



Photochemistry of long-lived $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ radicals

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ABSTRACT

The mechanism of the photodecomposition of the long lived radical $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ is explored by UV and ESR spectroscopy and quantum chemical calculations. The kinetics of the photodecomposition of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ are investigated in a matrix of glassy and liquid hexafluoropropylene trimer at 77 and 300 K, respectively. The mechanism of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ photodecomposition does not depend on the phase state of the matrix but differs from the thermal decomposition of the radical. Under UV light with $\lambda < 300$ nm, the CF_2-CF_3 bond of the perfluoro-ethyl group of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ is broken. Thermal decomposition of the radical above 373 K occurs by breaking a $CF-CF_3$ bond in the perfluoro-isopropyl group. The experimental results are consistent with the calculated bond dissociation energies and UV–vis excitation spectra of the radical. Additional calculated C–C BDEs for a number of fluorocarbon radicals show that radicals can be designed with very low C–C BDEs for the generation of $CF_3^{\bullet}$ radicals.

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1. Introduction

Stable radicals are of broad interest, for example, as reactive acceptor or donor intermediates in organic chemistry or as paramagnetic probes and spin labels. They are effective inhibitors of polymerization processes as they frequently inhibit oxidation and are used as the working material in radio-frequency masers and magnetometers. Radicals can be stabilized in a variety of ways and a range of such species is known [1]. Fluorinated long-lived radicals (LLRs) in liquid perfluoro-organic compounds were first detected by Allayarov et al. [2] during the radiolysis of perfluoroorganic compounds, such as the hexafluoropropylene trimer $(HFP)_3$ [2] and subsequently synthesized by Scherer and co-workers [3] by the fluorination of $(HFP)_3$. Allayarov [4] explored the formation of fluorinated LLRs by the γ -radiolysis of more than fifty fluoro-organic compounds and identified ten types of stable radicals in twenty fluoro-organic compounds. One of the most interesting radicals is the LLR $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ formed by the radiolysis of $(HFP)_3$.

The radical $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ is a colorless liquid [5] with a density $d_{25} = 2.05$ g/cc. It is stable in ambient oxygen and slowly reacts with fluorine. When the $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ radical was sealed in Pyrex tubes with excess chlorine or bromine, no reaction was observed over a period of months at room temperature, suggesting that chlorine molecules and certainly bromine molecules are too large to get close enough to the radical center of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ for the reaction to occur. Excess hydrogen bromide was condensed into a Pyrex tube containing $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ and also showed no reaction over months at room temperature. However, the radical is easily and quantitatively reduced by iodide ion. Treatment of a solution containing $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ (3.9 M) with excess sodium iodide in acetone gives a rapid one electron transfer reaction yielding a mixture of isomers $[(CF_3)_2CF]_2C=CF_3$ and $(CF_3)_2CF-C_2F_5=C(CF_3)_2$ of $(HFP)_3$ in a ratio of 44:1 [6]. From the iodide ion experiment, one can deduce that the reduction potential of $R_F^{\bullet}$ radical is greater than 0.535 V, the oxidation potential of iodide ion. Cyclic voltametry provides a more quantitative measurement, so a 10^{-3} M $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ solution in acetonitrile containing tetraethylammonium tetrafluoroborate as the electrolyte was used. The cyclic voltammogram of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ indicated that a non-reversible reduction takes place in the range of 0.550–0.575 V. This nonreversible behavior is expected as the anion can readily eliminate fluoride ion. The first ionization potential of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ is 10.75 eV showing that the unpaired electron of the $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ radical is tightly bound [7]. $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$

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can undergo β -scission to yield an olefin and a new radical on heating above 353 K [5,7] or under UV irradiation [8,9,10]. There have only been a few studies of the use of this radical for chemical applications [11,12].

The current work explores features of the photodecomposition of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$, formed by direct fluorination or by γ -irradiation of $(HFP)_3$.

2. Results and discussion

2.1. Structure of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$

The structure of the radicals formed upon fluorination were explored by analyzing the doublet ESR spectrum with $\Delta H = 4.44$ mT. The unpaired electron gives rise to a narrow line spectrum due to the interaction with one β fluorine in the C_2F_5 group [8]. The angular orientation of the β fluorine can be determined from the ESR spectrum (Fig. 1) using the equation $\alpha_F(\beta) = Q_\beta \rho \cos^2 \theta$, where $\alpha_F(\beta)$ equals the β -fluorine hyperfine coupling, Q_β is a constant, ρ is the spin density of the unpaired electron at the α -carbon atom, and θ is the angle between a projection of the C–F bond and the axis of the orbital of the unpaired electron. For fluorine atom F(27) (see Fig. 2), the hyperfine constant equals 4.44 mT whereas F(26) on the CF_2 of the perfluoroethyl fragment of the radical lies close to the nodal plane ($\theta = 69.5^\circ$) and is characterized by a small coupling. These measurements can be compared to previously published data on fluorocarbon radicals [13].

The structure of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ was optimized using density functional theory (DFT) with the B3LYP functional and the DZVP2 basis set [14,15,16] and is given in Fig. 2; the orientations of the fluorine atoms are consistent with the ESR spectra. It has been

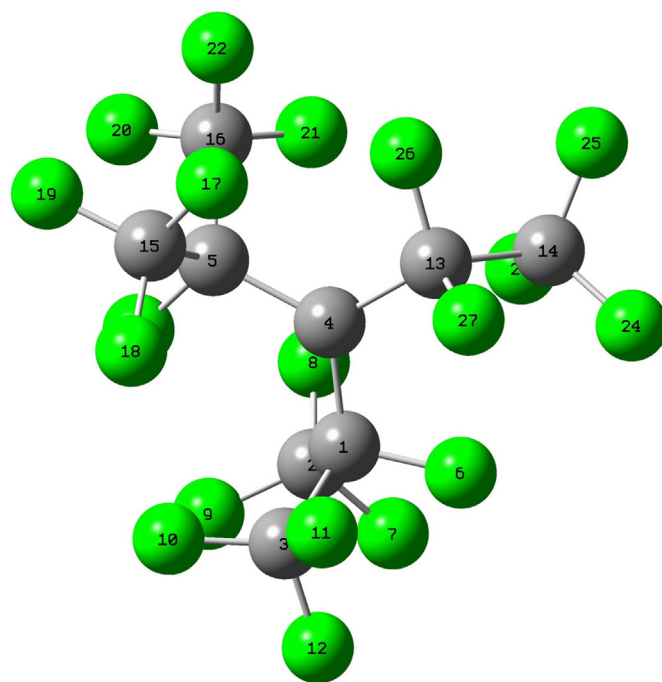


Fig. 2. Optimized structure of $R_F^*(I)$, $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$, at the B3LYP/DZVP2 level.

established that the structure of the radical in the liquid state does not differ from that found in the solid state, i.e. the conformation is apparently locked.

2.2. Mechanism of the photodecomposition of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$

The ESR spectrum of the solid solution of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ in a glassy matrix of $(HFP)_3$ upon photolysis shows appreciable changes (Fig. 1). The disappearance of the ESR spectrum of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ (Fig. 1a) is accompanied by the appearance of a complex ESR signal (Fig. 1b) with a splitting of 75.5 mT and four characteristic lines separated by 25.15 mT. In addition, the central part of the spectrum contains two asymmetric lines. The dependence of these lines with the time of UV irradiation and their appearance and disappearance as a function of heating was determined. All lines of the spectrum belong to $^{\bullet}CF_3$ radicals with axial symmetry and the three fluorine atoms of the radical are equivalent (Fig. 1b). The principal components of the g-tensor and hyperfine couplings are: $A_{||} = 25.15$ mT, $A_{\perp} = 9.1$ mT and $g_{||} = 1.9996$, $g_{\perp} = 2.0056$ respectively. These spectra are representative of samples irradiated for a short time. Total decomposition of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ in the solid phase happens only after UV-irradiation for a long time.

Photolysis of a solution of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$ radicals at 300 K generates new types of long-lived radicals (Fig. 3a versus b). Upon UV irradiation, a new fluorocarbon radical $R_F^*(II)$, (Fig. 3b) is formed and subsequently radical $R_F^*(III)$ is formed (Fig. 3c). The ESR spectrum for $R_F^*(II)$ is due to $[(CF_3)_2CF]_3C^{\bullet}$ formed by addition of $^{\bullet}CF_3$ to $[(CF_3)_2CF]_2C=CFCF_3$. Henderson [5] and Fernandez [7] have studied the addition of $^{\bullet}CF_3$ to $[(CF_3)_2CF]_2C=CFCF_3$ to give the triisopropyl radical and have observed the same ESR spectra growing in due to this addition. In the liquid state, about 90% of the $CF_3^{\bullet}$ radicals recombine with each other at 300 K. Other radicals can also add to $(HFP)_3$ leading to the formation of long-lived radical $R_F^*(II)$.

The ESR spectrum of $R_F^*(III)$ (Fig. 3c) is observed after the disappearance of $[(CF_3)_2CF]_2C^{\bullet}C_2F_5$. We speculate on the structure of $R_F^*(III)$ from the ESR spectrum and the mechanism of its

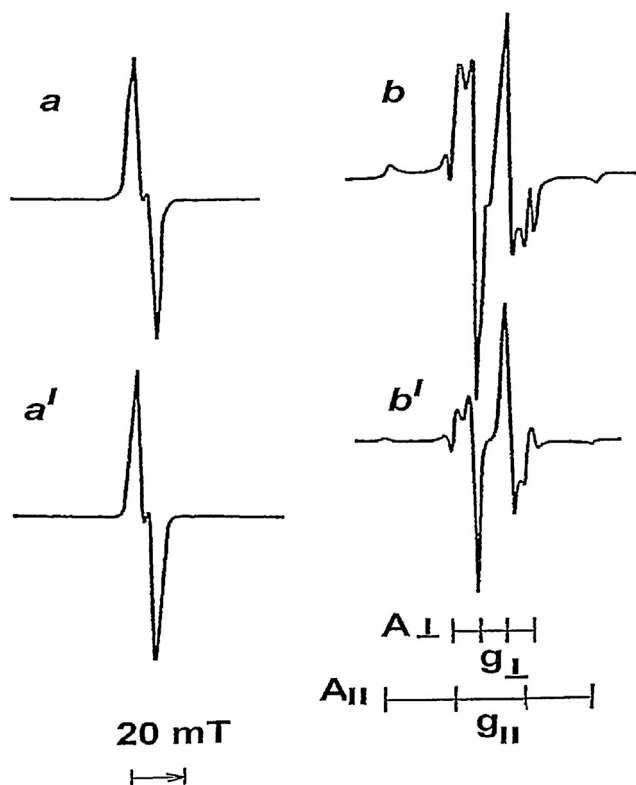


Fig. 1. (a, b) Experimental and (a', b') simulated ESR spectra of the R_F^* radicals in a glassy matrix of $(HFP)_3$ observed (a, a') before and (b, b') after 800 min UV photolysis at 77 K. The stick diagram for the $^{\bullet}CF_3$ radical spectrum is shown below spectrum b'.

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