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Formation and decay of trifluoromethyl radicals during photodecomposition of the long-lived perfluoro-2,4-dimethyl-3-ethylpent-3-yl radical

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UV irradiation of the long-lived radical $[(CF_3)_2CF]_2C^{\cdot}C_2F_5$ (**1**) in a hexafluoropropylene trimer (HFPT) glassy matrix at 77 K and in a HFPT solution at 300 K leads to its decomposition to the $^{\cdot}CF_3$ radical and perfluoroolefin molecule. About 90% of the $^{\cdot}CF_3$ radicals formed recombine at 300 K. The remaining radicals add to the HFPT molecules generating the long-lived radicals $[(CF_3)_2CF]_3C^{\cdot}$. Unlike the $^{\cdot}CF_3$ radicals produced by the photodecomposition of radicals **1**, the $^{\cdot}CF_3$ radicals formed during radiolysis of HFPT are not stabilized in the glassy HFPT matrix at 77 K.

Key words: long-lived perfluoroalkyl radical, photodecomposition, $^{\cdot}CF_3$ radical, ESR spectroscopy.

Numerous publications on ESR studies of the $^{\cdot}CF_3$ radicals formed upon low-temperature radiolysis of fluoroorganic compounds are available in the literature.[1] Meanwhile, the kinetics of their accumulation in solid matrices is poorly studied. This is associated with difficult separation of a complicated ESR spectrum of the $^{\cdot}CF_3$ radicals from the spectrum of irradiated fluoroorganic compounds and with a very low concentration of the stabilized $^{\cdot}CF_3$ radicals.

The products of radical photodecomposition of the $[(CF_3)_2CF]_2C^{\cdot}C_2F_5$ radicals (**1**) have previously[2] been studied in a solid HFPT matrix (77 K). Radicals **1** were shown to decompose to form the $^{\cdot}CF_3$ radicals. The absorption spectra of HFPT and radicals **1** and the excitation spectrum during the photodecomposition of radical **1** have been studied.[3] The optical absorption spectrum of liquid HFPT exhibits two absorption bands: at $\lambda_{max} < 185$ nm and at $\lambda_{max} < 250$ nm ($\varepsilon_{250} = 6$ L mol^{-1} cm^{-1}). The maximum of the optical absorption band of radicals **1** appears at $\lambda_{max} < 220$ nm ($\varepsilon_{250} = 4.9$ L mol^{-1} cm^{-1}). The study of the action spectrum showed that the photodecomposition of radical **1** begins with irradiation at $\lambda < 350$ nm. When photolysis is conducted in quartz ampules with the full light from a high-pressure mercury lamp for ≥400 min, an almost complete conversion of radicals **1** can be achieved in the glassy HFPT matrix at 77 K and an individual ESR spectrum of the $^{\cdot}CF_3$ radicals can be observed.

In this work, we studied the specific features of accumulation and decay of the $^{\cdot}CF_3$ radicals during photodecomposition of radicals **1** in the glassy (77 K) and liquid (300 K) HFPT matrices.

Experimental

A solution containing $3 \cdot 10^{20}$ g^{-1} of radicals **1** in HFPT was prepared according to a described procedure.[2] To prepare samples with a lower concentration of radicals **1**, this solution was diluted with the starting HFPT. HFPT samples contained two isomers: $[(CF_3)_2CF]_2C{=}CFCF_3$ (47%) and $(CF_3)_2CF{-}C(C_2F_5){=}C(CF_3)_2$ (53%).

ESR spectra were recorded on an EPR-21 radiospectrometer (Institute of Problems of Chemical Physics, RAS). An error of determination of the absolute concentration of paramagnetic species was 20—30%, and that for determination of the relative concentration was 5—10%. Samples were UV irradiated *in vacuo* at 77 K in quartz ampules 4—5 mm in diameter. A DRSh-1000 high-pressure mercury lamp with a sufficiently intense continuous emission spectrum in the 210—750 nm range was used as UV source. Samples photolyzed at 77 K were heated by cooled nitrogen vapor and stored at each temperature of experiment for 10 min.

Results and Discussion

The ESR spectrum of the sample photolyzed at 77 K is the superposition of the spectra of radicals **1** and $^{\cdot}CF_3$. The accumulation kinetics of the latter was monitored by a change in the intensities of broad lines[2] with splittings at ~75.5 and 27.3 mT.

As can be seen in Fig. 1, after photolysis for ~400 min an increase in the concentration of the stabilized $^{\cdot}CF_3$ radicals virtually stops. The limiting concentration of the $^{\cdot}CF_3$ radicals depends on the concentration of radicals **1** in the sample. When the concentration of radicals **1** increases from $6 \cdot 10^{17}$ to $3 \cdot 10^{20}$ g^{-1}, the limiting concentration of the stabilized $^{\cdot}CF_3$ radicals ~100-fold increases (see Fig. 1). The photodecomposition rate of **1** is $[R]/dt = \Phi I_0(1 - 10^{-D})$, where [R] is the current concentration of radicals **1**, I_0 is the intensity of the incident light, Φ is the quantum yield of the reaction, t is the time of irradiation, and D is absorbance. The absorbance of the samples containing radicals **1** in concentrations of $6 \cdot 10^{17}$ g^{-1} and $3 \cdot 10^{20}$ g^{-1} at 250 nm ($\varepsilon_{250} = 49$ m^2 mol^{-1}) is 0.245 and 122.5,

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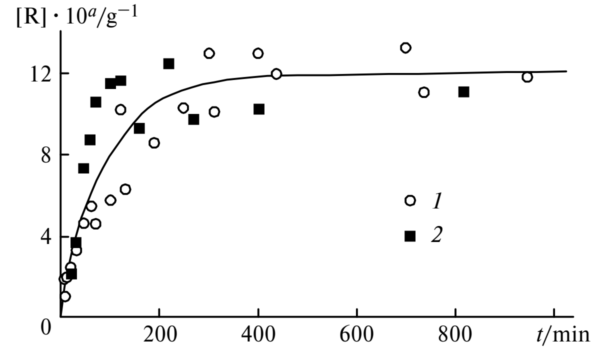

Fig. 1. Kinetics of accumulation of the $^{\cdot}CF_3$ radicals during photolysis (77 K) of samples containing $3 \cdot 10^{20}$ (*1*, $a = -18$) and $6 \cdot 10^{17}$ g^{-1} (*2*, $a = -16$) radicals **1** in the HFPT matrix.

respectively. At low absorbances (0.245), the k value equal to $(184\pm7) \cdot 10^{-4}$ s^{-1} can be determined from the equation $\log([R]_0/[R]) = kt$ ($k = \Phi I_0 \varepsilon l$). At higher D values (122.5), the photodecomposition kinetics of radicals **1** is more complicated but a decrease in the decay rate of the radicals in the samples with $3 \cdot 10^{20}$ g^{-1} we attribute to a sharp increase in D. In the case when all photochemically generated $^{\cdot}CF_3$ radicals are stabilized in the sample, the overall concentration of radicals **1** and $^{\cdot}CF_3$ during photolysis should remain unchanged. The change in the overall concentration of these radicals during photolysis at 77 K is presented in Fig. 2. It is seen that when photolysis is carried out for 400 min the concentration of the radicals decreases, and further the concentration remains unchanged up to the time of irradiation of 1000 min.

A reason for the decrease in the overall concentration of radicals $^{\cdot}CF_3$ and **1** is radical decay during photolysis at 77 K. Quantum-chemical calculations showed that radicals **1** cannot recombine between each other or with the $^{\cdot}CF_3$ radicals because of electronegative and sterically bulky CF_3 groups. Therefore, it is reasonable to attribute the decrease in the overall concentration of radicals **1** and $^{\cdot}CF_3$ to the decay of the $^{\cdot}CF_3$ radicals. The decay of the $^{\cdot}CF_3$ radicals due to F atom abstraction from the HFPT molecule or C—C bond cleavage is thermodynamically unfavorable. Therefore, the $^{\cdot}CF_3$ radicals recombine during photolysis at 77 K.

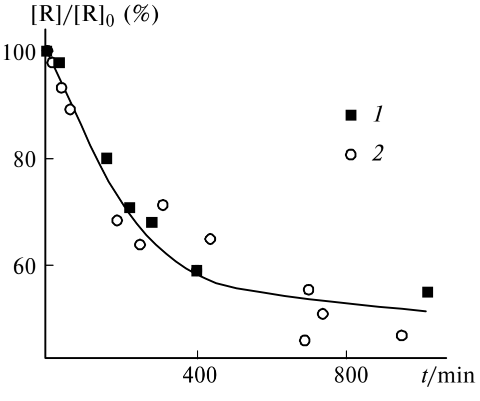

Fig. 2. Plots of the total concentration of radicals **1** and $^{\cdot}CF_3$ detected in the ESR spectra of samples containing $3 \cdot 10^{20}$ (*1*) and $6 \cdot 10^{17}$ g^{-1} (*2*) of radicals **1** *vs.* time of UV irradiation at 77 K.

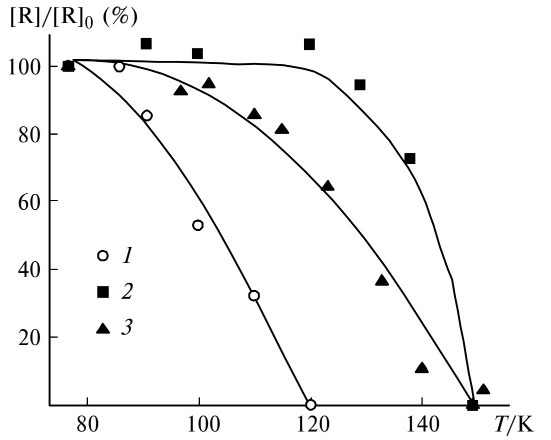

Fig. 3. Temperature plots of the concentration of the $^{\cdot}CF_3$ radicals in samples containing $1.2 \cdot 10^{19}$ (*1*), $1.2 \cdot 10^{18}$ (*2*), and $1.2 \cdot 10^{17}$ g^{-1} (*3*) of $^{\cdot}CF_3$ radicals in the HFPT matrix at 77 K.

We studied the thermal stability of the $^{\cdot}CF_3$ radicals in the HFPT matrix. As can be seen in Fig. 3, on heating the $^{\cdot}CF_3$ radicals stabilized in the solid matrix of glassy HFPT, radical decay begins at temperatures much lower than the vitrification temperature of the HFPT matrix. The beginning of their decay shifts toward lower temperatures with an increase in the concentration of the $^{\cdot}CF_3$ radicals in the sample. This is related, most likely, to the fact that at high concentrations of radicals **1** due to high absorbances of the samples, the $^{\cdot}CF_3$ radicals are mainly formed in the narrow near-boundary layer, and the average distance between them is much shorter than that in other cases considered. When the sample is devitrified (~150 K), the $^{\cdot}CF_3$ radicals decay completely. The $^{\cdot}CF_3$ radicals generated during photolysis at 300 K cannot be stabilized in the liquid and decay. Unlike photolysis in the solid HFPT matrix, in the liquid some $^{\cdot}CF_3$ radicals add to the $[(CF_3)_2CF]_2C{=}CFCF_3$ molecule to form the long-lived $[(CF_3)_2CF]_3C^{\cdot}$ radical (**2**). Quantum-chemical calculations showed that due to steric factors the addition of the $^{\cdot}CF_3$ radical to the second isomer of the HFPT molecule is impossible. The ESR spectrum of radical **2** at 300 K exhibits a multiplet with splitting $\Delta H \approx 0.27$ mT, whose each line is subsplit to a quadruplet with $\Delta H \approx 0.03$ mT. On cooling to 77 K, the ESR spectrum of radical **2** reversibly transforms into a singlet with a width of 2.2 mT. The formation of radical **2** has previously[4] been observed due to the addition of the $^{\cdot}CF_3$ radical, appeared during the thermal decomposition of radical **1**, at the double bond of the HFPT molecule. Thus, the $[(CF_3)_2CF]_2C{=}CFCF_3$ isomer of the HFPT molecule can be used as a spin trap for the $^{\cdot}CF_3$ radicals.

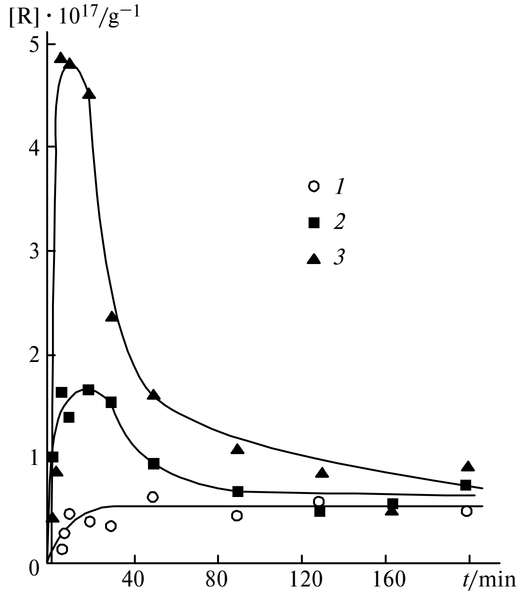

Fig. 4. Plots of the concentration of radicals **2** formed during photolysis of samples containing $6 \cdot 10^{17}$ (*1*), $3 \cdot 10^{18}$ (*2*) and $6 \cdot 10^{18}$ g^{-1} (*3*) of radicals **1** *vs.* time of UV irradiation at 300 K.

The accumulation curves of radicals **2** (Fig. 4) in the samples containing before irradiation at 300 K $6 \cdot 10^{17}$, $3 \cdot 10^{18}$, and $6 \cdot 10^{18}$ g^{-1} of radicals **1** have a maximum after ~15 min of irradiation. Therefore, during photolysis the decay of radicals **2** occurs along with their accumulation. Since the $^{\cdot}\mathrm{CF}_3$ radicals cannot recombine with radicals **2** due to steric hindrances, the decay of radicals **2** is related to their photochemical transformations.

Unlike the $^{\cdot}\mathrm{CF}_3$ radicals generated during the photodecomposition of radicals **1**, the $^{\cdot}\mathrm{CF}_3$ radicals formed by the radiolysis of HFPT are not stabilized in it at 77 K. No spectrum of the $^{\cdot}\mathrm{CF}_3$ radicals is observed in the ESR spectra of the HFPT samples exposed to γ-^{60}Co radiation (a dose of $6 \cdot 10^{-3}$—19 MGy) at 77 K. Our analysis of the HFPT products shows that CF_4 composes a considerable fraction of molecular products. During radiolysis of perfluororganic compounds, the CF_4 molecule can be formed by the recombination of the $^{\cdot}\mathrm{CF}_3$ radicals with the F atoms, which explains, most likely, the absence of a signal from the $^{\cdot}\mathrm{CF}_3$ radicals in the ESR spectrum of HFPT γ-irradiated at 77 K.

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