields were nearly identical for low pyrolytic pressure of *I*, $p_I = 0.6$ Pa, and pyrolytic tempera-tures (T_p) up to 910 K. For higher values of p_I and T_p, the yields of the allyl radical declined from continuously increasing yields of the peroxyl radical and diminished as it is shown in Fig. 2. This diminution of allyl radical yields was attributed to insuf-

ficient cooling of the matrix surface at high values of p_I and T_p, which resulted in the radical decay during condensation[11]. The increasing yields of the peroxyl radicals, under conditions which were even less favorable for the radical trapping due to additional heat transfer to the matrix by dioxygen, thus indicate that the allylperoxyl radical is more stable than the allyl radical in the range of low temperatures.

The decay of radicals during the gas-phase transport from pyrolyser to trap was studied under conditions $\left(p_I = 0.5 \text{ Pa}, \quad T_p = 910 \text{ K}, \quad p_{O_2} : p_I = 5\right)$ giving equal yields of allyl and allylperoxyl radicals in the absence and presence of dioxygen, respectively. In this case, the results are valid for both types of radicals as their decay in the condensed phase is eliminated. The fraction of radicals decaying during the transport was estimated by comparing the degree of decomposition of I (corrected for non-radical decomposition) with the number of the trapped radicals, as it is shown below for $p_I = 0.5$ Pa and $T_p = 910$ K. In this case, about $3 . 10^{18}$ molecules of I passed through the pyrolyser during 1 h and about 10% of them were decom-
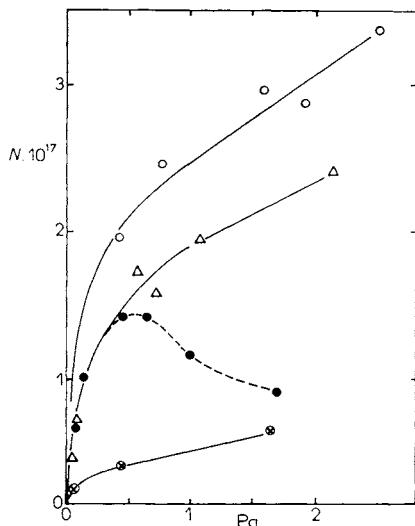

FIG. 2

Dependence of the number of allylperoxyl radicals N trapped in the adamantane matrix during 1 h on partial pressure of I (p_I), for various temperatures of pyrolysis (T_p). ○ 1 030 K, △ 910 K, ⊗ 790 K; constant ratio $p_{O_2} : p_I = 5$. ● Analogous dependence for the allyl radical prepared by pyrolysis of I at 910 K in the absence of dioxygen
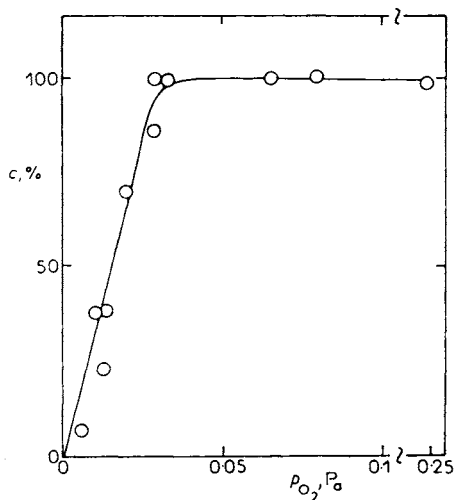
FIG. 3

Dependence of the allylperoxyl radical content (c) in the paramagentic products of pyrolysis (mixture of allyl and allylperoxyl radicals) on partial pressure of dioxygen (p_{O_2}) ($T_p = 910$ K, $p_I = 0.6$ Pa, adamantane pressure 9 Pa)

posed[11]. Since the MS analysis of the annealed pyrolytic products revealed that c. $20-25\%$ of the decomposed *I* yielded allene and propene in a non-radical process, the number of allyl radicals produced per 1 h was estimated to be $3-5 \cdot 10^{17}$. The number of radicals $1 \cdot 5 \cdot 10^{17}$ trapped in the adamantane matrix under the same conditions then represents c. $30-50\%$ of the produced radicals. Since this figure concerns the gas-phase decay, it strongly depends on the geometry of the pyrolyser--trap arrangement. Actually, an enlargement of the distance between pyrolyser and trap 3-times by inserting a glass tube loop decreased approximately equally the yields of either radical about 5-times.

The ESR investigation of pyrolytic products over a wide range of low $p_{O_2} : p_I$ ratios (minimum ratio $3 \cdot 10^{-3}$) showed the dependence of the conversion of allyl radicals into the allylperoxyl ones on p_{O_2} (Fig. 3), with the sum of both radicals remaining approximately constant. The minimum partial pressure of dioxygen which is necessary for effective conversion of the allyl radicals to peroxyl radicals ($p_{O_2} = 0 \cdot 03$ Pa against $p_I = 0 \cdot 6$ Pa) approaches the stoichiometrical requirement. The insertion of the loop decreased the value of the minimum dioxygen pressure required for complete conversion of allyl radicals. This decrease corresponds to the amount of the allyl radicals decaying during the prolonged gas-phase transport.

The dependencies found for the 2-methylallylperoxyl and 2-methylallyl radicals were similar to those ones depicted in Figs 2 and 3.

All the above results indicate that the allylic radicals dominate in the gas phase, their conversion to allylic peroxyl radicals being governed by the thermal dependence of the equilibrium (A). Since the temperature of the trapping device at the point for sealing off the Dewar vessel (point F in Fig. 1 of ref.[11]) remained above 370 K we can assume that the peroxyl radicals are mainly formed during the condensation at 77 K and/or in the condensed phase. The reaction in the condensed phase seems to account for complete conversion of the allylic radicals by a nearly stoichiometric amount of dioxygen under low partial pressure of dioxygen and at c. 300-times higher pressure of adamantane. We suggest that both the allylic radicals and dioxygen are trapped in the excess of condensing adamantane, but while the radicals are localized in cages, the adsorbed dioxygen migrates through the matrix and reacts with them. This suggestion is further supported by softness of the adamantane matrix as follows from the ESR spectra of the trapped radicals.

The ESR *Spectra of Allylperoxyl and 2-Methylallylperoxyl Radicals in the Adamantane Matrix*

The allylperoxyl and 2-methylallylperoxyl radicals displayed typical anisotropic spectra of peroxyl radicals[1,12,13] when they were trapped in the absence of adamantane or in the adamantane metrix at partial pressures of *I* or *II* higher than $1 \cdot 5$ Pa (Figs 4a and 5a). The decrease of p_I or p_{II} below $1 \cdot 5$ Pa led to the occurrence

of new, less anisotropic spectra. In this way, the allylperoxyl radical spectrum approached the single-line appearance (Figs $4b - d$), and the 2-methylallylperoxyl radical gave a spectrum (Fig. $5c$) which can be interpreted in terms of an axially symmetric g-tensor and nearly isotropic doublet splitting $A_{\parallel} = 0.8$ mT and $A_{\perp} = 0.7$ mT. The difference between $g_{\parallel}$ and $g_{\perp}$ is in this case much lower than in the known anisotropic spectra of the peroxyl radicals[1,12,13] (Table I). The doublet splitting can arise from the through-space interaction of the unpaired electron, residing mainly on the outer oxygen atom, with one proton of the methyl group the rotation of which is hindered at 77 K. Such a structure can be constructed using parameters calculated for the methylperoxyl radical[14] and normal bonding parameters for the C=C, C—C, and C—H bonds.

Both the allylperoxyl and 2-methylallylperoxyl radicals displayed reversibly isotropic singlet signals ($\Delta H = 1.2$ mT) at 110 K (Figs $4e$ and $5d$), providing p_I or p_{II} were lower than 2 Pa. Their g-values (Table I) agree with the literature data for peroxyl radicals in solution[15].

The hydroperoxyl radical, which is suggested to take part in the high temperature oxidations[10], gives the doublet splitting in the ESR spectrum of rigidly trapped
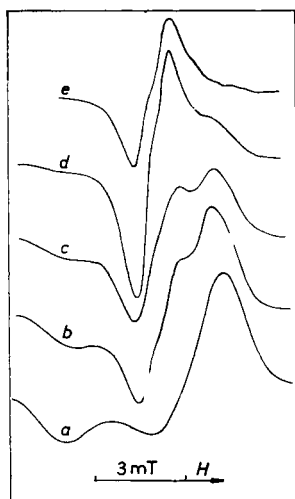

FIG. 4

ESR spectra of the allylperoxyl radical obtained at different partial pressures of I (p_I) and at constant ratio $p_{O_2} : p_I = 5$. a $p_I = 1.7$ Pa, b 0.7 Pa, c 0.06 Pa, d 0.01 Pa, e $p_I = 1.7$ Pa, 110 K
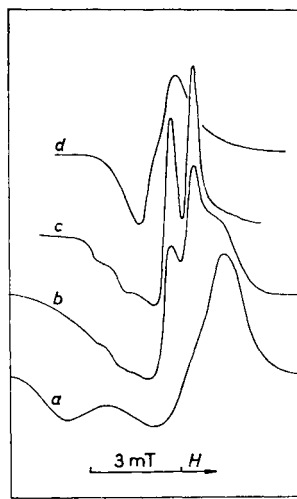
FIG. 5

ESR spectra of the 2-methylallylperoxyl radical obtained at different partial pressures of II(p_{II}) and at constant ratio $p_{O_2} : p_{II} = 5$. a $p_{II} = 1.8$ Pa, b 0.4 Pa, c 0.01 Pa, d $p_{II} = 1.8$ Pa, 110 K

radical but its parameters $\left(g_{\parallel} = 2.0393, g_{\perp} = 2.0044, A_{\parallel} = 1.35\text{ mT}, A_{\perp} = 0.86\text{ mT}\right)$ (ref.[16]) differ from those obtained by us for the 2-methylallylperoxyl radical. Another arguments against possibility that the trapped radical is mainly $HO_2^{\bullet}$ are the difference in appearance of ESR spectra obtained from *I* and *II* at high dilution and no doublet splitting in the regular anisotropic as well as isotropic ESR spectra.

The changes in the anisotropy of ESR spectra of the trapped peroxyl radicals (Figs 4 and 5) are obviously connected with the extent of contamination of the adamantane matrix by hydrocarbons *I* or *II*. The radicals were trapped rigidly in highly contaminated matrix, while those trapped in relatively pure adamantane matrix exerted some reorientational motion as indicated by the low anisotropy of their ESR spectra. In comparison with the allyl and 2-methylallyl radicals, which give isotropic ESR spectra in adamantane matrix even at 77 K (ref.[11]), the allylic peroxyl radicals require, due to their larger size, higher thermal activation for their free rotational motion.

In contrast to the crystalline adamantane matrix, which stabilizes the allylic radicals up to the room temperature[18], the adamantane matrix condensed from the gas phase is apparently softer[11]. It probably possesses very fine polycrystalline and porous structure with large cages allowing relatively high motional freedom to the trapped radicals even at low temperature. The coincidence of decay of both the allylic[11] and peroxyl radicals (Table I) in the temperature range 160−170 K

TABLE I

ESR spectra of allylperoxyl and 2-methylallylperoxyl radicals

Hydro-carbon	Matrix[a]	Tempe-rature, K	ESR parameters	Stability
I	−AD	77	$g_{\parallel} = 2.032, g_{\perp} = 2.008$	110 K
I	+AD	77	$g_{\text{iso}} = 2.016^{b}$	
		130	$g_{\text{iso}} = 2.016$	160 K, $\tau_{1/2} = 10\text{ min}^{c}$
II	−AD	77	$g_{\parallel} = 2.033, g_{\perp} = 2.008$	110 K
II	+AD	77	$g_{\parallel} = 2.024, g_{\perp} = 2.013$ $A_{\parallel} = 0.82\text{ mT}, A_{\perp} = 0.72\text{ mT}$	
		120	$g_{\text{iso}} = 2.016$	160 K, $\tau_{1/2} = 10\text{ min}^{c}$

[a] −AD Matrix of pyrolyzed hydrocarbon and non-paramagnetic products of pyrolysis (ESR spectra are identical with those ones in Figs 4a and 5a). +AD The low-contaminated adamantane matrix obtained at p_I or $p_{II} = 0.01$ Pa (cf. Figs 4d,e and 5c,d). [b] Only approximately isotropic, cf. Fig. 4d,e. [c] Kinetics of the radicals decay is similar to that found for the crystalline adamantane matrix (biexponential)[11,17]; the values of $\tau_{1/2}$ are only approximate due to differing warm-up conditions.

may be accounted for either similar reactivities of both radical species or the rearrangement of the adamantane matrix.

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