

## TRAPPING OF ALLYLIC RADICALS FROM THE GAS PHASE PYROLYSIS IN THE ADAMANTANE MATRIX — ISOTROPIC ESR SPECTRA AT 77 K

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A simple device has been developed and tested for trapping radicals from the gas phase onto a cold finger kept at 77 K. The yields of allylic radicals obtained by pyrolysis of allyl hydrocarbons were studied by ESR spectroscopy in dependence on the temperature and pressure of pyrolysis, both in the absence and presence of adamantane. The co-deposition of the radicals with adamantane increased considerably the radical yields and afforded isotropic ESR spectra of allyl radicals ( $\Delta H_{\min} = 0.21$  mT) even at 77 K. The adamantane matrix formed from the gas phase appeared to be less rigid than the crystalline one, as the allylic radicals decayed already at 160–177 K. Yields of the trapped allyl radicals were also compared with the radical yields measured by mass spectrometry using analogous pyrolytic device.

ESR detection of radicals trapped from the gas phase has been widely used in the pyrolytic, photolytic, oxidation and combustion studies of low molecular weight organic substances<sup>1–3</sup> and polymers<sup>4,5</sup>. The radicals were usually trapped in the matrix of other non-paramagnetic reaction products or added inerts, condensed simultaneously on a cold finger<sup>1–3</sup> or in a rotating cryostat<sup>4–6</sup>. The obtained ESR spectra were predominantly anisotropic because the radicals had been trapped in random orientations.

Crystalline adamantane forms one of the few matrices permitting rotational motion of the trapped radicals even at low temperatures stabilizing them up to relatively high temperatures<sup>7</sup>. Since adamantane is relatively insensitive to high energy radiation and non-reactive towards the organic radicals it has been frequently used for stabilization of the radicals generated by  $\gamma$ - or x-irradiation<sup>7–10</sup> and photolysis<sup>11</sup>. In most cases, the studied compounds were incorporated into the adamantane matrix by slow crystallization of the adamantane solution containing minute amounts of the respective compound. A successful attempt was also made to use the adamantane matrix in the rotating cryostat, using separate leaks for admittance of adamantane and the acetyl radicals<sup>12</sup>.

In this paper we report on application of the adamantane matrix for stabilization of allylic radicals generated in the gas phase pyrolysis. In a very simple arrangement, the radicals and adamantane are co-deposited on a cold finger inside a Dewar vessel which, after sealing off, is inserted into the cavity of the ESR spectrometer. Yields and stabilities of the radicals have been studied in dependence on various pyrolytic and trapping conditions, both in the absence and presence of adamantane.

The yields of radicals are compared with those determined by mass spectrometry using the same type of pyrolyser placed in front of the ionisation chamber<sup>13,14</sup>.

### EXPERIMENTAL

**Chemicals.** 1,5-Hexadiene (*I*) and 2,5-dimethyl-1,5-hexadiene (*II*) (Fluka) were distilled *in vacuo* and degassed carefully by repeated thawing under pumping. Adamantane (Koch-Light) was purified by liquid column chromatography (silica gel, n-hexane, column 2 m × 2 cm), however, identical results were obtained also with the commercial product.

**Apparatus.** The all sealed apparatus consisted of a pyrolyser *P* and a trapping Dewar vessel *D*, as shown in Fig. 1. The pyrolyser was made of a quartz tube which was heated from the outside by a resistor wire. The temperature of the pyrolyser was controlled by means of a Pt/PtRh thermocouple *C* which was located in the centre of the pyrolyser. Partial pressure of the biallyl compound (inlet *A*) and adamantane (inlet *B*) were adjusted by dosing metal valves. The gaseous mixture was pumped through the region of *P* and *D*, using an oil diffusion pump equipped with liquid nitrogen trap. After filling *D* with liquid nitrogen, all volatile materials were condensed at the bottom of cold finger and a vacuum  $3 \cdot 10^{-4}$  Pa was restored behind the cold finger. The experiment was terminated by closing the valves *A* and *B*. The Dewar vessel *D* was then sealed off at points *E* and *F* and inserted into the cavity of the ESR spectrometer blown with dry nitrogen.

**Measurements.** ESR spectra were registered on a commercial ESR-220 spectrometer (ZWG, German Academy of Sciences, Berlin, GDR) in the X-band, using 100 kHz modulation. The number of radicals was obtained by double integration of the ESR spectra. The *g*-values were related to the  $Mn^{2+}$  standard ( $g = 1.9860$ ) and the DPPH solution of known concentration was used as the standard for quantitative measurements. The cold finger was warmed up in a controlled way, by blowing cold nitrogen at required temperature through the Dewar vessel *D*.

The mass spectrometric measurements of the radicals were performed on a MI 1305, 60° sector field mass spectrometer, using ionisation with low energy electrons (11–12 eV) as described

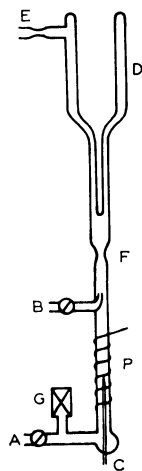


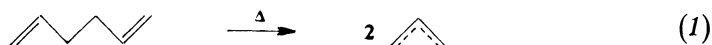
FIG. 1

Device for trapping the radicals generated in gas phase pyrolysis. *A* Inlet of a pyrolyzed hydrocarbon, *B* inlet of adamantane, *C* thermocouple, *D* Dewar vessel, *E*, *F* narrowings for sealing off the Dewar vessel, *G* Pirani gauge, *P* pyrolyser

elsewhere<sup>13-14</sup>. The allyl and 2-methylallyl radicals were measured at the mass-to-charge ratio 41 and 55, respectively.

## RESULTS AND DISCUSSION

Pyrolysis of 1,5-hexadiene (*I*) and 2,5-dimethyl-1,5-hexadiene (*II*) yields selectively the corresponding allyl and 2-methylallyl radicals, *e.g.*, according to equation (1):



Both compounds dissociate in the temperature range 790–1 100 K in comparable amounts as illustrated by the mass spectrometric measurements of decomposed *I* and *II* (Table I).

### Radical Yields in the Absence of Adamantane

The radical yields of pyrolyses of both *I* and *II*, measured by mass spectrometry using low energy electrons, increased both with the temperature of pyrolysis in the range 790–1 110 K (Fig. 2) and with the inlet pressure of the diallyl hydrocarbon ( $5 \cdot 10^{-3}$ – $5 \cdot 10^{-1}$  Pa). At such low pressures, the radical yields were too low to be determined by the ESR method. In this case the radicals were trapped in the matrix formed by the undecomposed fraction of a pyrolyzed hydrocarbon and diamagnetic pyrolytic products. Measurable yields of radicals were obtained only at considerably higher pressures ( $> 1$  Pa) and at temperatures below 1 000 K. The obtained ESR spectra were anisotropic (Fig. 3a,c) and the measured radical yields were little dependent on the temperature and pressure of pyrolysis; the magnitudes of the radical signals varied between  $1 \cdot 10^{16}$  and  $2 \cdot 5 \cdot 10^{16}$  spins within the range of pyrolytic temperatures 790–1 000 K and hydrocarbon pressure 4–32 Pa. Results were generally poorly reproducible; *e.g.*, radical yields  $1 (\pm 0.2) \cdot 10^{16}$  and  $2 (\pm 0.3) \cdot 10^{16}$  spins were obtained for the pyrolyses of *II* carried out at 790 and 950 K, respectively, both at pressure of 8 Pa.

TABLE I

The thermal decomposition of 1,5-hexadiene (*I*) and 2,5-dimethyl-1,5-hexadiene (*II*) measured by mass spectrometry as diminution of *I* (*m/e* 67) and *II* (*m/e* 95), in percent

Temperature, K	790	910	950	990	1 070
<i>I</i> ( <i>m/e</i> 67)	1	12	20	26	48
<i>II</i> ( <i>m/e</i> 95)	1	8	15	26	50

Since the collisions of radicals with the walls are frequent at the low pressures used, we have attempted to improve the radical yields and reproducibility of the results by work-up of the glass surface with radicals prepared by pyrolysis. For this purpose,

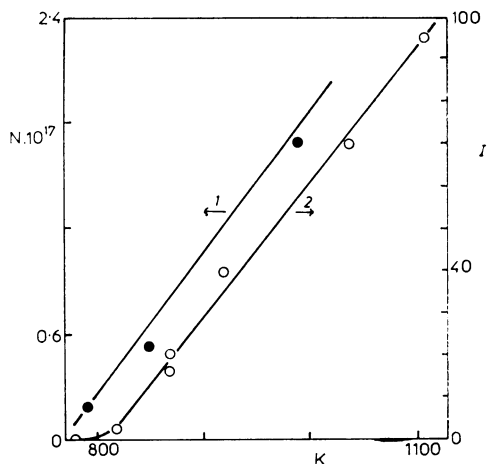


FIG. 2

Thermal dependences of the yields of 2-methylallyl radicals. 1 Measured by ESR using the adamantane matrix (pressure of  $II$   $2.6 \cdot 10^{-2}$  Pa, pressure of adamantane 9.0 Pa); 2 measured by mass spectrometry (pressure of  $II$   $2.3 \cdot 10^{-2}$  Pa). The yields are expressed as a number of radicals  $N$  (left) and intensity  $I$  of  $m/e$  55 in arbitrary units (right)

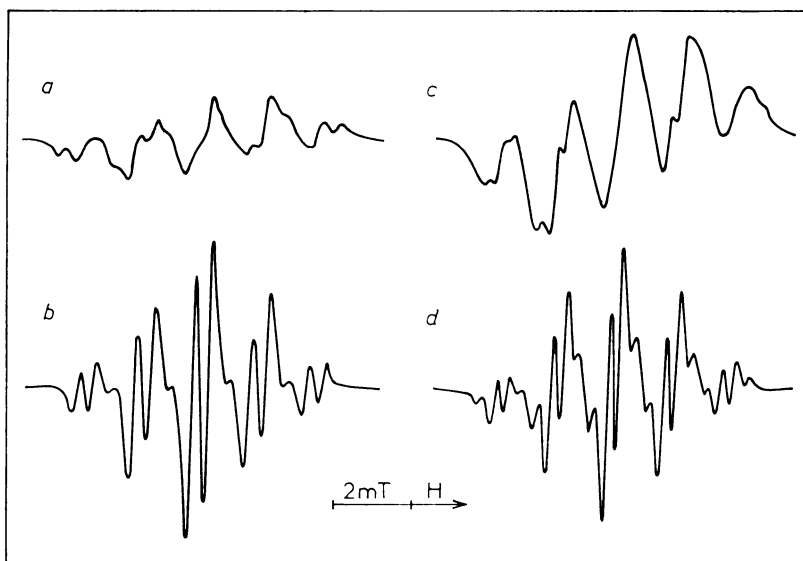


FIG. 3

The ESR spectra of allylic radicals trapped at 77 K. *a* Allyl radical in 1,5-hexadiene; *b* the same in adamantane; *c* 2-methylallyl radical in 2,5-dimethyl-1,5-hexadiene; *d* the same in adamantane

the respective biallyl hydrocarbon was pyrolyzed at 1 100 K, for 1 h at 8 Pa, without cooling the finger trap. In an immediately following experiment, the yield of the trapped radicals increased in average about four times, giving ESR signals corresponding to  $4 \cdot 10^{16} - 1 \cdot 10^{17}$  spins. Nonetheless, a poor reproducibility and little dependence of the radical yields on temperature of pyrolysis have not improved.

### Radical Yields in the Adamantane Matrix

Application of the adamantane matrix condensed together with the pyrolytic products increased generally the yields of trapped radicals, improved substantially the reproducibility of results and provided isotropic ESR spectra of the trapped radicals. Optimum yields were obtained after one hour pyrolysis at partial pressure of adamantane 9 Pa, giving approximately a 6 mg matrix. Further prolongation of the pyrolysis did not lead to proportional increase of the radical yields, presumably as a consequence of insufficient cooling of the matrix surface.

The dependences of radical yields on pyrolytic temperature and pressure were studied in detail for *II* (Fig. 4); the results obtained with *I* were analogous, only the maximum radical yields were about twice as low as those of *II*. At the lowest partial pressure of *I* and *II* which we were able to adjust ( $2.6 \cdot 10^{-2}$  Pa), the radical yields in the adamantane matrix increased proportionally to the temperature of pyrolysis (Fig. 2), following the linear dependence of the radical yields obtained by mass spectrometry in the absence of adamantane (Fig. 2). At higher pressures, the radical yields varied with the temperature of pyrolysis, as one can see in Fig. 4. Optimum radical yields were obtained at 910 K, for pressures near 0.6 Pa. Above these values, the radical yields decreased with the increase of both the temperature and the pres-

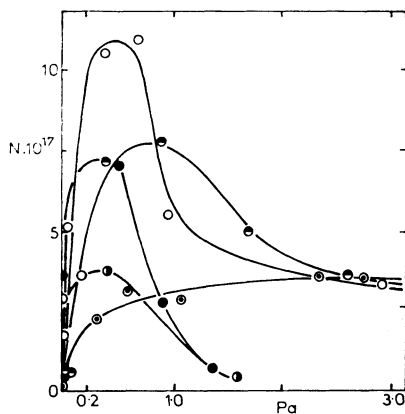


FIG. 4

Dependence of the number of 2-methylallyl radicals  $N$  trapped in the adamantane matrix on partial pressure of 2,5-dimethyl-1,5-hexadiene at different temperatures of pyrolysis.  $\circ$  790 K,  $\circ$  910 K,  $\bullet$  950 K,  $\bullet$  990 K,  $\bullet$  1070 K

sure, except the dependence obtained at the lowest temperature 790 K. These effects can be explained by the increased probability of mutual interaction of radicals in the gas phase and in the solid phase though the influence of the dilution of the adamantane matrix and possible increased temperature of the surface of matrix should be taken into account, too.

Decrease of the radical yields at high temperature and pressure was also observed in the mass spectrometric measurements, in the pyrolysis carried out at 1 070 K and at about  $5 \cdot 10^{-1}$  Pa. Under these conditions, disproportionation products of allyl radicals (propylene and allene) were clearly detected along with *I* and allyl radicals. On the other hand, at pressures below  $1 \cdot 10^{-1}$  Pa, no products besides allyl radicals were detected.

We have also tried to separate the possibly existing stabilizing influence of adamantane on the radicals in the gas phase, from the stabilization effect of the solid adamantane matrix. For this purpose, adamantane ( $\leq 3$  Pa) was admitted into the pyrolyser connected to the mass spectrometer through a leak and equipped with a by-pass pumping. In this arrangement, nevertheless, the concentration of the detected allyl radicals considerably decreased and no reasonably accurate dependence of the number of detected radicals on the adamantane pressure was established. We assume, that though some stabilization of allyl radicals in the flow of gaseous adamantane cannot be excluded, stabilization of the allyl radicals in the solid adamantane matrix is clearly the most important factor enhancing the trapped radicals yields.

#### *ESR Spectra and Stability of Radicals*

In the absence of adamantane, only anisotropic spectra of the allyl and 2-methylallyl radicals (Fig. 3a,c) were observed. Both these radicals decayed after the samples had been warmed up to 133 K. In the case of application of the adamantane matrix, isotropic ESR spectra of the above radicals were found as it is illustrated in Fig. 3b,d. The minimum line halfwidth  $\Delta H = 0.21$  mT at 77 K was obtained for radical yields below  $4 \cdot 10^{16}$  spins (corresponding to the radical/adamantane molar ratio 1 : 600) and partial pressures of pyrolyzed hydrocarbons lower than 0.2 Pa. Under other conditions, the resolution was partly smeared by the radical-radical interactions and by dilution of the adamantane matrix with the hydrocarbon. Coupling constants of both allylic radicals in the adamantane matrix are comparable with the values measured in the solution<sup>15</sup>, within the limit given by the larger linewidth (Table II).

A controlled warming of the samples during the ESR measurement led to further improvement of the resolution to minimum 0.18 mT for the 2-methylallyl radical at 177 K and 0.19 mT for the allyl radical at 167 K. At these temperatures, the radical decay was, however, so rapid that the ESR spectra were diminishing during the measurements. The comparison with the decay temperatures of the allylic radicals in the crystalline adamantane matrix (allyl: > 175 K, 2-methylallyl: > 298 K — ref.<sup>11</sup>)

indicates that the probably microcrystalline adamantane matrix prepared from the gas phase is less rigid than the crystalline one.

A typical kinetics of the allyl radical decay at 163 K (Fig. 5) reflects a broad distribution of energy potentials of the trapping sites affording a fraction of long-lived radicals even at this temperature. Simultaneously, it proves the absence of possible phase transition in the adamantane matrix<sup>16</sup> between 77 and 163 K, usually inducing the sudden fast radical decay. Thermal annealing experiments have also proved that the radical-radical interaction has minor influence on the ESR line width compared to the effect of the dilution of adamantane matrix with the diallyl hydrocarbons. *E.g.*, the thermal annealing of the sample prepared by pyrolysis of *I* at 950 K

TABLE II  
Coupling constants of allylic radicals

Radical		Coupling constants, mT	
		present work	in solution <sup>15</sup>
Allyl	$a_{\text{H}}(1,3\text{-syn})$	1.46	1.481
	$a_{\text{H}}(1,3\text{-anti})$		1.390
	$a_{\text{H}}(2)$	0.42	0.406
2-Methylallyl	$a_{\text{H}}(1,3\text{-syn})$	1.43	1.468
	$a_{\text{H}}(1,3\text{-anti})$		1.382
	$a_{\text{H}}(\text{CH}_3)$	0.34	0.319

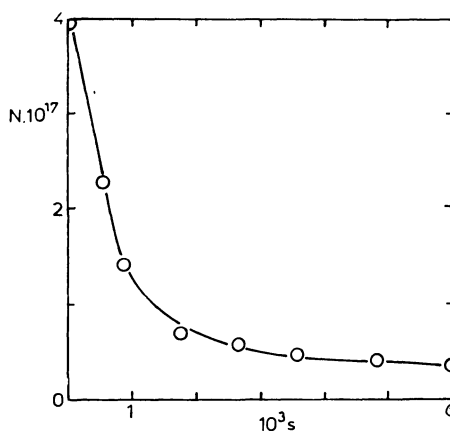


FIG. 5

Decay of the allyl radicals in adamantane matrix at 163 K. Pyrolysis of *I* at 950 K, pressure of *I* 1.0 Pa, pressure of adamantane 9.0 Pa, duration 1 h

and at the partial pressure of  $I$  1.0 Pa (Fig. 5) was accompanied with a change of  $\Delta H = 0.25$  mT of the original sample at 77 K to  $\Delta H = 0.19$  mT at 163 K, measured after annealing of the sample. The latter sample containing very diluted radicals ( $\sim 4 \cdot 10^{16}$  spins) exhibited the value  $\Delta H = 0.24$  mT after re-cooling down to 77 K which is considerably higher than the value (0.21 mT) found in samples containing the same concentration of radicals but prepared at low partial pressures of  $I$  ( $\leq 0.2$  Pa).

#### *Limitations and Advantages of the Method*

The application of the adamantane matrix for trapping of pyrolytic radicals in the described apparatus is limited by the insufficient pumping rate of the arrangement which allows the gaseous adamantane to enter the pyrolyser, and hence to be pyrolyzed together with the substrate. Blank experiments on the adamantane pyrolysis showed that no radical products were trapped below 1 070 K, yet, a mixture of radicals was detected above this temperature. Among the observed radicals, only the allyl radical was identified with high probability. Other species, characterized by the outermost doublet  $a = 0.44$  mT separated by 7.7 mT, was assigned only tentatively to some derivative of the cyclohexadienyl radical<sup>16</sup>. Nevertheless, for pyrolysis carried out below 1 070 K the application of the adamantane matrix promises the enhanced radical yields and easier identification of radicals from their isotropic ESR spectra, at least for radicals similar in stability and size to the allyl radicals tested in this work.

The present device, though not suitable for quantitative kinetic studies of radical reactions in the gas phase, is assumed to be a useful tool in the studies of pyrolytic and photodissociative mechanisms as well as in studies of the reactions of radicals with small molecules. A study of the allyl radical reactions with dioxygen is in progress.

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