Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 1992, **2(4)**, 141–143

Mendeleev Communications

The Role of Multiple Bonds in the Radiolysis of Linear Perfluorocarbons

Elena V. Sablina, Sadulla R. Allayarov and Igor M. Barkalov*

Institute of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 095 938 2156

The presence of a double bond in a perfluorocarbon molecule under radiolysis, on the one hand, increases the yield of stabilized radicals and, on the other hand, decreases the destruction of the main carbon chain of the molecule; these interrelated factors result from the reaction of a fluorine atom with the double bond.

Perfluoroalkanes are known[1] to have greater radiational stability than their hydrocarbon analogues owing to the specific characteristics of a fluorine atom formed during the radiolysis of perfluorocarbons.[2–6] The drop in the yield of stabilized radicals in perfluorohexane, as compared with n-heptane, is connected, on the one hand, with elimination of radicals stabilized during radiolysis at 77 K by fluorine atoms and, on the other hand, with the absence of abstraction of a fluorine atom from a perfluoroalkane molecule by another fluorine atom.[6]

The aim of this work is to elucidate the effect of C=C bonds on the radiolysis mechanism of linear perfluoroalkanes. The radiolysis mechanism of perfluoroocta-2,6-diene (PFD) is compared with that of its saturated analogue, perfluorooctane (PFO).

The presence of a double bond in the molecule of perfluorocarbons affects markedly the accumulation of radicals during their solid phase radiolysis. The kinetics of radical accumulation during radiolysis at 77 K in perfluorooctane [Fig. 1(*a*)] and perfluoroocta-2,6-diene [Fig. 1(*b*)] differ widely. The radiation yield of radicals for PFO is almost four times lower than that for PFD, the accumulation coming to an end with doses of

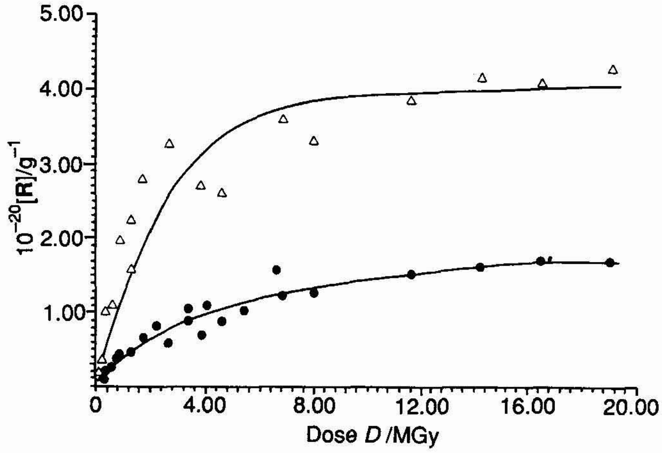

Fig. 1 Kinetics of radical accumulation for radiolysis at 77 K of n-perfluorooctane (●) (*a*) and n-perfluoroocta-2,6-diene (△) (*b*)

Mendeleev Commun., 1992, 2(4), 141–143

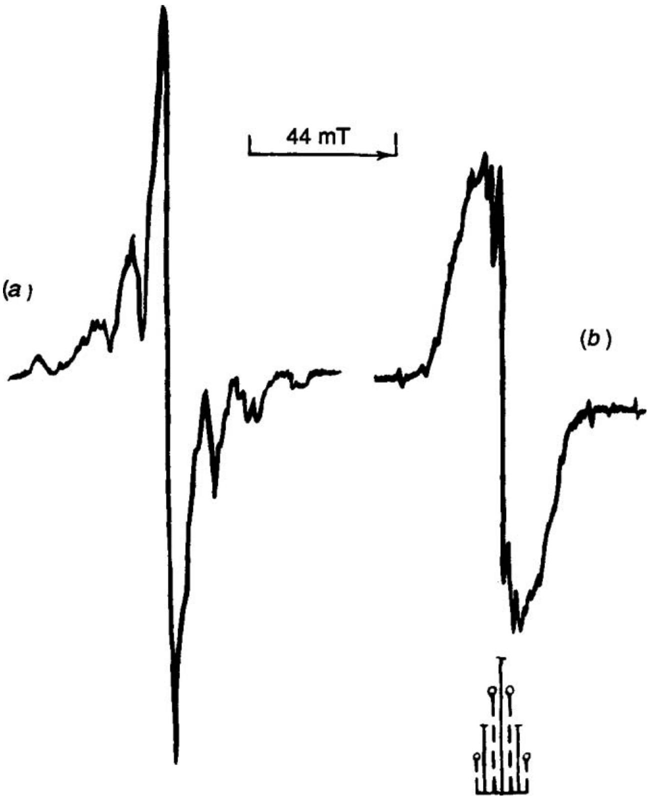

Fig. 2 EPR spectra of samples of n-perfluorooctane (*a*) and n-perfluoroocta-2,6-diene (*b*) irradiated at 77 K with a dose of 66.7 (*a*) and 24.7 kGy (*b*)

~8 mGy.† On the contrary, the radiolysis of hydrocarbons in saturated compounds leads to a greater yield of stabilized radicals than in their unsaturated analogues.[7,8] Therefore, the double bond influences the kinetics of radical accumulation in different ways during the course of radiolysis for linear perfluorocarbons and their hydrocarbon analogue. The radicals arising as a result of the rupture of C—C and C—F bonds are stabilized at 77 K. EPR spectra at 77 K register peaks with splittings of 45.5 and 22.5 mT [Fig. 2(*a*)]. The peaks with splitting 45.5 mT are characteristic of the radicals **r** formed on C—C bond rupture. Radicals **R** with characteristic peaks with splitting 22.5 mT are formed on the rupture of a C—F bond.

The central region of the EPR spectrum of PFO [Fig. 2(*b*)] has a quadruplet and a triplet with close splittings ~5.0 mT. The triplet spectrum is due to superfine interactions (SFI) of an unpaired electron with two fluorine α-atoms of a perfluoroallyl radical formed on abstraction of a fluorine atom from a PFD molecule [eqn. (1)].

$$\text{n-}C_8F_{14}\xrightarrow{\gamma}CF_3CF^{a}{=}CF^{0}\dot{C}F^{\alpha}CF_2CF{=}CFCF_3+F \qquad (1)$$

The formation of an allyl radical may also occur as a result of detachment of F in another part of the PFD molecule [eqn. (2)].

$$\text{n-}C_8F_{14}\xrightarrow{\gamma}\dot{C}F_2^{a}CF^{0}{=}CF^{\alpha}CF_2CF_2CF{=}CFCF_3+F \qquad (2)$$

A perfluoroallyl radical with three fluorine α-atoms is formed in reaction (2), and as a result of an SFI of an unpaired electron with these atoms an EPR quadruplet spectrum appears with a splitting of ~5.0 mT.

Peaks with a splitting 22.4 mT [Fig. 2(*a*)] are registered both in the spectrum of PFD irradiated at 77 K and in the EPR spectrum of PFO. However, the intensity of this signal in PFD is much higher than that in PFO. This spectrum is attributable to the radicals produced on addition of a fluorine atom to the double bond of a PFD molecule. Other radicals can also be added to the PFD double bond but, owing to the limited mobility of radicals in the solid phase, only the fluorine atoms are mobile at 77 K and can thus approach the reaction centre [eqn. (3)].

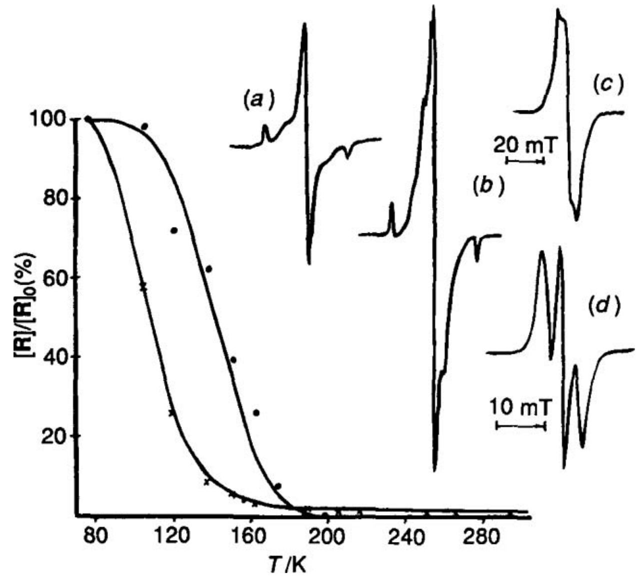

Fig. 3 Concentration of radicals *versus* temperature in samples of n-perfluorooctane irradiated with a dose of 4.804 (●) and 18.98 MGy (×) at 77 K. EPR spectra of an n-perfluorooctane sample irradiated with a dose of 18.98 MGy before (*a*) and after thermostating at 163 (*b*) and 300 K (*c*, *d*). Registration temperature 77 K.

$$\text{n-}C_8F_{14}+F\longrightarrow\begin{matrix}CF_3\dot{C}FCF_2CF_2CF_2CF{=}CFCF_3\\ CF_3CF_2\dot{C}FCF_2CF_2CF{=}CFCF_3\end{matrix} \qquad (2)$$

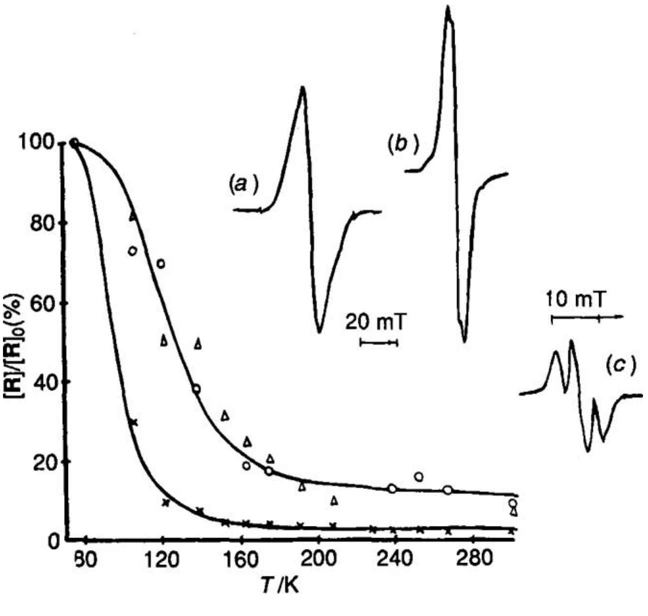

Fig. 4 Concentration of radicals *versus* temperature in samples of n-perfluoroocta-2,6-diene irradiated with a dose of 1.019 (×) and 18.98 MGy (○, △). EPR spectra of a sample of n-perfluoroocta-2,6-diene irradiated with a dose of 1.019 MGy before (*a*) and after thermostating at 300 K (*b*, *c*). Registration temperature 77 (*a*, *b*) and 300 K (*c*).

---

† Gy = J kg^{-1}.

Mendeleev Commun., 1992, 2(4), 141–143

Therefore, the double bonds of PFD are effective traps for fluorine atoms. As a result of addition of fluorine atoms a radical stabilized at 77 K is formed. Hence, a greater yield of radicals is observed in the radiolysis of PFD than in the radiolysis of its saturated analogue.

The temperature necessary for effective destruction of radicals on heating PFO decreases with increase in the irradiation dose while for PFD it increases (*cf.* Figs. 3 and 4). Let us consider the reasons for these differences. Stabilization of active radicals **R** and **r** occurs in the crystal lattice. Since PFO radiolysis is followed by destruction of the crystal lattice, the rigidity of the lattice decreases and the mobility of the radicals and the probability of their recombination both increase.

As distinct from PFO, the EPR spectrum of PFD shows more perfluoroallyl radicals. Owing to the delocalization of an unpaired electron in the double bond they possess higher thermal stability and lower chemical activity than perfluoroalkyl radicals. With an increase of irradiation dose in PFD the proportion of such chemically passive and thermally stable radicals grows, hence, the temperature region for effective destruction of radicals increases (Fig. 4).

An analysis of the EPR spectra shows that at 300 K radicals formed by reaction (1) remain stable in liquid PFD. The EPR spectra at 300 K register a triplet with a splitting 3.975 mT [Fig. 4(*c*)]. Such a signal is due to SFI of an unpaired electron with two fluorine α-atoms. The observed value of the splitting in this radical is in good agreement with the splitting constant for fluorine α-atoms in a chloroperfluoroallyl radical.[9]

On cooling down to 77 K, the EPR spectrum reverts to a poorly resolved triplet showing peaks with splitting 11.4 mT [Fig. 4(*b*)]. Peaks with splitting 11.4 mT are also registered in the spectrum of a PFD sample irradiated at 77 K [Fig. 4(*a*)]. An analysis of changes in the spectrum on heating the irradiated sample shows that the peaks with splitting 11.4 mT in the sample irradiated at 77 K correspond to the radicals that are stable at 300 K. These radicals are, therefore, formed during radiolysis at 77 K.

In the process of heating the perfluorooctane irradiated at 77 K (Fig. 3), a small portion (<1%) of the radicals also remains stable as a liquid. The EPR spectra of these radicals coincide with those of long-lived radicals in PFD. These are obviously perfluoroallyl radicals with two fluorine α-atoms. The absence of a superfine structure in the spectrum of this radical does not allow us to interpret it directly. Since the existence of a double bond is necessary for the formation of an allyl radical, then the latter can arise in perfluorooctane only with the unsaturated radiolysis products available. Hence, perfluoroalkyl radicals stable in the liquid phase can form in PFO, as distinct from PFD, in low yields and only after rather high irradiation doses.

For the radiolysis products of PFO and PFD, we have succeeded in isolating 15 and 18 organofluorine compounds, respectively. However, we have been unable to identify all of them. Table 1 gives chromatographic results for the radiolysis products. Rupture of a C—C bond during the radiolysis of these perfluorocarbons results in the destruction of their main carbon chain. Hence, one can deduce the degree of destruction of the carbon chain in the compounds studied from the yield of products containing up to seven fluorine atoms. The yield of such products in PFD is an order of magnitude lower than that in PFO, so the probability of carbon chain rupture is evidently higher than that in PFD.

Thus, the presence of a double bond in a perfluorocarbon molecule under radiolysis, on the one hand, increases the yield of stabilized radicals and, on the other hand, reduces the destruction of the main carbon chain of the molecule. These interrelated factors arise from the reaction of a fluorine atom with the double bond.

NMR data also testify to the greater radiation stability of PFD. There are no new lines in the NMR spectrum of PFD irradiated with a dose of 1.7 MGy and the relative intensity of the main lines is preserved. At the same time, marked changes occur in the NMR spectrum of irradiated PFO, and the observed widening of the spectral lines is connected with a disturbed ratio of intensities in the main components of the spectrum.

Table 1 Relative yields[a] of radiolysis products from perfluorooctane and perfluoroocta-2,6-diene

Radiolysis products	n-C_8F_{18}	$CF_3CF{=}CFCF_2CF_2CF{=}CFCF_3$
CF_4	2.87	–
C_2F_6	0.7	–
C_2F_4	0.2	28.43
C_3F_8	1.0	1.0[b]
cyclo-C_3F_6	–	0.25
$CF_3CF{=}CF_2$	0.066	35.38
n-C_4F_{10}	0.46	0.33
$CF_2{=}CFCF_2CF_3$	0.05	10.65
$CF_3CF{=}CFCF_3$	0.016	39.90
C_5F_{10}	0.0024	3.82
n-C_5F_{12}	0.2	1.10
C_6F_{12} (F-62)	0.005	9.86
n-C_6F_{14}	0.06	10.81

[a] The yield of perfluoropropane was arbitrarily assigned as 1. [b] The quantity of C_3F_8 obtained is ten times less than that from radiolysis of n-C_8F_{18}. The yield of products in PFD is an order of magnitude lower than that in PFO.

Linear perfluorooctanes are the main gaseous products of PFO radiolysis. They are formed by recombination of fluorine atoms with radicals **R** and **r**. This means that the destruction of the carbon chain in PFO is determined by the reaction of fluorine with the radicals formed on the rupture of a C—C bond. The double bond in PFD prevents such destruction of the carbon chain involving the fluorine atoms. As a result, the degree of carbon chain destruction decreases on PFD radiolysis. It is thought that this protective action of the C=C bond will also be displayed in two-component system. Therefore, the radiation stability of fluoropolymers could be enhanced by introducing a C=C bond into a macromolecule or producing compositions with perfluoroalkane additives.

References

1 J. H. Simons and E. H. Taylor, *J. Phys. Chem.*, 1959, **63**, 636.

2 R. F. Heine, *J. Phys. Chem.*, 1962, **66**, 2116.

3 J. C. Mailen, *Diss. Abstr.*, 1965, **25**, 5812.

4 E. Yu. Astakhov, *Autoreferal Kandidatskoi Dissertatsii*, Moscow, 1988, p. 22 (in Russian).

5 V. A. Khramchenko, *At. Energ.*, 1964, **17**, 53.

6 S. R. Allayarov, E. V. Sablina, I. M. Barkalov, *Khim. Vys. Energ.* in the press (in Russian).

7 V. V. Saraeva, *Radioliz uglevodorodov v zhidkoi faze* (Radiolysis of hydrocarbons in the liquid phase), MGU, Moscow, 1986, p. 62 (in Russian).

8 S. Ya. Pshezhetskii, A. Y. Kotov, V. K. Milinchuk, V. A. Roginski and V. I. Tupikov, *EPR svobodnykh radikalov v radiatsionnoi khimii* (ESR of free radicals in radiation chemistry), Khimiya, Moscow, 1972, p. 176 (in Russian).

9 B. E. Start, R. J. Krusic, P. Meakin and R. C. Bingham, *J. Am. Chem. Soc.*, 1974, **96**, 7382.

Received: Moscow, 22nd January 1992
Cambridge, 24th February 1992; Com. 2/00483F