# ESR spectra of trifluoromethyl radical formed during the solid-phase photodecomposition of long-lived perfluoro-2,4-dimethyl-3-ethylpentyl-3 radicals

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The products of photolysis of the long-lived radical $[(CF_3)_2CF]_2C^{\cdot}C_2F_5$ at 77 K were studied by ESR. The mechanism of photodecomposition to form $^{\cdot}CF_3$ radicals was proposed. The ESR spectra of the trifluoromethyl radicals stabilized at 77 K in a glassy hexafluoropropylene trimer matrix were simulated, and the parameters $A_\parallel$ = 25.15 mT, $A_\perp$ = 9.1 mT, and $g_\parallel$ = 1.9996, $g_\perp$ = 2.0056 were determined.

**Key words:** trifluoromethyl radical, ESR spectroscopy.

The $^{\cdot}CF_3$ radical probably exceeds the other low-molecular perfluoroalkyl radicals by the number of the ESR studies. In the ESR spectrum of the $^{\cdot}CF_3$ radical in the liquid phase,[1] the dipole interactions are averaged, the lines are narrowed, and a quadruplet with splitting $\Delta H$ = 14.24 mT is detected. The quadruplet is resulted from the interaction of an unpaired electron with three equivalent F nuclei. Studies of the $^{\cdot}CF_3$ radicals in the solid phase[2—8] exhibited complex multicomponent ESR spectra. The ESR spectrum of the $^{\cdot}CF_3$ radicals randomly oriented in the matrix of zeolite I3X was also studied.[3] However, it is difficult to interpret all lines of the multicomponent spectrum of the $^{\cdot}CF_3$ radicals stabilized in polycrystalline or amorphous matrices because of the superposition of signals from other paramagnetic centers (PC).

In this work, we investigated the spectrum of the $^{\cdot}CF_3$ radicals in the solid matrix of the hexafluoropropylene trimer (HFPT) without admixtures of other PC during the photodecomposition of the long-lived radicals $[(CF_3)_2CF]_2C^{\cdot}C_2F_5$ (**1**).

## Experimental

Samples of HFPT contained two isomers: $[(CF_3)_2CF]_2C{=}CFCF_3$ (47%) and $(CF_3)_2CF_2C(C_2F_5){=}C(CF_3)_2$ (53%). To obtain long-lived radicals **1**, HFPT samples were evacuated to a residual pressure of 3—10 Torr and exposed to γ-irradiation from the $^{60}Co$ source at 77 K with a dose of 1.4 mGy. Then the samples were heated and stored at 300 K for 1 month, after which they represented a solution of radical **1** in HFPT with a concentration of $3 \cdot 10^{20}$ $g^{-1}$.

Radiolysis of samples at 77 K was carried out in ampules of the SK-4B glass, which gave no ESR signal during radiolysis. The power of the irradiation dose was 28 Gy $s^{-1}$. Photolysis of samples at 300 K was performed by the full light from a high-pressure DRSh-1000 mercury lamp in quartz cells 4—5 mm in diameter, which gave no ESR signal.

ESR spectra were detected on a small-size PS100.Kh radiospectrometer. ESR spectra of the radicals were automatically detected and simulated on a computer using the programs of the Scientific Technical Cooperative Center of Radiospectroscopic Instrument Making "Tsentrospektr" (Minsk).

## Results and Discussion

Significant changes occur in the ESR spectrum during photolysis at 77 K of radicals **1** in the glassy HFPT matrix (Fig. 1). The disappearance of the spectrum of radicals **1** is accompanied by the appearance of a complex ESR signal (see Fig. 1, *c*) with a total splitting of 75.5 mT and characteristic four lines with a distance of 25.15 mT. In addition, two asymmetric lines are detected in the central region of the spectrum. These two groups of lines were tentatively ascribed[5] to different PC. However, we found that the intensities of all the lines depend equally on the UV irradiation time. Moreover, the kinetics of the appearance and decay upon heating is the same for these lines, and this is parallel to the kinetics of changing the overall PC concentration during the low-temperature (77 K) photolysis of the sample with radicals **1** followed by its heating. This suggests that all lines of the spectrum belong to the same PC. As shown by the analysis of the spectrum (see Fig. 1, *c*), this PC is the $^{\cdot}CF_3$ radical with axial symmetry.

The line-image reconstruction of the spectrum of the $^{\cdot}CF_3$ radical (see Fig. 1, *c*) shows that all three F atoms of the $^{\cdot}CF_3$ radical are equivalent. The following main values of the components of the *g* factor and the components of the HFC tensor for the F atom were determined: $A_\parallel$ = 25.15 mT, $A_\perp$ = 9.1 mT, and $g_\parallel$ = 1.9996, $g_\perp$ = 2.0056.

Figure 1, *f* presents the results of simulation of the ESR spectra of the $^{\cdot}CF_3$ radicals in the glassy HFPT

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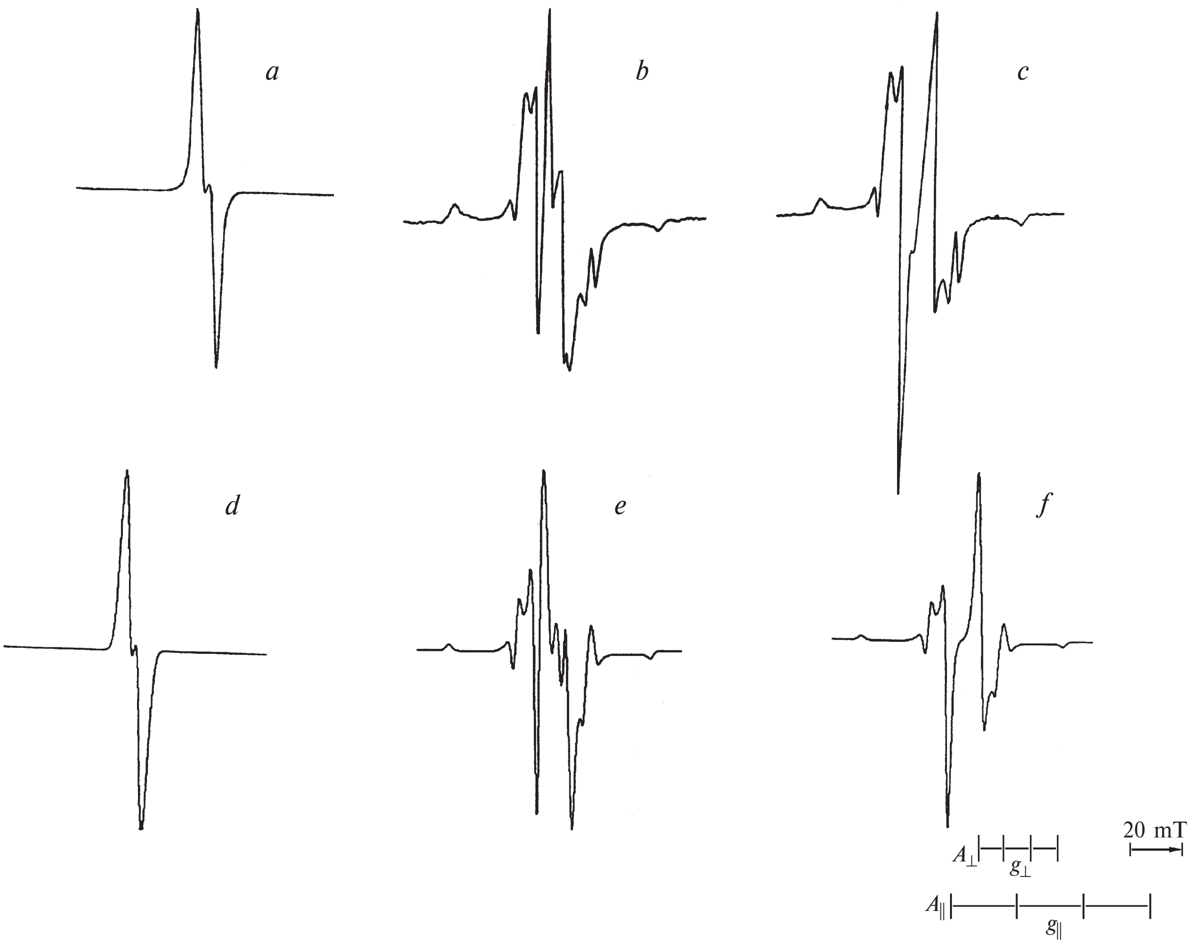

**Fig. 1.** Experimental (*a—c*) and model (*d—f*) ESR spectra of the $[(CF_3)_2CF]_2C^{\cdot}C_2F_5$ radical in the HFPT matrix before (*a*, *d*) and after UV irradiation at 77 K for 280 (*b*, *e*) and 800 min (*c*, *f*) and line-image reconstruction of the ESR spectrum of the $^{\cdot}CF_3$ radical (*f*).

matrix at 77 K based on the experimental data. As known,[9] the shape of the asymmetric ESR line of the Gaussian or Lorentzian type depends only on one anisotropy parameter $\delta = (|H_{\parallel} - H_{\perp}|)/\Delta H_i$, where $\Delta H_i$ is the individual linewidth between the points of maximum slope; $H_{\parallel}$ and $H_{\perp}$ are the magnetic field intensities corresponding to the limiting positions of the individual line for changing the angle between the $H_0$ direction and symmetry axis from 0 to $\pi/2$. The spectra of the $^{\cdot}CF_3$ radical (see Fig. 1, *c*, *f*) allows the determination of four values of the δ parameter: two values from lateral ($\delta_{1,2} \approx 9$) and two values from inner ($\delta_{3,4} \approx 3$) components of the $H_{\parallel}$ and $H_{\perp}$ components of quadruplets. According to earlier published data,[9] analysis of experimental spectra is simple at these δ values, and the $H_{\parallel}$ and $H_{\perp}$ values can be determined with a high accuracy (to 5%) at $\delta \geq 5$. The theoretical spectrum (see Fig. 1, *f*) simulated taking into account the above parameters agrees well with the experimental spectrum (see Fig. 1, *c*). Thus, simulation confirms that the central lines are, in fact, the components of the spectrum of the $^{\cdot}CF_3$ radical.

By analogy to thermal decomposition,[10] we can assume that the photodecomposition of radicals **1** with the elimination of the trifluoromethyl radical occurs according to the reaction

$$[(CF_3)_2CF]_2C^{\cdot}C_2F_5 \longrightarrow$$
$$\longrightarrow [(CF_3)_2CF]C(C_2F_5){=}CF(CF_3) + {}^{\cdot}CF_3.$$

Only prolonged (≥400 min) photolysis allows the almost complete decomposition of radical **1** to be achieved during a long time (see Fig. 1, *c*). The ESR spectrum of the samples irradiated for a relatively short time (see Fig. 1, *b*) is a superposition of the spectra of the $^{\cdot}CF_3$ and **1** radicals. The fraction of the $^{\cdot}CF_3$ radicals can rather exactly be determined by simulation of experimental spectra. The ESR spectrum of radical **1** in the glassy HFPT matrix at 77 K exhibits a doublet with a splitting of 4.6 mT (see Fig. 1, *a*). The *g* factor for radical **1** is[10] 2.00286. Simulation of the spectrum of radical **1** (see Fig. 1, *a*) shows that the shape of its individual components is described by the Gaussian function and their width is ~4.4 mT. Analysis of the

ESR spectrum of a solution of radical **1** in HFPT UV-irradiated at 77 K for 280 min showed that in this sample the ratio of concentrations of the radicals is [$^{\cdot}CF_3$] : [**1**] ≈ 1 : 3 (see Fig. 1, *b*, *e*). Thus, the simulation of the experimental spectra of the irradiated samples containing radicals **1** and $^{\cdot}CF_3$ allows the determination of the fractions of the radicals in the sample.

Based on the interpretation of the ESR spectra of the $^{\cdot}CF_3$ radical, which is the decomposition product, we can assume that the photodecomposition mechanism of radicals **1** includes the formation of the $^{\cdot}CF_3$ radical. However, the selectivity of the C—CF bond cleavage remains unclear. The ESR spectra of the $^{\cdot}CF_3$ radicals similar to that detected in the glassy HFPT matrix were also recorded in the γ-irradiated at 77 K polycrystalline samples of an aqueous solution of $CF_3COOH$ [4] and photolyzed at 77 K $CF_3COCF_3$ samples[3] adsorbed on zeolite I3X. The parameters of these spectra almost coincide with those obtained in this work and, therefore, the simulated spectrum of the $^{\cdot}CF_3$ radicals in the HFPT matrix (see Fig. 1, *f*) can be used for the identification of these radicals in other matrices.

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