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Free-radical and ion chemistry of fluoro derivatives: the mechanism of γ-radiolysis of perfluoropolypropene and perfluoropolytrimethylene oxides

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Abstract

The radiation chemistry of perfluoropolypropene and perfluoropolytrimethylene oxides has been investigated by ESR spectroscopy of the intermediate free radicals and by NMR spectroscopic detection of the major changes occurring in the structure of the oligomers. The major radiolytic products have been related to C—C and C—O bond scissions and to a minor participation of C—F bond cleavage. The results have been rationalized in terms of ionic and free-radical reactions stemming from the formation of primary ether cation-radicals.

Introduction

Chemical processes induced by high-energy radiation are characterized by complex ionic and radical reactions which finally lead to the stable end-products. Investigations of these mechanisms are essential for an understanding of the radiation behaviour of the materials, but are also the basis of a well-defined methodology for elucidating fundamental aspects of the ion and free-radical chemistry of the systems considered.

The radiolytic approach to ion and radical chemistry has important specific advantages over the technique of mass spectrometry due to the enhanced efficiency of collisional deactivation in the condensed phase which prevents extensive fragmentation of the ions and makes possible the identification and characterization of primary intermediates under the realm of kinetic and thermodynamic control. Following previous investigations [1], this work deals with the radiolytic behaviour and related ion and free-radical chemistry of perfluoropolyethers with the following structures:

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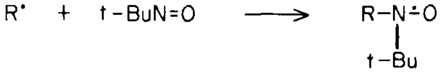
$CF_3CF_2CF_2O-(CF_2CF_2CF_2O)_n-CF_2CF_3$ (PFNPO); and $CF_3CF_2CF_2O-(CF_2CF(CF_3)O)_n-CF_2CF_3$ (PFPO).

The study is based on the identification by ESR spectroscopy of the free-radical intermediates and on an NMR analysis of the major radiation-induced changes in the structure of the oligomers. This methodological approach represents a major advance in respect of previous studies [2–4] since it allows a more direct insight to the radiolysis mechanisms.

Experimental

The detection by ESR spectroscopy of the free-radical intermediates in the radiolysis process was performed via the spin-trapping technique using 2-methylnitrosopropane (MNP) according to the equation:



$$R^{\bullet} + t\text{-}BuN{=}O \longrightarrow \underset{t\text{-}Bu}{\underset{|}{R-\dot{N}-O}}$$

The nitroxide adducts are relatively stable and show characteristic ESR *hf* patterns for the $R^{\bullet}$ precursors which can thus be identified. In the experimental approach adopted, samples of the polyethers containing 0.1–0.3% of MNP were γ-irradiated at 77 K under vacuum (^{60}Co source) and successively allowed to warm up gradually in the cavity of the ESR spectrometer with a continuous recording of the spectra. The analysis of the solution spectra was performed by computer simulation using a first-order isotropic Hamiltonian with electron Zeeman and hyperfine terms. No corrections were made for the motional modulation of the g and *hf* tensor anisotropy of the nitroxides since this effect only influences the high-field half ($m_I + 1$) of the spectra, and consequently does not cause problems for the interpretation and identification of the species.

Samples for GM and NMR analysis were irradiated at room temperature under vacuum with total doses of 27 Mrad. After irradiation, the gas fraction and part of the low molecular weight products were extracted with a Toepler pump and analyzed by GM spectrometry. Analyses of the structural changes induced by radiation on the polymers and determination of the number average molecular weights (M_n) were made by NMR spectroscopy using a 200 MHz Varian XL spectrometer.

Results

ESR spectra from the γ-radiolysis of PFNPO/MNP

The spectrum recorded at 77 K after irradiation [Fig. 1(a)] is identical to that obtained from the neat compound; this can be considered as evidence

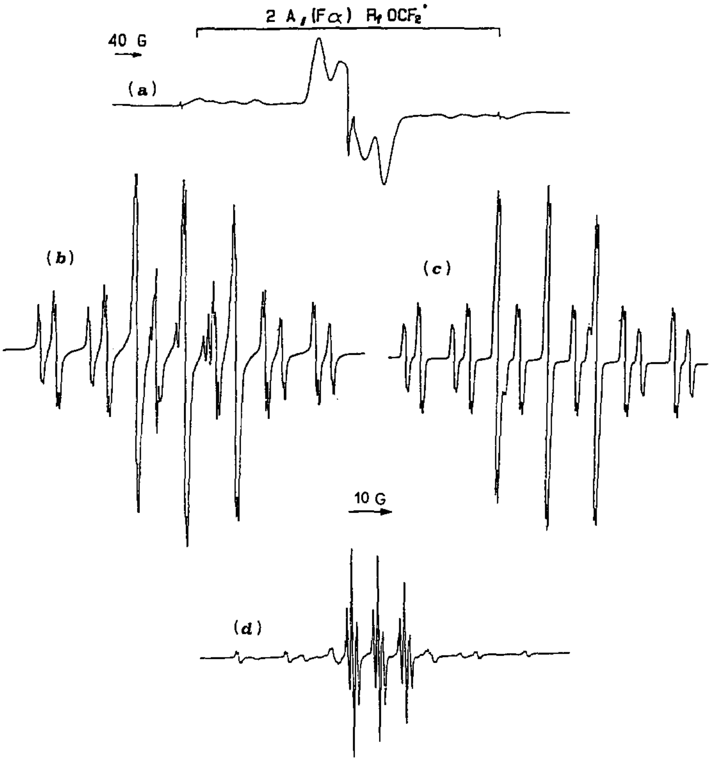
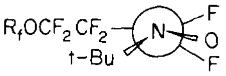
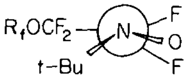
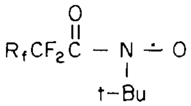


Fig. 1. ESR spectra from γ-irradiated perfluoropolytrimethylene oxide recorded (a) at 77 K and (b) after spin-trapping with 2-methylnitrosopropane at room temperature; (c) is the computer simulation of (b) based on the linear combination of the signals of radical A, B in the ratio 1.8:1 (see text). The narrow extra lines in the centre of the experimental spectrum are due to (d) the pattern of the acyl nitroxide which is enhanced at 40 °C.

of the fact that, at the concentration level used, MNP does not interfere with the primary events in the radiolysis mechanism. The outer peaks at *c.* $+250$ G in this spectrum are in the positions expected for the parallel components of the F_α tensors in the $R_fO\dot{C}F_2$ radical [5]:

$R_fO\dot{C}F_2 \quad 2A(F_\alpha)_\parallel = 243$ G

The presence of the $R_fCF_2\dot{C}F_2$ radical may also be tentatively inferred from the triplets of *c.* 35 G superimposed on the parallel features of the F_α tensors at *c.* $+190$ G. On warming at 170 K, spin-trapping occurs giving rise to a partially resolved nitroxide spectrum. A sufficient resolution for the interpretation is attained at *c.* 300 K where three different nitroxides can be identified arising from the trapping of the primary perfluoroalkyl radicals: $R_fOCF_2CF_2\dot{C}F_2$, $R_fOCF_2\dot{C}F_2$ (relative abundance *c.* 1:2) and the perfluoroacyl radical $R_fCF_2\dot{C}{=}O$.

Trapped radicals	Adducts	*hf* Couplings
$R_fOCF_2CF_2\dot{C}F_2$ (A)		N = 11.5 G $2F_\beta$ = 21.75 G 2F = 0.57 G
$R_fOCF_2\dot{C}F_2$ (B)		N = 11.6 G $2F_\beta$ = 18.1 G 2F = 0.60 G
$R_fCF_2\dot{C}(=O)$ (C)	 $R_fCF_2\overset{O}{\overset{\|}{C}}-\underset{t\text{-}Bu}{\underset{\vert}{N}}\dot{-}O$	N = 5.95 G 2F = 1.0 G

The two perfluoroalkyl adducts A and B show small but significant differences in the β-fluorine couplings. This is due to slight differences in the average conformations induced by the different structure of the perfluoroalkyl units adjacent to the radical centres. The assignment of the signal with the largest F_β coupling to the nitroxide adduct of $-OCF_2\dot{C}F_2$ is based on the fact that it is consistent with the NMR detection of the intrachain units $-OCF_2CF_2CF_2CF_2O-$ as the major products expected from radical couplings (Table 1). The acyl nitroxide has a greater thermal stability so that it can be seen as a major component at higher temperatures [Fig. 1(d)]. No evidence of trapping of the R_fOCF_2 species could be obtained. However, the presence of this species is reasonably inferred from the parallel features of the F_α tensors observed in the 77 K spectrum [Fig. 1(a)].

ESR spectra from the γ-radiolysis of PFPO/MNP

The 77 K spectrum shows a composite pattern where the $R_fO\dot{C}F_2$ radicals can be recognized from the outer peaks at *c.* +235 G:

$R_fO\dot{C}F_2$ $\quad 2A(F_\alpha)_\parallel = 230$ G

The part of the spectrum in the +150 G region shows the characteristic features of the radical $R_fO\dot{C}F(CF_3)$ with a doublet of *c.* 60 G corresponding to the parallel coupling of one β-fluorine located in an eclipsed position with respect to the unpaired electron orbital [5]:

$R_fO\dot{C}F(CF_3)$ $\quad A(F_\alpha)_\parallel = 240$ G
$\qquad A(F_\beta)_\parallel = 55$ G

The doublets are superimposed on a more complex structure, probably due to the $R_fCF_2\dot{C}F(CF_3)$ radical. On warming near 200 K, spin-trapping takes place giving a typical 'immobilized' nitroxide spectrum [Fig. 2(b)]. Further warming to room temperature affords resolved spectra which are

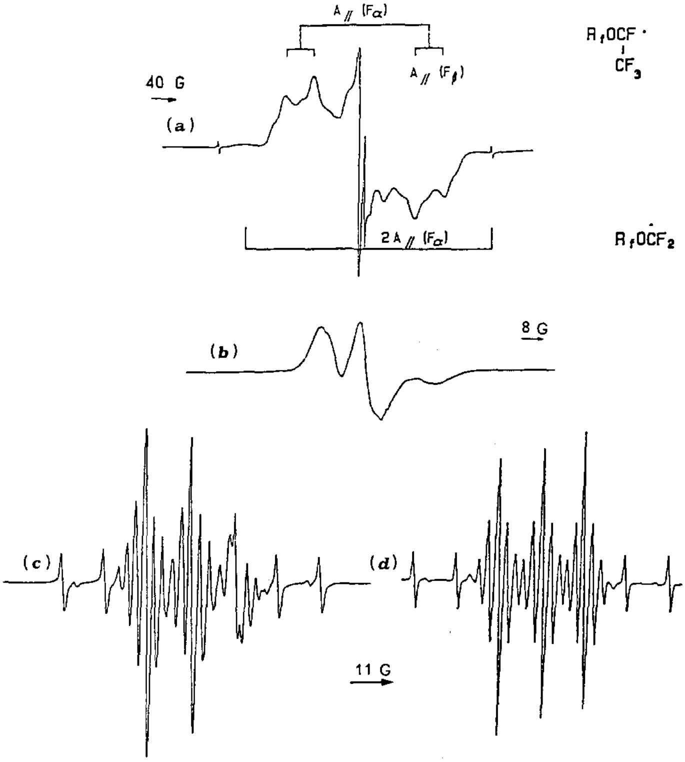
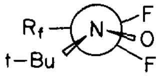
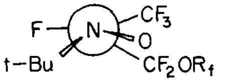
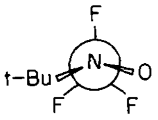


Fig. 2. ESR spectra from γ-irradiated perfluoropolypropene oxide recorded (a) at 77 K, (b) after spin-trapping with 2-methylnitrosopropane at −50 °C and (c) at room temperature; (d) is the computer simulation based on the linear combination of the signals from the radicals D, E and F in the ratio 1:4:0.1 (see text).

interpreted by computer simulation in terms of adducts of the species listed below.

Trapped radicals	Adducts	*hf* Couplings
$R_fO\dot{C}F_2$ (D)		N = 11.25 G $2F_\beta$ = 22.6 G
$R_fOCF_2\dot{C}F(CF_3)$ (E)		N = 11.6 G F_β = 2.4 G 5F = 2.4 G
$\dot{C}F_3$ (F)		N = 11.6 G $3F_\beta$ = 12.6 G

By computer simulation, the relative abundance of the secondary species $R_fO\dot{C}F(CF_3)$ and $R_fOCF_2\dot{C}F(CF_3)$ was found to exceed that of the $R_fO\dot{C}F_2$ species by a factor of *c.* 2. No definite evidence for the trapping of the $R_fO\dot{C}F(CF_3)$ radical could be obtained, but the presence of this species is safely inferred from the similarity of the features of the F_β tensors observed in the 77 K spectrum.

Gas product analysis

The gas fractions recovered from 100 g of material after 27 Mrad irradiation amounted to 47.9 cm^3 and 67.5 cm^3 (normal conditions) for PFNPO and PFPO respectively, which correspond to *G*(gas) values of 0.66 and 0.34 [molecules $(100\ eV)^{-1}$]. By GM spectrometry, the major product was COF_2 in both cases; other compounds detected in trace amounts were the epoxide C_2F_4O, and C_2F_6 in the case of PFNPO and C_2F_6, C_3F_8 for PFPO. In addition to the gases, a number of volatile oligomers with polyether structures and molecular weights >250 could be recovered by prolonging the extraction with the Toepler pump.

NMR spectroscopic analysis

The major structural changes induced in the oligomers by irradiation as detected by NMR spectroscopy are summarized in Table 1. In both the polyethers, irradiation caused a significant decrease in the average molecular weight as a consequence of degradation of the chains. The irradiation of PFNPO leads to the formation of terminal acyl fluorides and to branching; other significant changes are the appearance of C-1 and C-4 units in the chains and a drastic increase in the concentration of CF_3O- terminal groups. The limited increase in the relative yields of perfluoroethyl and perfluoropropyl units, which are the major terminals in the unirradiated material, is not considered significant since this is mostly a consequence of the decrease in the molecular weight.

The irradiation of PFPO also leads to the formation of acyl fluoride terminal groups, $R_fOCF(CF_3)C(=O)F$, $R_fCF_2C(=O)F$, to the appearance of C-1 and C-4 units in the chains and to the enhancement of CF_3O- and, to a lesser extent, of perfluoro-isopropyl and -isobutyl terminals. As in the previous case, the small relative increase in the relative yield of the perfluoroethyl and -propyl terminals are attributed to the decrease in the chain length due to degradation.

Discussion

From the nature of the intermediate radicals identified by ESR spectroscopy and the structural changes detected by NMR spectroscopy, the radiolytic behaviour of the perfluoropolyethers is characterized by chain degradation involving C–O and C–C bond rupture. In addition, indirect evidence has been obtained from the formation of perfluoromethyl terminals

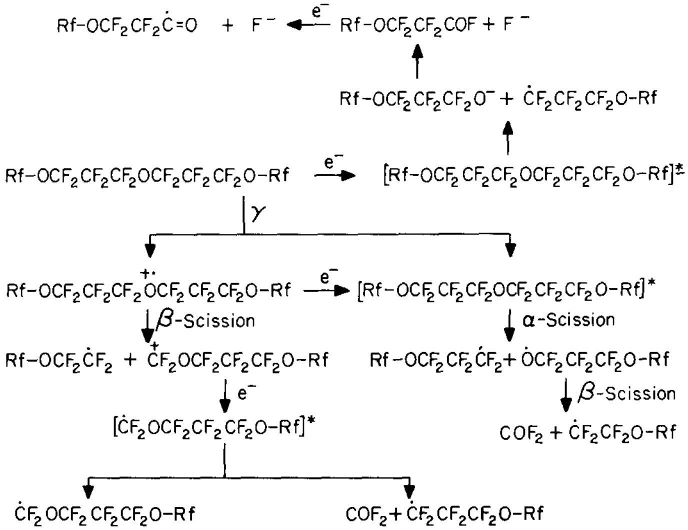
TABLE 1

The effect of γ-irradiation on the structure of perfluoropolytrimethylene oxide (PFNPO) and perfluoropolypropene oxide (PFPO) as determined by NMR spectroscopy

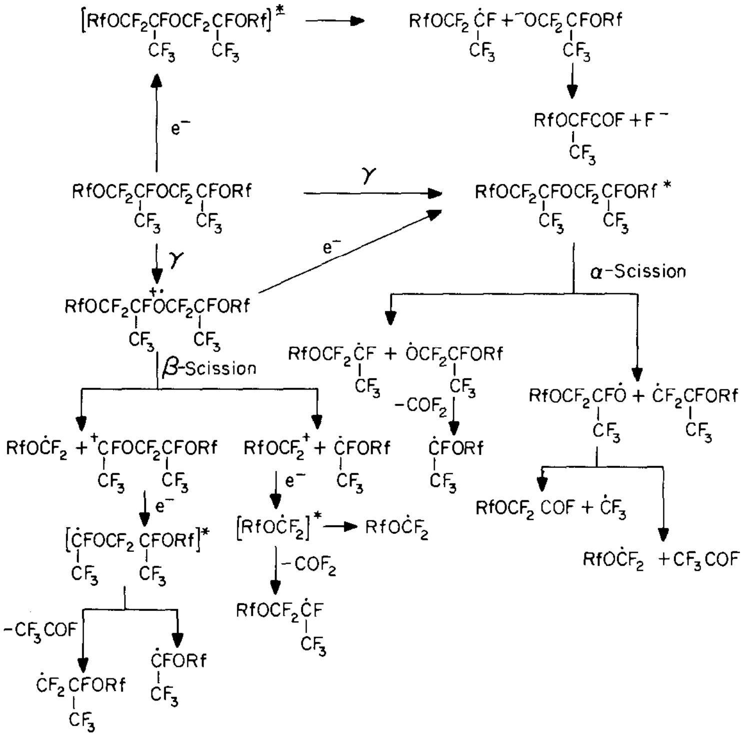
Structure	Relative abundance[a]		Chemical shift, δ (ppm ref. $\mathrm{CFCl_3}$)
	A	B	
PFNPO			
$\mathrm{-CF_2\underline{CF_2}CF_2O-}$	100	100	−129
$\mathrm{-CF_2\underline{CF_2}\underline{CF_2}CF_2O-}$	0.08	0.80	−125.3
$\mathrm{-CF_2CF_2\underline{CF}(R_f)CF_2O-}$	–	0.16	−182.8
$\mathrm{-CF_2O\underline{CF_2}OCF_2-}$	–	0.31	−51.1
$\mathrm{\underline{CF_3}OCF_2O-}$	–	0.04	−57.7 (t, $J=9.2$ Hz)
$\mathrm{\underline{CF_3}O-}$	0.03	0.45	−55.7 (t, $J=9.2$ Hz)
$\mathrm{\underline{CF_3}CF_2O-}$	7.10	7.40	−87.5(s)
$\mathrm{CF_3\underline{CF_2}CF_2O-}$	7.10	7.90	−130(s)
$\mathrm{-OCF_2CF_2CO\underline{F}}$	–	0.20	+23.2(bs)
M_n	2640	2500	
PFPO			
$\mathrm{-CF_2\underline{CF}(CF_3)O-}$	100	100	−145
$\mathrm{-O\underline{CF_2}O-}$	–	0.16	−49.5
$\mathrm{-OCF_2\underline{CF}(CF_3)\underline{CF}(CF_3)CF_2O-}$	–	0.19	−180
$\mathrm{\underline{CF_3}O-}$	0.02	0.39	−54, −56
$\mathrm{\underline{CF_3}CF_2O-}$	3.70	4.10	−87.5(s)
$\mathrm{CF_3\underline{CF_2}CF_2O-}$	4.70	4.90	−130(s)
$\mathrm{-OCF_2\underline{CF}(CF_3)_2}$	0.09	0.23	−187(s)
$\mathrm{-OCF(\underline{CF_3})_2}$	0.10	0.20	−81(s)
$\mathrm{-OCF(CF_3)CO\underline{F}}$	–	0.58	+25.8(bs)
$\mathrm{-OCF_2CO\underline{F}}$	–	0.04	+12(bs)
M_n	4220	3980	

[a] The results are reported in moles relative to the main regular structural units set equal to 100. Columns A and B refer to the unirradiated and irradiated material, respectively.

which suggests the occurrence of homolytic or etherolytic cleavage of the C−F bonds. The reaction sequences shown in Schemes 1 and 2 attempt to rationalize the ESR and NMR spectroscopic observations on the basis of the following general assumptions: (a) the polarity of the medium is sufficiently high to prevent a significant fraction of the primary ions undergoing geminate recombinations with electrons; (b) the primary positive charges are mainly localized on the oxygen atoms; (c) as a consequence of (b), the excitation energy arising from ion–electron recombination is mainly concentrated on the ether moiety; (d) in agreement with mass-spectrometric observations, the major mechanism of electron capture is assumed to be that leading to the formation of $\mathrm{R_fO^-}$ ions [4]; and (e) multiple chain fragmentations are



Scheme 1. The mechanism of the radiolysis of PFNPO.



Scheme 2. The mechanism of the radiolysis of PFPO.

excluded because of the high efficiency of collisional deactivation in the condensed phase.

In accord with the above assumptions, the mechanism of radiolysis of the linear polyether PFNPO may be based on three main reaction sequences: a cationic path, an anionic path and an excitation path (Scheme 1). Because of the lower energy of the C—C bond in comparison to the C—O bond [6, 7], the favoured reaction mode of the cations is expected to be β-scission leading to the formation of neutral free radicals and carbonium ions, the latter species generating other neutral radicals by neutralization. In this process the positive charge is likely to be located preferentially on the carbon atom adjacent to the oxygen because of resonance stabilization which may be expressed by the structures:

$$^{+}CF_2{-}O{-} \leftarrow\rightarrow CF_2{=}\overset{+}{O}{-}$$

Those cation radicals which undergo neutralization will give rise to excited structures with most of the excitation energy concentrated in the ether moiety: bond scission at positions adjacent to the oxygen atoms is a likely process in this case giving neutral perfluoro-alkyl and -alkoxyl radicals, with the latter being unstable toward β-scission to yield other neutral radicals and COF_2. In agreement with mass-spectrometric observations, the anionic path is assumed to be based on dissociative electron capture giving neutral perfluoroalkyl radicals and diamagnetic alkoxy anions [4, 8]. The latter species may be suggested as precursors of the acyl fluoride terminals by splitting of F^- ions. These acyl fluorides are suggested as the source of the acyl radicals detected by ESR spectroscopy because of the high electron affinity of the carbonyl group:

$$R_fOCF_2CF_2C({=}O)F + e^- \longrightarrow R_fOCF_2CF_2C(O^-)F \longrightarrow R_fCF_2CF_2\dot{C}{=}O + F^-$$

In order to complete the rationalization of the structural changes detected by NMR spectroscopy, it is also necessary to add to the reaction scheme the coupling of neutral free radicals and ions. Thus the formation of the $-OCF_2O-$ units calls for neutralization of the alkoxide anions with what are thought to be the most abundant carbonium ions in the system:

$$R_fO^- + {}^{+}CF_2O- \longrightarrow R_fO{-}CF_2O-$$

The C-4 sequences are mainly accounted for in terms of the couplings of $-OCF_2\dot{C}F_2$ radicals which are the most abundant species in the system. The C-5 and C-6 intrachain sequences, which would result from the cross and direct couplings of the $-OCF_2\dot{C}F_2$ and $-OCF_2CF_2\dot{C}F_2$ radicals, have been tentatively identified by NMR spectroscopy but the exceedingly low intensity of the signals prevented any definite assignment and quantitative evaluation. The NMR signal of the C-2 units formed by coupling of the $-O\dot{C}F_2$ radicals was below the limit of detection. The existence of chain branching implies the presence of species arising from the rupture of C—F bonds not adjacent to the oxygen atoms. This is a common event in the radiolysis of perfluoropolyolefins [9], but must be considered of minor importance in perfluoropolyethers judging from the very low branching yield and the apparent absence of $R_fR_f'\dot{C}F$ radicals in the ESR spectra.

The significant increase of CF_3O- terminals may be rationalized on the basis of the neutralization of the most abundant cations and anions via the processes:

$$-OCF_2^+ + F^- \longrightarrow -OCF_3$$

$$-OCF_2^+ + R_fCF_2CF_2CF_2O^- \longrightarrow -OCF_3 + R_fCF_2CF_2C(=O)F$$

The latter reaction is in competition with coupling leading to the $-OCF_2O-$ units and would also afford an alternative path to the formation of the acyl radicals detected by ESR spectroscopy.

The proposal for the mechanism of radiolysis of PFPO (Scheme 2) matches that for the linear polyether PFNPO, except for the possibility of side-chain scission with the formation of $\dot{C}F_3$ radicals and a loss of symmetry in the cleavage of the C$-$O bonds. All the reaction paths hypothesized can yield neutral free radicals and account for the structural changes of the oligomers detected by ESR and NMR spectroscopy. The observed major relative abundance of the secondary radicals $R_fR_f'\dot{C}F$ relative to primary radicals $R_f\dot{C}F_2$ may be explained by the prevalence of the β-scission mode leading to the $-OCF_2^+$ carbonium ion which is expected to be more stable than the $-O\overset{+}{C}F(CF_3)$ ion [10]. A contribution to the prevalence of the $R_fR_f'\dot{C}F$ radicals may also come from the asymmetry of α-scissions at the excited ether units favouring the cleavage of the weaker CF$-$O bonds with respect to the CF_2-O bonds. Preferred cleavage of the CF$-$O bond can also be expected to occur in dissociative electron capture leading to the alkoxide anions, for which direct evidence has been obtained from negative ion DCI/MS experiments performed on PFPO [8]. This latter reaction followed by splitting of F^- ions affords a reasonable path for the formation of the most abundant acyl fluoride terminals $R_fOCF(CF_3)C(=O)F$ detected by NMR spectroscopy.

The other acyl fluoride terminals $R_fOCF_2C(=O)F$, which are formed in much smaller amounts (Table 1), could arise from the side-chain scission of alkoxy radicals. Neutralization of the most abundant cations $-OCF_2^+$ with F^- and $R_fCF_2O^-$ anions provides an acceptable route for the formation of the CF_3O- and acyl terminals and the $-OCF_2O-$ units:

$$-OCF_2^+ + F^- \longrightarrow -OCF_3$$

$$-OCF_2^+ + R_fO^- \longrightarrow -OCF_2-OR_f$$

$$-OCF_2^+ + R_fOCF(CF_3)CF_2O^- \longrightarrow -OCF_3 + R_fOCF(CF_3)C(=O)F$$

Couplings between the neutral radicals identified by ESR spectroscopy account for the other significant structural changes reported in Table 1 in a simple manner:

$$2\ -\mathrm{OCF_2\dot{C}F(CF_3)} \longrightarrow -\mathrm{OCF_2CF(CF_3)CF(CF_3)CF_2O}-$$

$$-\mathrm{OCF_2\dot{C}F(CF_3)} + \mathrm{\dot{C}F_3} \longrightarrow -\mathrm{OCF_2CF(CF_3)_2}$$

$$-\mathrm{O\dot{C}F(CF_3)} + \mathrm{\dot{C}F_3} \longrightarrow -\mathrm{OCF(CF_3)_2}$$

References

1 A. Faucitano, A. Buttafava, F. Martinotti, G. Marchionni and R.J. De Pasquale, *Radiat. Phys. Chem.*, *37* (1991) 43.

2 J. Packansky and R.J. Waltman, *J. Phys. Chem.*, *95* (1991) 1512.

3 J. Packansky, C. Wang and R.J. Waltman, *J. Fluorine Chem.*, *32* (1986) 283.

4 I.V. Bletsos, D.M. Hercules, D. Fowler, D. van Leyen and A. Benninghoven, *Anal. Chem.*, *62* (1990) 1275.

5 A. Faucitano, A. Buttafava and G. Marchionni, *Tetrahedron Lett.*, *29* (1988) 4611.

6 G.E. Gerhardt and R.J. Lagow, *J. Org. Chem.*, *43* (1978) 4505.

7 B.E. Smart, *Molecular Structure and Energetics*, VCH, New York, 1986, Vol. 3, Chap. 4.

8 A. Guarini, M. Vincenti, P.A. Guarda and G. Marchionni, *12th Int. Mass Spectrom. Conf.*, Amsterdam, August 1991, Abs. No. C07, p. 392.

9 N. Tamura, *J. Chem. Phys.*, *37* (1962) 479.

10 G. Olah and Y.K. Mo, *Adv. Fluorine Chem.*, *7* (1973) 69.