

GAS-PHASE RADICALS IN CO-CONDENSED ADAMANTANE MATRIX: PROTON SPLITTING IN THE ESR  
SPECTRUM OF THE CYCLOHEPTATRIENYLPEROXYL RADICAL

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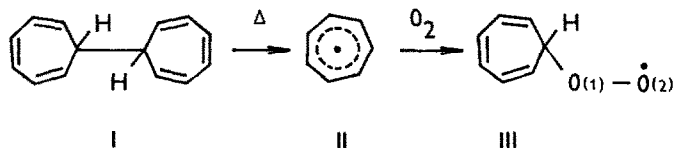
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**Abstract:** The cycloheptatrienyl (tropenyl) radical was generated by the gas-phase pyrolysis of ditropenyl at 473-723 K and was trapped in co-condensed adamantane at 77 K. Well-resolved isotropic ESR spectra of the tropenyl radical showed a linear temperature dependence of  $a_{iso}$  in the range 77-226 K. The tropenylperoxyl radical was obtained if the ditropenyl pyrolysis was carried out in the presence of dioxygen. The anisotropic ESR spectrum of the tropenylperoxyl radical obtained in the adamantane matrix at 77 K was characterized by  $g_1 = 2.035$ ,  $g_2 = 2.009$ ,  $g_3 = 2.002$  and  $a_1 = 8.4$  G,<sup>†</sup>  $a_2 = 9.6$  G and  $a_3 = 5.35$  G. The values of  $g_{iso}$  and  $a_{iso}$  were found experimentally in the freely rotating radical at 130 K to be  $g = 2.0157$  and  $a = 7.5$  G respectively. The hyperfine coupling arises from coupling to the  $\beta$ -H atom via a hyperconjugative mechanism.

Recently, we have found that the adamantane matrix, which is obtained by co-condensation of adamantane with radicals from the gas phase, is suitable for the investigation by ESR spectroscopy of these radicals at low temperatures.<sup>1</sup> In comparison with an adamantane matrix crystallized from solution, co-condensation from the gas phase stabilizes radicals only at relatively low temperature and so gives a greater range of motional freedom. Since adamantane itself is pyrolyzed only above 1000 K, radicals obtained from the gas phase pyrolysis of easily dissociating symmetric diallyl and dialkyl hydrocarbons can be studied by ESR using this type of matrix, as can radical products of their gas-phase reactions with, for example, dioxygen. The study by mass spectrometry and ESR of the pyrolysis of diallyl hydrocarbons in the presence of dioxygen led us to conclude<sup>2</sup> that the allylperoxyl radicals were formed only at low temperature in the condensing matrix, while in the hot gaseous phase the equilibrium  $R\cdot + O_2 \rightleftharpoons RO_2\cdot$  was shifted to the left. The temperature dependence of this equilibrium for the allyl radical was previously established by the mass spectrometric studies.<sup>3,4</sup> Anisotropic ESR spectra of the allyl- and 2-methylallylperoxyl radicals at 77 K as well as isotropic spectra of the same radicals freely rotating at 110 K in the adamantane matrix have been obtained.<sup>2</sup>

<sup>†</sup> 1G =  $10^{-4}$  T

In this work we describe the formation of the cycloheptatrienyl (tropenyl) radical from the pyrolysis of dicycloheptatrienyl (ditropenyl), and the cycloheptatrienylperoxyl (tropenylperoxyl) radical from the same pyrolysis performed in the presence of dioxygen.



The use of the adamantane matrix co-condensed from the gas phase enabled us to establish the thermal dependence of  $a_{\text{iso}}$  of the tropenyl radical at low temperatures, and also that of a new hyperfine splitting seen in the ESR spectrum of both the rigid and freely rotating tropenylperoxyl radical.

#### EXPERIMENTAL

The ESR measurements. - Pyrolysis of ditropenyl was carried out at temperatures in the range 473-723 K, both in the absence and the presence of dioxygen, in a quartz pyrolyser attached to the trapping Dewar vessel for the ESR measurement.<sup>1</sup> The pyrolytic products were condensed on a cool finger (77 K) of the trapping Dewar vessel both in the absence and the presence of adamantane and were studied by ESR. The partial pressure of ditropenyl was varied in the range of  $5 \times 10^{-4}$ - $5 \times 10^{-3}$  Torr<sup>†</sup> and that of dioxygen between  $1 \times 10^{-3}$ - $1.5 \times 10^{-2}$  Torr. The partial pressure of adamantane was  $7 \times 10^{-2}$  Torr. After pyrolysis, the Dewar vessel was sealed off and inserted into the ESR cavity. The temperature of the samples was kept at 77 K by liquid nitrogen or at higher temperatures ( $\pm 1$  K) by blowing cooled gaseous nitrogen over the sample in the cavity. The ESR spectra were recorded on an ERS-220 spectrometer [Centre for Scientific Instruments, German Academy of Sciences, Berlin, GDR]. The magnetic field was calibrated with a proton magnetometer MJ-110 R [Radiopan, Poznań, Poland]. The g-values were calibrated relative to the signal of a  $\text{Mn}^{2+}$  ( $M_T = -\frac{1}{2}$  line) standard at  $g = 1.9860$ .

The mass spectrometric analyses. - Gaseous pyrolytic products were analyzed using a device comprising a pyrolyser connected through a leak with the ionisation chamber of a MI 1302 mass spectrometer (USSR).<sup>5</sup> The formation of tropenyl radicals in the range of temperatures 473-723 K was indicated by a decrease of fragment peaks of ditropenyl (in the order of decreasing intensity:  $m/e$  91, 104, 78, 181) and increase in intensity of the fragment peaks of the tropenyl radical ( $m/e$  65, 39, 63). The peak  $m/e$  91 was decreasing in intensity with increasing temperature of pyrolysis when measured at 50 eV of ionisation energy, but when measured at 9 eV it grew in intensity with the temperature which was due to the increasing content of easily ionized tropenyl radical. The non-radical isomerization of ditropenyl to dibenzyl at temperatures above 623 K was indicated by the increasing intensity of the  $\text{M}^+$  peak  $m/e$  182. All these measurements agreed with results by Harrison

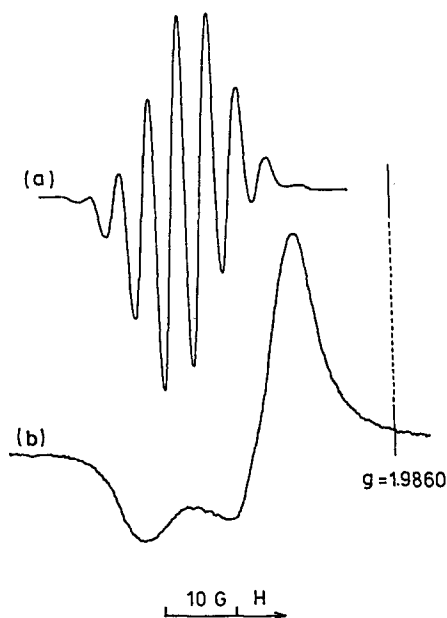
<sup>†</sup> 1 Torr = (101325/760)Pa.

*et al.*<sup>6</sup> Addition of dioxygen to the pyrolyzed ditropenyl vapour did not change the fragmentation pattern; no products of oxidation were detected. This is in line with the prevailing dissociation of allylperoxyl radicals at the temperature of the ionisation chamber ( $> 470$  K).<sup>2</sup>

The pyrolytic products were also analyzed after their condensation in the Dewar vessel (*vide supra*) and thawing at room temperature. The Dewar vessel was attached through a break seal to the reservoir for gas injection to a JEOL D-100 mass spectrometer. The analyses showed that the pyrolysis of ditropenyl in the absence of dioxygen yielded, in addition to dibenzyl, mainly benzene and lower amounts of styrene, toluene, ethylbenzene and indene. In the presence of dioxygen the pyrolytic products contained, besides dibenzyl and benzene, mainly  $\text{CO}_2$  and lower amounts of benzaldehyde, benzyl alcohol and formic acid. All the products can be accounted for by the reactions of the tropenyl radical, although dibenzyl was suggested to be formed largely in a non-radical way.<sup>6</sup>

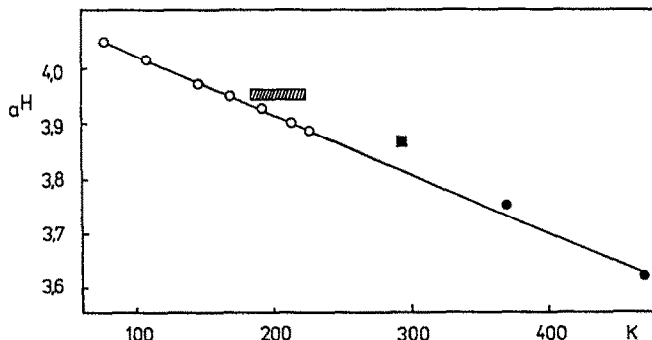
## RESULTS AND DISCUSSION

The tropenyl radical in the co-condensed adamantane matrix. - The ESR measurements at 77 K on the trapped products of pyrolysis at 682 K of ditropenyl vapour revealed the presence of the tropenyl radical  $\text{C}_7\text{H}_7$  only. Its isotropic eight-line ESR spectra were obtained both in the absence and the presence of co-condensed adamantane; however, in the adamantane matrix, the tropenyl radical spectrum was much better resolved (Fig. 1a). The tropenyl radicals decayed in the adamantane matrix at temperatures above 226 K while in its absence, decay



**Figure 1** ESR spectra at 77 K of the tropenyl radical trapped in the co-condensed adamantane matrix (a), the tropenylperoxyl radical trapped in the absence of adamantane (b).

started at 145 K. The improved thermal stability of radicals in the adamantane matrix and well-resolved ESR spectra (peak-to-peak linewidth  $\Delta H$  (77 K) = 2.0 G;  $\Delta H$  (226 K) = 1.75 G) allowed us to establish the thermal dependence of  $a^H$  in the range 77-226 K (Fig. 2), which

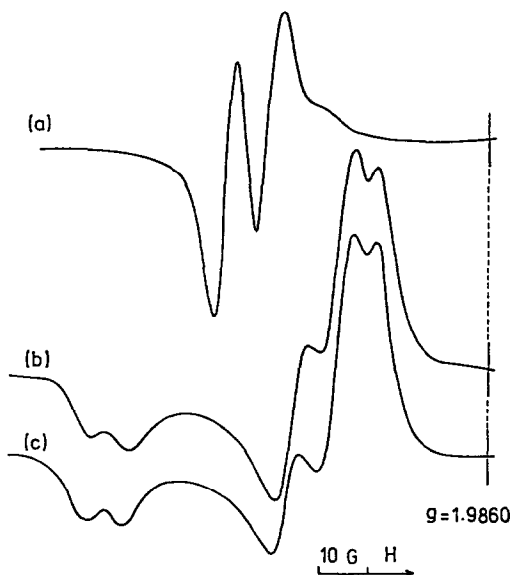


**Figure 2** Dependence of isotropic coupling ( $a^H$  in G) of the tropenyl radical with temperature in various media: (O) adamantane matrix co-condensed from the gas phase; (////) in hydrocarbon solvents (ref. 17); (■) in cyclohexane or n-heptane (ref. 7); (●) in ditrophenyl (ref. 7).

could not be previously done in solution.<sup>7</sup> Reproducible results for the thermal dependence of  $a^H$  were obtained in all but the first thermal cycle which afforded initial  $a^H$  at 77 K higher ( $4.08 \pm 0.02$  G) than in the following thermal cycles. The magnitude of the coupling constant decreased linearly with increasing temperature from  $4.045 \pm 0.015$  G at 77 K to  $3.885 \pm 0.015$  G at 226 K, the rate of increase being  $-1.074 \times 10^{-3}$  G/K, compared with the dependence found in solution at higher temperatures, viz.  $-1.33 \times 10^{-3}$  G/K in the region 353-469 K.<sup>7</sup> The extrapolation of the present temperature dependence correlates well with the highest temperature splitting obtained in liquid ditrophenyl.<sup>7</sup> This suggests that the use of the adamantane matrix eliminates the solvent effects which may influence the ESR spectra, especially at low temperature.

The cycloheptatrienylperoxyl radical in the co-condensed adamantane matrix. - The cycloheptatrienylperoxyl (trophenylperoxyl) radical,  $C_7H_7O_2^{\cdot}$  (III in Scheme) was formed as the only paramagnetic product from pyrolysis of a gaseous mixture containing a slight excess of dioxygen over ditrophenyl (I), e.g.  $p_{O_2} = 1 \times 10^{-2}$  Torr,  $p_I = 8 \times 10^{-3}$  Torr. An insufficient amount of dioxygen resulted in the occurrence of both trophenyl and trophenylperoxyl radical spectra. The ESR spectrum of III trapped in the absence of adamantane (Fig. 1b) gave  $g_1 = 2.035$ ,  $g_2 = 2.009$  and  $g_3 = 2.002$  and did not differ from typical anisotropic spectra of organic peroxyl radicals showing a nearly axially symmetric  $g$ -tensor. Such spectra are virtually invariant with respect to the nature of the organic substituent.<sup>9-11</sup>

If co-condensed with adamantane at 77 K, the trophenylperoxyl radical displayed the anisotropic spectrum differing from the former one by additional splitting in all  $g$ -tensor components (Fig. 3b). This anisotropic spectrum turned to an isotropic doublet with  $g = 2.0157$ ,  $a = 7.5$  G upon warming to 140 K (Fig. 3a). It reversibly turned to the anisotropic



**Figure 3** ESR spectra of the tropanylperoxyl radical in the co-condensed adamantane matrix (a) at 140 K, (b) at 77 K, (c) simulated spectrum (b).

spectrum on recoiling to 77 K. The latter spectrum appeared to be slightly better resolved than the original one. The peroxyl radical rapidly decayed at 150 K. The simulation of the anisotropic spectrum gave best agreement with the experimental spectrum for following values of the  $g$ - and  $a$ -tensors:  $g_1 = 2.035$ ,  $g_2 = 2.009$ ,  $g_3 = 2.002$ ;  $a_1 = 8.4$  G,  $a_2 = 9.6$  G,  $a_3 = 5.35$  G. The line width about 2.0 G is typical for this type of adamantane matrix<sup>1,2</sup> (*vide supra*) and the simulated spectrum (Fig. 3c) was obtained with the linewidth values  $\Delta H_1 = 2.4$  G,  $\Delta H_2 = 2.0$  G and  $\Delta H_3 = 1.7$  G with Lorentzian line shape.

A doublet splitting in the ESR spectra of some organic peroxyl radicals derived from some unsaturated esters has been observed for the freely rotating radicals in cyclopropane ( $g = 2.015$ ,  $a = 4.4$ - $5.1$  G, 160 K)<sup>12</sup> while the splitting was not mentioned for peroxyl radicals derived from decalin and 2,6,10,14-tetramethylpentadecane at 403-424 K.<sup>13</sup> We have recently observed a small unresolved doublet splitting in the freely rotating allylperoxyl and 2-methylallylperoxyl radicals in the same adamantane matrix; the latter radical showed additionally a distinct splitting in the anisotropic spectrum.

Proton hyperfine coupling in the anisotropic spectrum is well established for the hydroperoxyl radical  $\text{HOO}^\cdot$  ( $g_{\parallel} = 2.0303$ ,  $g_{\perp} = 2.0044$ ;  $a_{\parallel} = 13.5$  G,  $a_{\perp} = 8.6$  G).<sup>14</sup> Although the  $g$ -tensor is practically very similar to that of  $\text{ROO}^\cdot$  radicals, the proton splitting was clearly observed in soft (Ar)<sup>11,14</sup> and hard ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ )<sup>15</sup> matrices. The possibility that we were actually observing the hydroperoxyl radical seems to be excluded by (i) the differences in the proton coupling constants, (ii) the absence of proton splitting when no adamantane is present, and (iii) the mechanism of generation: the reaction  $\text{R}^\cdot + \text{O}_2 \rightarrow \text{RO}_2^\cdot$

is more probable than  $R' + O_2 \rightarrow HO_2' + R:$ .

The proton splitting in the tropenylperoxyl radical must arise from a  $\beta$ -proton to the peroxy group by a hyperconjugation mechanism since the signs of the proton hyperfine couplings are all the same and the couplings are almost isotropic. The coupling is much smaller than in rotationally averaged  $H_\beta$  coupling (e.g. 25 G in  $CH_3CHCOOH$ )<sup>16</sup> because the unpaired electron in the 0-0  $\pi$  molecular orbital is divided between the two oxygen atoms. Calculations by Rakoczi *et al.*<sup>11</sup> show that the unpaired electron spin density on O(2) is 3-4 times that on O(1) (see III in Scheme).

We have also considered the possibility that the benzyl radical could be a congener of the tropenyl radical since the dibenzyl was found to be formed in pyrolysis of ditropenyl above 623 K (*vide supra*). Our experiments on pyrolysis of dibenzyl, however, showed that thermolysis to benzyl radicals occurred only above 673 K. The isotropic spectrum of the benzyl radical at 77 K (formed by pyrolysis at 773 K) in the co-condensed adamantane matrix was characterized by  $a^H(CH_2) = 16.4$  G,  $a^H(o- \text{ and } p-) = 5.5$  G (for solution spectrum see ref. 17). The spectrum was much broader than that of the tropenyl radical and has never been observed in the pyrolysis of ditropenyl.

In conclusion, trapping radicals from the gas phase in adamantane matrix offers possibility to differentiate between organic peroxy radicals on the basis of the magnitude of their proton coupling constant. Comparative studies on a number of organic peroxy radicals are under way.

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