

# EPR Spectrum of Radicals from Thermal Decomposition of 1,1,2,2-Tetraphenyl-1,2-bis(trimethylsiloxy)ethane

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Free radicals generated by thermal decomposition of tetraphenyl-1,2-bis(trimethylsiloxy)ethane were studied by EPR spectroscopy. The maximum amount of free radicals was obtained at temperature 403 K. Hyperfine splitting constants of diphenyl-(trimethylsiloxy)methyl radicals were determined and a good agreement between experimental and simulated EPR spectra has been found.

Various types of hexasubstituted ethanes are known to decompose into relatively stable alkyl radicals which are capable of initiating free radical polymerization. This represents some practical interest since the initiator moiety attached to the polymer molecule may become the site of further transformation processes.

In this paper we present EPR spectrum of the free radicals formed in thermal decomposition of tetraphenyl-bis(trimethylsiloxy)ethane (TPSE). These radicals were studied first by *Neumann et al.* [1, 2], who UV-irradiated benzene solutions of TPSE and determined hyperfine splitting constants of radicals observed. Our contribution is based on determination of hyperfine splitting constants of thermally prepared radicals which are confirmed by a parallel simulation of corresponding EPR spectrum and on measuring the equilibrium dependence of amount of radicals on temperature.

## EXPERIMENTAL

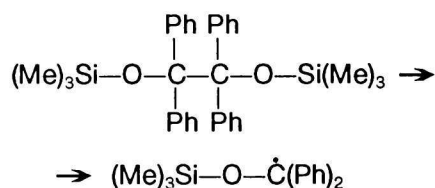
1,1,2,2-Tetraphenyl-1,2-bis(trimethylsiloxy)ethane was synthesized from trimethylchlorosilane and benzophenone in the presence of metallic magnesium in tetrahydrofuran. The reaction was facilitated by a small amount of hexamethylphosphotriamide [3].

A solution of  $5 \times 10^{-2}$  M TPSE in hexachloro-1,3-butadiene was used for EPR measurements which were performed on a spectrometer ER 200D SRC (Bruker) with X-band cavity resonator ER 4102 ST at 12.5 kHz modulation frequency. The experiments were carried out in the temperature interval 320–460 K. Acquisition of spectra and their simulations were done on a data system ER 140 based on a computer ASPECT 2000.

The hyperfine splitting constants were determined by the autocorrelation method using an FT EPR spectrum [4] and the method of proton coupling constant extraction [5, 6]. These constants were used for simulation of theoretical spectrum. The splitting constants were optimized in order to obtain the best agreement between simulated and experimental spectra.

## RESULTS AND DISCUSSION

The decomposition of TPSE can be registered on EPR spectrometer when temperature of a sample exceeds 340 K. The formation of free radicals is schematically depicted by the equation



Free radicals ( $g = 0.0030 \pm 0.0001$ ) generated at lower temperatures can be observed for hours. As temperature is increased the amplitude as well as the resolution of the spectrum gradually increases. This occurs up to temperature of 400 K when an equilibrium level of radicals starts to decrease. Figs. 1a and 1b show the spectrum recorded at 370 K and the computer-simulated spectrum based on hyperfine splitting constants  $a_o = 0.324$  mT,  $a_m = 0.126$  mT, and  $a_p = 0.360$  mT ( $\pm 0.0003$  mT). The line shape is assumed to be Gaussian and the line width is  $\Delta B_{pp} = (0.006 \pm 0.0005)$  mT. As we can see a good correspon-

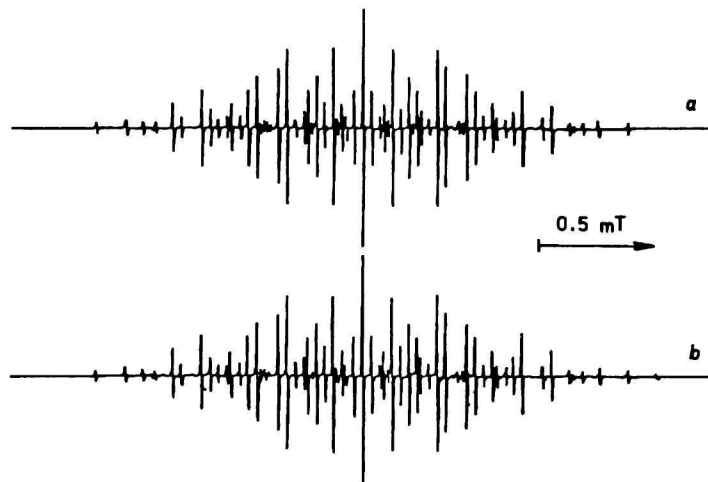


Fig. 1. EPR spectrum of diphenyl-(trimethylsiloxy)methyl radicals at 370 K: a) experimental, b) simulated.

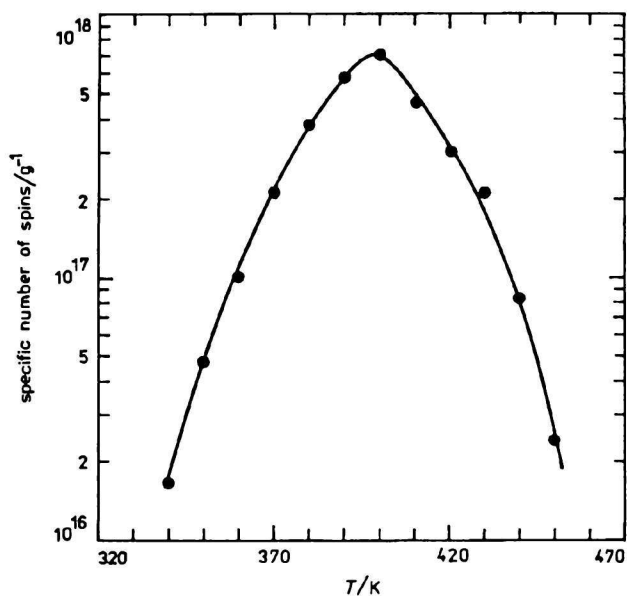


Fig. 2. Temperature dependence of the amount of diphenyl-(trimethylsiloxy)methyl radicals determined by the specific number of spins.

dence between both the experimental and simulated spectrum indicates that the hyperfine splitting constants were well determined.

Fig. 2 shows the equilibrium dependence of the amount of free radicals on the temperature of the sample. The amount of free radicals in the mea-

suring cell (ampoule) was determined with standard precision. There are some imprecisions in the values of the TPSE concentrations in solutions. The problem consists in the fact that the solubility of TPSE in the particular solvent is not perfect. The solubility also depends on the temperature and stirring of the solution in the ampoule. In spite of the complications indicated, the curve in Fig. 2 characterizes well the temperature dependence of the amount of diphenyl-(trimethylsiloxy)methyl radicals. The maximum radical content is achieved at 403 K. This value was determined on the basis of several measurements with the accuracy of  $\pm 5$  K.

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