

The persistent tertiary F-4-ethyl-3,4-dimethyl-3-hexyl radical: a selective trap for monitoring atomic fluorine

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Abstract

The title radical **1** was obtained by elemental fluorination of perfluoro-3,4-dimethyl-4 ethyl-hex-*cis*-2-ene (tetrafluoroethylene pentamer). Its high resolution EPR-spectrum was measured consisting of more than 960 lines. Based on semiempirical quantum chemical calculations, the simulation of the experimental spectrum was performed. This way, structural parameters such as torsion angles, coupling constants of hyperfine splitting (HFS), charge and spin densities were obtained. On this bases the geometric structure of a sterically locked radical is presented, which shows only a small deviation from planarity at the radical site. The chemical and thermal stability was also studied and the kinetics of the thermal pyrolysis of the radical was investigated. The thermal decomposition obeys a first-order kinetic law with an enthalpy of activation of 19.6 kcal/mol. Because the formation of the title radical depends on the existence of atomic fluorine, this fact is used for the detection of intermediate radical fluorine atoms in fluorination processes and the evaluation of their mechanistic pathway. Thus, the stable radical is formed from reactions with XeF₂, CF₃OF and by the electrochemical fluorination process (ECF). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Stable radical; High resolution EPR; Spectra simulation; Kinetics of pyrolysis; Atomic fluorine monitor

1. Introduction

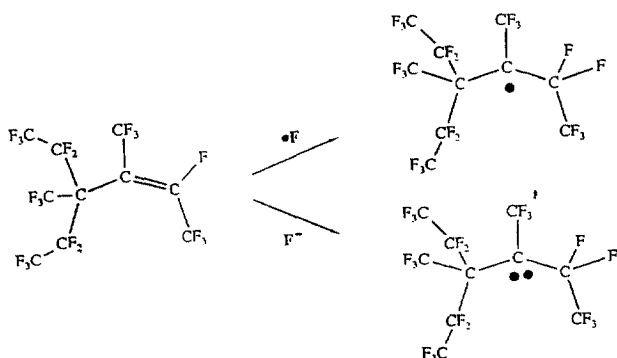
Steric and electronic requirements favour according to the subsequent equation the formation and stability of the title fluorocarbon radical and the corresponding perfluorinated carbanion, which differ only by one electron at carbon atom 3. Concerning the structure at this site of the molecule the question is raised, whether it is planar (sp²) or tetrahedral (sp³). Therefore, a comparison of the geometric structure of the two, their spectroscopic data and chemistry are of interest.

Whereas α-fluororadicals prefer to be pyramidal to minimize inductive repulsions, β-fluorination does not significantly affect the radical geometry [1]. Thus, the F₃C· radical is tetrahedral with a high barrier of inversion of about 25 kcal/mol. On the contrary, the perfluoro *tert*-butyl radical (CF₃)₃C· exhibit a more planar geometry. Scherer et al. [2] has discovered a new type of persistent tertiary fluororadicals, e.g., *iso*-C₃F₇)₂C₂F₅C·, by addition of elemental fluorine to branched fluoro-olefins. Functionalized radicals of this type are reported by Sterlin et al. [3].

Structural peculiarities of the comparable and isolable carbanion (see scheme) obtained by an extensive NMR investigation will be reported elsewhere. Specifically, at low temperatures all alkyl-group rotations are frozen and the rotational barriers were calculated from the ¹⁹F-NMR parameters. In accordance with the splitting pattern of signals and from quantum chemical calculations the carbanion centre is essentially planar. These data contribute in elucidating the radical structure to a great extent.

2. Experimental details

The title radical was obtained by elemental fluorination of the corresponding parent fluoro-olefin under definite condi-



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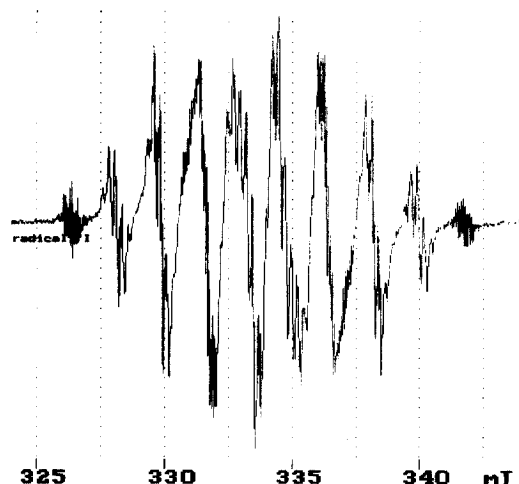


Fig. 1. High resolution EPR-spectrum of F-4-ethyl-3,4-dimethyl-3-hexyl radical.

tions [4]. EPR-spectra were measured from degassed and diluted samples in the X-band at 9.5 GHz microwave frequency. The kinetics of the thermal decay of the radical **1** was studied diluted in perfluorodecalin as solvent in a temperature range from 80–140°C. The formed radical **2** perfluoro 3-methyl-3-pentyl was analyzed by spectra simulation.

The solid fluorination agents xenon difluoride, cobalt(III)-fluoride or Barnette's salt (up to 2 g) were placed in a reaction tube with the F-olefin and if necessary, gently warmed up to about 50°C. The obtained persistent radical in admixture with excess F-olefin were separated from solid or gaseous materials and then transferred to 4 mm sealed quartz tubes for monitoring the EPR-spectrum (see Fig. 1).

3. Results and discussion

The complex hyperfine splitting (HFS)-spectrum was measured in high resolution at 120°C. Based on calculations, the hyperfine splittings of more than 960 lines were analyzed and an assignment was undertaken. Simulation of the observed EPR-spectrum of **1** is based on semiempirical quantum chemical calculations. Using the AM1 method and the UHF-approximation, geometry optimization was achieved from a graphically designed molecular model of the radical.

Together with INDO-UHF calculations torsion angles of atoms in β - and γ -positions to the radical site, spin and charge densities and HFS coupling constants were calculated. With the help of these parameters the fit of the measured and simulated spectrum was performed. The coincidence of the spectra is so high, that a graphical comparison of the two is unnecessary.

Six sets of coupling nuclei were included in the spectra simulation. Additionally, torsion angles and coupling constants are reported (Table 1).

The scheme of Fig. 2 presents the geometric feature of the radical, reflecting the structural properties given in Table 1.

Table 1
Molecular parameters of the $C_{10}F_{21}$ radical

Group	Site	Sets of nuclei	HFS (mT)	Torsion angle (deg)
F	[C ₄]	1	3.56	11.4
F	[C ₄]	1	3.02	49.5
F	[C ₂]		1.83	56.4
F	[C ₂]	2	1.83	59.4
CF ₃	[C ₄]	3	1.69	3.12
CF ₃ CF ₂	[R ₃]		0.23	34.0
CF ₃ CF ₂	[R ₂]		0.23	26.2
CF ₃	[C ₃]	3	0.08	89.4

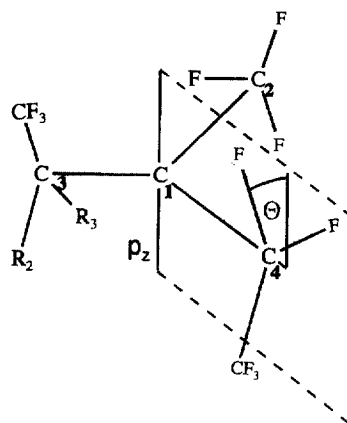


Fig. 2. Scheme of the angular arrangement of substituents in relation to the p_z -orbital plane level.

The radical bearing carbon atom is in the center of this representation and is numbered accordingly. The plane level through the perpendicular p_z -orbital gives the relative angular positions of the locked neighbouring groups.

The assumption made is consistent with a conformationally locked molecular structure, where two β -fluorines of the trifluoromethyl group at carbon atom 1 are eclipsed and those two at carbon 4 are in staggered position related to the half-filled p_z -orbital at the paramagnetic centre. While the first couple with 1.83 mT, the latter present the strongest couplings in the molecule with 3.56 mT and 3.02 mT, respectively. However, the terminal γ -CF₃-group rotates with one coupling constant of 1.69 mT. The long-range interaction of the CF₂-group in R_2 and R_3 with the unpaired electron is only 0.23 mT, that of CF₃ at carbon 3 is 0.08 mT. The inspection of this structure implies that the arrangement at the paramagnetic carbon is nearly planar with only small distortion from sp^2 . According to AM 1 calculations, the deviation from planarity at this molecular site is about 8°.

The comparable carbanion is planar as well due to NMR-measurements and in agreement with calculations. Expectedly, calculated charge densities are decisively different at carbon 3 (radical—0.200; carbanion—0.712).

The unprecedented stability of the radical results from the steric hindrance as well as from charge delocalization. Obviously, its persistence is not a thermodynamic but a kinetic effect which arises from shielding by the sheer bulk

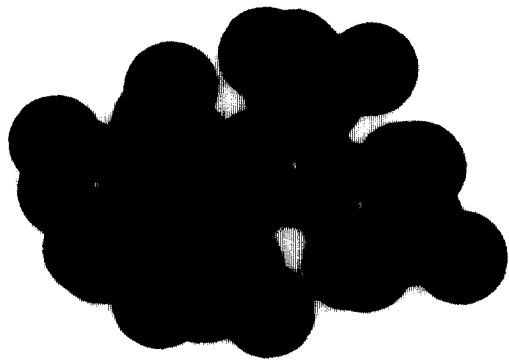


Fig. 3. Front view of the space filling model of the radical 1.

of the perfluoroalkyl group. On the contrary, the radical is thermally relatively unstable, because of considerable steric strain.

The long-term stability of radical 1 was measured by EPR over a period of several month at a storage temperature of 8°C. The loss of radical intensity followed a first-order kinetics with a half-live $\tau_{1/2}$ of 89 days and a rate constant of $8.9 \cdot 10^{-8}$.

The space filling drawing of Fig. 3 gives a front view of the radical centre and its surrounding. Steric hindrance as represented in Fig. 3 is undoubtedly responsible for the sluggish reaction of the radical with fluorine and for its stability towards oxygen, chlorine and to dimerization. On the other hand, as a strong oxidant the radical is less stable to mild

reducing agents: e.g., secondary amine destroys the radical in a vigorous reaction. The reaction with NO was observed in the EPR-spectrometer. The signals of the radical rapidly disappeared, probably the oxidation of NO to NOF has taken place.

3.1. Kinetic investigations of the thermal decomposition of radical 1

When the diluted radical is heated to 120°C, its spectrum disappears over hours, superimposed in a complex way and finally replaced by a new radical 2. The symmetric spectrum consists of eight major signals. According to spectra simulations this radical and its HFS-couplings of β -fluorines (CF_2 1.66 mT; CF_3 1.84 mT) is consistent with the perfluoro-3-methyl-3-pentyl radical [5]. Obviously, the weakest bond at the quaternary carbon is broken to give a relatively stable tertiary perfluoro-3-methyl-3-pentyl radical, which was obtained previously by Scherer et al. [6] and Krusic et al. [7] from photochemical and thermal decomposition.

The thermal decomposition of radical 1 dissolved in the inert, nonpolar solvent perfluorodecalin was carried out in a temperature range from 100° to 130°C obeying first-order kinetics (see Fig. 4). The radical concentrations are not absolute values, but a spectroscopic measure from which in dependence on time the kinetic law is obtained.

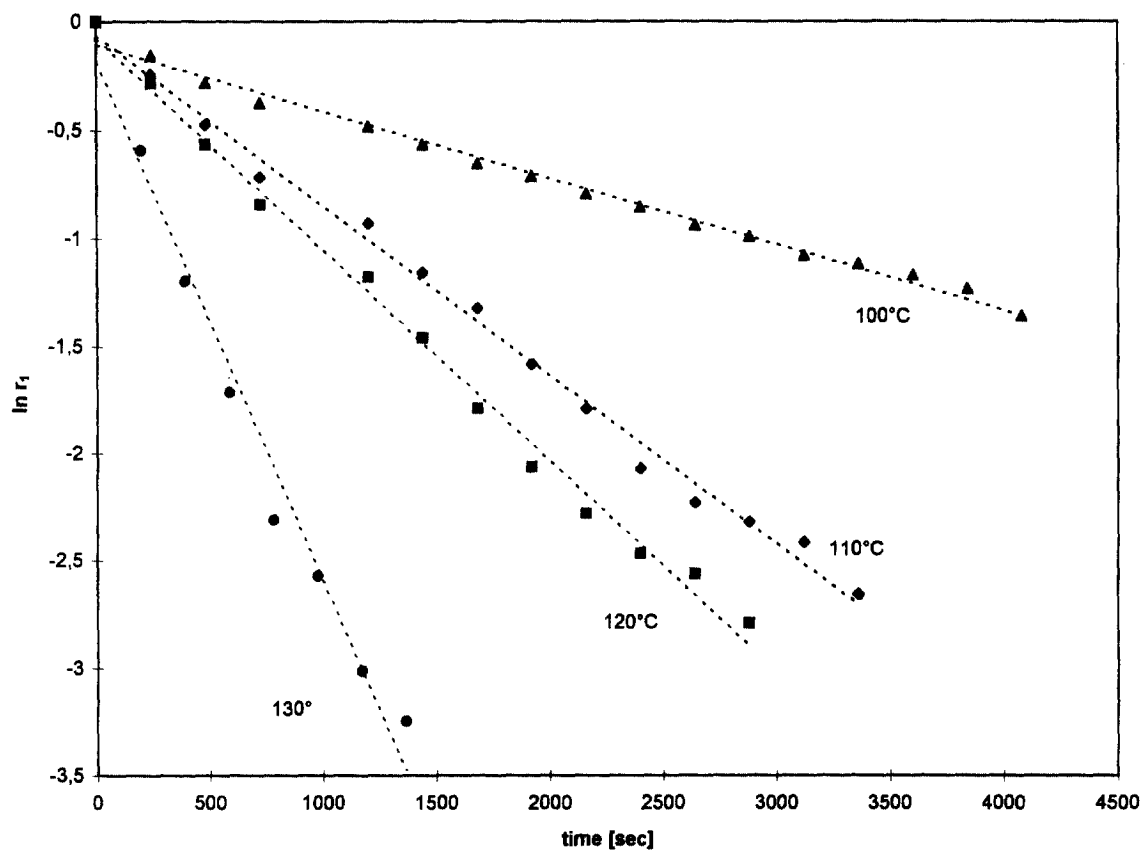


Fig. 4. First-order kinetics of thermal pyrolysis of radical 1 at different temperatures.

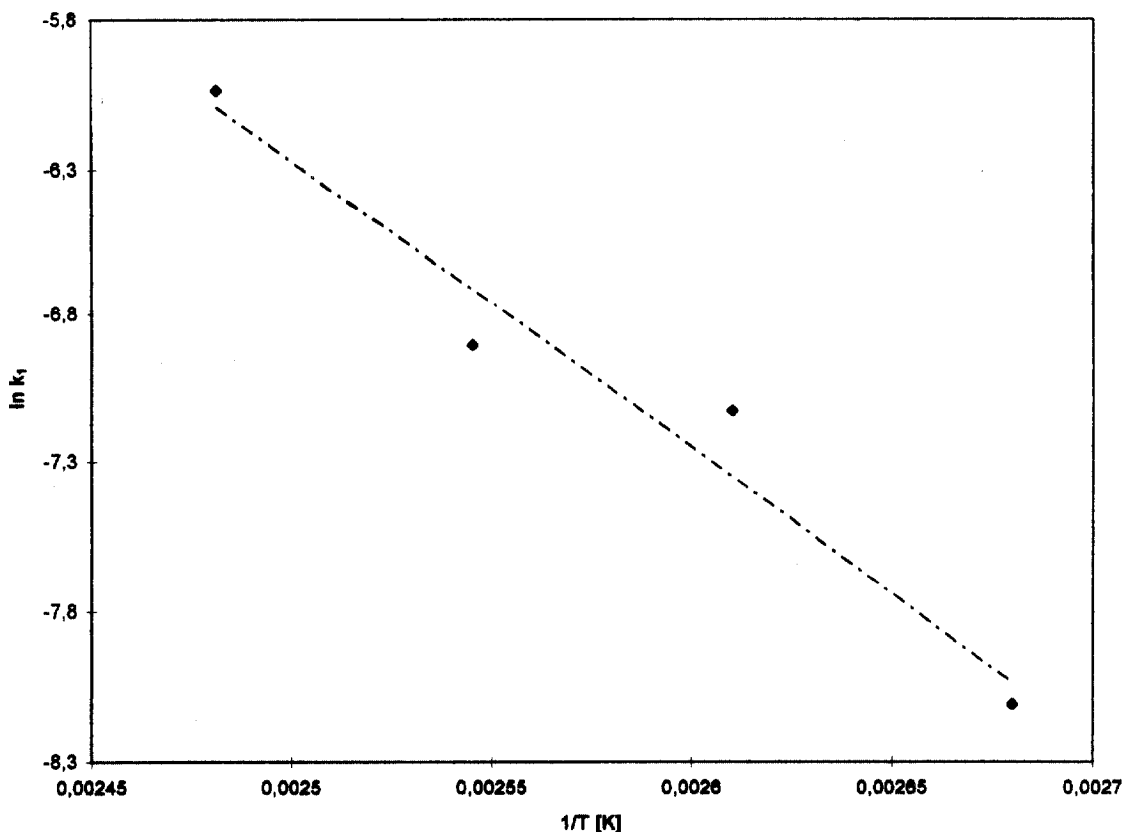


Fig. 5. Arrhenius plot of the thermal decomposition of radical 1: estimation of E_A .

Table 2
Kinetic parameter of the thermal decomposition of radical 1

Sample	t (K)	k (s^{-1})	τ (min)	E_A (kcal/mol)
1	281	$8.9 \cdot 10^{-8}$	128 160	19.6
2	373	$3.0 \cdot 10^{-4}$	38.3	
3	383	$8.0 \cdot 10^{-4}$	14.4	
4	393	$1.0 \cdot 10^{-3}$	11.5	
5	403	$2.4 \cdot 10^{-3}$	4.8	

The half time life τ at 100°C is in the order of 39 min and is thus comparable with that of 60 min for the Scherer radical [2]. From the Arrhenius plot of the rate constants in Fig. 5 the activation enthalpy of decomposition is obtained with 19.6 kcal/mol. The tabulated k -value at 281 K (sample 1) fits the straight line in Fig. 5 as well.

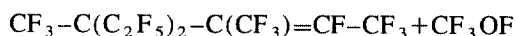
The activation enthalpy of decomposition of 19.6 kcal/mol corresponds to a very low bond energy between the tertiary and quaternary carbon atoms. Tortelli et al. [5] have shown in a recent pyrolysis study of branched fluorocarbons that homolytic cleavage takes place at the most substituted C–C bonds, whereby the ethyl-group weakens the neighbouring bond stronger than methyl (see Table 2 for the kinetic parameter of the thermal decomposition of radical 1).

Therefore, these fluorocarbons are thermolabile. The lowest bond energy reported in this respect is 36 kcal/mol in the sterically stressed (*iso*-C₃F₇)₂C(CF₃)C₂F₅ [8].

3.2. Radical 1 as a monitor for atomic fluorine in fluorination reactions

The fact that the title radical is formed only in the presence of radical fluorine makes the F-olefin (CF₃CF₂)₂CF₃C–C(CF₃)=C(CF₃)F a selective trap for fluorine radicals and the resulting organic radical a monitor in EPR-spectroscopy. Using this method it was found that the electrochemical fluorination process in anhydrous hydrogen fluoride generates radical fluorine, because the expected radical 1 was formed from the F-olefin [4].

Applying this methodology to fluorinations with XeF₂ and CF₃OF the radical was observed as well. In contrast to expectations, these electrophilic fluorinating agents [9,10] do not fluorinate the electron rich but the charge deficient site of the double bond, thus underlining the pure radical nature of these two processes. Obviously, the direction of fluorine addition is essentially determined by steric reasons of the strongly branched F-olefin.



It is interesting to note that in the above reaction, unlike the work of Corvaja et al. [11], fluorine but not the CF₃O·-moiety is added to the double bond.

Attempts to generate the radical 1 by reaction with the highly reactive interhalogens ClF and ClF₃ as fluorinating

agents failed. Certainly, their much higher dissociation enthalpy (60.3 kcal/mol and 41.6 kcal/mol, respectively) as compared to that of fluorine ($\Delta H_{\text{Diss}} = 37.8$ kcal/mol) is one reasonable explanation.

As expected, elemental chlorine ($\Delta H_{\text{Diss}} = 58.1$ kcal/mol) did not give a comparable radical and also the solid fluorinating agents CoF_3 and $\text{CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{N}(\text{CH}_3)_2\text{F}$ (Barnette's salt) are not able to release fluorine in the temperature range up to 50°C.

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