other than migration of iodide is limiting the reaction. We shall only set a lower limit of ca. 10^8 M^{-1} s^{-1} for the bimolecular rate constant of the iodide reaction. It is quite possible that the observed rate constant for the reaction with base is also a lower limit.

Conclusions

In this study we have examined the relative reactivities of H_2O and H_2O_2 toward F_2 and HOF and have obtained support for a simple mechanism for the fluorine-water interaction. We have obtained for the first time an order-of-magnitude estimate for the rate of reaction of dissolved fluorine with water. This rate is considerably greater than the analogous rates for the heavier halogens. This aspect of our present results should be regarded as preliminary in nature. Refinement of the technique should make possible the evaluation of a variety of rate constants for reaction of fluorine with aqueous substrates, at least on a relative basis.

Acknowledgment. We express our thanks to Col. C. J. Dymek, Jr., and Capt. David Neumann, USAF, for discussions that first put us on the track of an approach to problems of mass transfer with chemical reaction, and to Drs. J. D. Kelley, R. A. Pierotti, G. Astarita, and M. M. Sharma for helpful discussions relating to their respective specialties. We thank E. I. du Pont & Co. for the sample of Albone 70 DG. Oxygen isotope analyses were carried out by A. G. Engelkemeir of the Argonne Analytical Laboratory. R.C.T. acknowledges partial support from the Argonne Division of Educational Programs.

Registry No. H_2O, 7732-18-5; F_2, 7782-41-4; HOF, 14034-79-8; H_2O_2, 7722-84-1; O_2, 7782-44-7.

ESR of Intermediate Radicals in Thermolysis Mechanisms: Peroxidic Perfluoro Polyethers

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Abstract: The photothermolysis between 100 and 250 °C of polymers with perfluorooxymethylene, oxyethylene, and oxypropylene structures and containing perioxidic units as photoactive initiators has been studied by ESR and the INDO MO method. Following the initial homolysis of peroxidic bonds and the β scission of resulting alkoxy radicals, alkoxyfluoroalkyl radicals are formed which, above 100 °C, undergo thermal decomposition by β scission, initiating a chain depolymerization with formation of carbonyl compounds and C_2F_4 and C_3F_6 monomers; the latter add to $RCF_2\cdot$ species yielding C_n ($n \geq 3$) units. By extension of these results, it is inferred that this mechanism is of major importance in the high-temperature pyrolysis of this class of compounds. Among the intermediates of the C2P and C3P photothermolysis, of special interest are some novel primary alkoxyfluoroalkyl radicals with strongly bent structures at the radical centers and showing unusually large long-range interactions with γ- and δ-fluorine atoms, which are actually being investigated by MO methods.

ESR has a great potentiality as a method for elucidating the thermolysis mechanism;[1] however, its applications to this field is severely hindered by difficulties inherent to the high temperature and pressure that must be attained within the sample cavity. Furthermore, at high temperature, the lifetime of the radicals is shorter so that most of the species do not attain the limit of detection. We have tried to avoid these difficulties, in polymer thermolysis studies, by taking advantage of the fact that the radical reactions in the propagation stage have a much lower activation energy as compared to the initiation stage; as a consequence they can occur at a lower temperature provided initiation is obtained in a nonthermal way. Several methods for nonthermal initiation can be proposed, such as ionizing radiations (radiation-assisted thermolysis) or UV radiations; in the latter case photoactive groups must be inserted within the polymer chains. We have attempted to apply the latter method to investigate the major features of the mechanism of thermolysis of perfluoro polyethers[2] containing structural units of formula

$$-(OCF_2CF_2)_m-(OCF_2)_n- \quad n/m \sim 1 \quad \text{C2P}$$

$$-(OCF_2CF(CF_3))_x-(OCF_2)_y \quad x/y \sim 10 \quad \text{C3P}$$

When obtained by photooxidation of C_2F_4 and C_3F_6, C2P and C3P contain about 1% of peroxidic units of formula

$$\left.\begin{array}{ll} \text{a} & -OCF_2CF_2OOCF_2CF_2O- \\ \text{b} & -OCF_2CF_2OOCF_2O- \\ \text{c} & -OCF_2OOCF_2O- \end{array}\right\} \text{C2P}$$

$$\left.\begin{array}{ll} \text{d} & -OCF_2CF(CF_3)OOCF_2CF(CF_3)O- \\ \text{e} & -OCF_2CF(CF_3)OOCF(CF_3)CF_2O- \end{array}\right\} \text{C3P}$$

which are suitable as photoactive initiators of the thermolysis. In addition to the mechanism of thermal degradation, a major interest of this investigation is the characterization of the expected intermediates alkoxyfluoroalkyl radicals; only few examples belonging to this important class of radicals are reported in literature,[3c,4,5] and no information pertaining to their stability and reaction at relatively high temperature are available.

Experimental Section

Peroxidic C2P and C3P were prepared by photooxidation at low temperature of perfluoroethylene and perfluoropropylene according to the methods described in ref 2. For the ESR measurements, samples of C2P and C3P were sealed in quartz tubes under high vacuum and submitted to UV irradiations from a 100-W high-pressure mercury lamp within the cavity of an E-109 ESR Spectrometer equipped with an authomatic temperature-control device. Photothermolysis experiments were performed in the range 60–250 °C.

MO Calculations. The INDO method has become the standard technique for studying the geometry and electronic structure of organic

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(2) Sianesi, D.; Pasetti, A.; Fontanelli, R.; Bernardi, G. C.; Caporiccio, G. *Chim. Ind. (Milan)* **1973**, *55* (2), 221.

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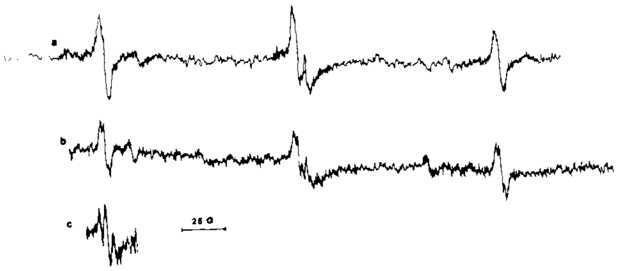


Figure 1. ESR spectra of UV-irradiated peroxidic C2P at low and intermediate temperatures: (a) 60 °C; (b) 100 °C; (c) details of the low-field peak of the $OCF_2\cdot$ signal, showing the triplet structure due to γ-CF_2 group.

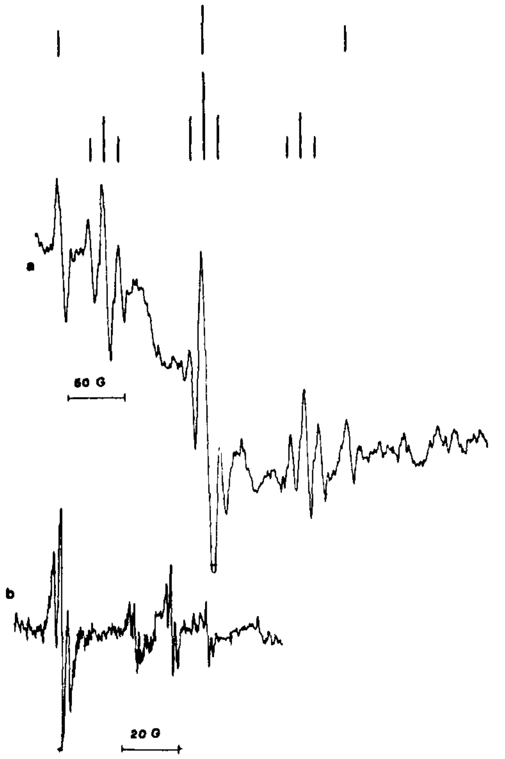


Figure 2. ESR spectra of UV-irradiated peroxidic C2P at high temperature: (a) recorded at 270 °C; (b) details of the low-field peaks of the $OCF_2\cdot$ and $CF_2CF_2\cdot$ triplets showing the hf interactions of γ-CF_2 groups.

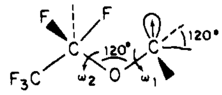
free radicals.[8] However, a word of caution is in order about the significance of calculated splittings when dealing with fluoroalkyl radicals, owing to the parametrization based on limited experimental data.[6] Actually this method seems to work nicely with α and long-range F couplings, which are matched in correspondence to the expected geometries,[3-5] while it is low accurate with β-F couplings, which appear to be overestimated.

INDO MO calculations were performed on a Honeywell DPS 8 Computer according to the method of Pople and Beveridge.[6] Standard bond lengths, $D_{C\text{-}F} = 1.35$, $D_{C\text{-}O} = 1.36$, $D_{C\text{-}C} = 1.53$ Å, and bond angles, $F\hat{C}F$ (except at the radical center), $C\hat{C}F$, and $C\hat{C}O$ equal to 109.5°, were assumed; the geometries of radical centers and the $C\hat{O}C$ angles were allowed to change in order to fit the experimental Fluorine hfs and the energy minima.

Results

Photothermolysis of C2P. The ESR spectrum obtained at 60 °C consists of a triplet of 126.5 G, which is diagnostic of a species bearing two α-fluorine atoms (Figure 1a). At 100 °C each peak of this signal appears to be further resolved into triplets 1:2:1 of 2.5 G (Figure 1b). When the temperature is rised up to 200–250 °C, a new spectrum is obtained, which can be analyzed in term of the signal of Figure 1b superimposed to a new pattern consisting of a triplet 1:2:1 of 87.3 G further split into triplets 1:2:1 of 13.0 and 1.5 G (Figure 2).

Table I. INDO MO Calculations on the Angular Dependence of the Long-Range γ- and δ-Fluorine Couplings in the Model Radical $CF_3CF_2OCF_2\cdot$



μ_1, deg	ω_2, deg	α-F	α-F_α	γ-F	γ-F	δ-$F(CF_3)_{av}$
0	0	115.2	115.2	−7.1	−7.1	0.0
45	0	115.1	116.8	−18.8	1.9	0.3
90	0	122.6	109.5	−12.9	0.7	0.6
135	0	122.1	101.9	−1.7	−2.0	2.8
180	0	106.9	106.9	0.4	0.4	4.1
0	45	117.6	118.3	7.9	−1.1	0.0
0	90	117.9	114.8	2.1	−5.7	0.8
0	135	114.8	129.8	−2.6	−9.8	60.0
0	180	122.6	122.6	−3.6	−3.6	64.0

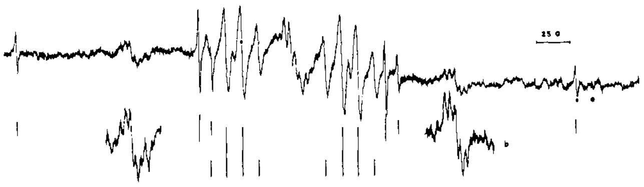
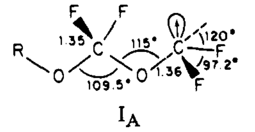


Figure 3. ESR spectrum of UV-irradiated peroxidic C3P at low temperatures: (a) recorded at 60 °C; (b) details of the M ± 1 peaks of the $OCF_2\cdot$ triplet showing interaction with γ- and δ-F atoms.

This ESR change is reversible, for relatively short irradiation times. On the basis of INDO calculations, the triplet of 126.5 G is assigned to primary alkoxyfluoroalkyl radicals of type $ROCF_2OCF_2\cdot$ (I_A):



I_A

exptl	calcd (INDO)
$2a_\alpha{}^F = 126.5$ G	$2a_\alpha{}^F = 122.5$ G
$2a_\gamma{}^F = 2.5$ G	$2a_\gamma{}^F = 3.1$ G

An other species that might in principle account for this spectrum is the radical $ROCF_2CF_2OCF_2\cdot$ (I_B) provided that the two δ-fluorine couplings are too small for being resolved. So that this point may be clarified, INDO calculations were performed on the model radical $CF_3CF_2OCF_2\cdot$ (Table I); the results predict that δ-fluorine couplings are strongly dependent on the angles of rotations about the O–C· and the O–C_β bonds[7] and that a variety of conformations exist where these constants are of magnitude equal or greater as compared to γ-fluorine couplings. These results, together with the observation that δ-fluorine couplings are clearly detectable in the radical III (see next section), point to the radical I_B not being present at 100 °C although it seems reasonable to assume that it contributes to the lower temperature (60 °C) spectrum (Figure 1a). The high-temperature pattern is diagnostic of a radical with two α-, two β-, and two γ-fluorine atoms; furthermore the magnitude of the α splitting is typical of α-difluoroalkyl radicals,[3-5] therefore the most acceptable hypothesis is $RCF_2CF_2CF_2\cdot$ (II):

$$2a_\alpha{}^F = 87.3\ \text{G} \qquad 2a_\beta{}^F = 13.0\ \text{G} \qquad 2a_\gamma{}^F = 1.5\ \text{G}$$

Reaction Mechanism. The spectra recorded below 100 °C are likely to be related to the photolysis of peroxide units to produce alkoxy radicals of type $OCF_2CF_2O\cdot$ and $OCF_2O\cdot$; these species are not stable and, in absence of reactive substrates, are expected

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[8] Hudson, A. In "Electron Spin Resonance"; Royal Society of Chemistry: London, 1980; Vol. 6, p 2.

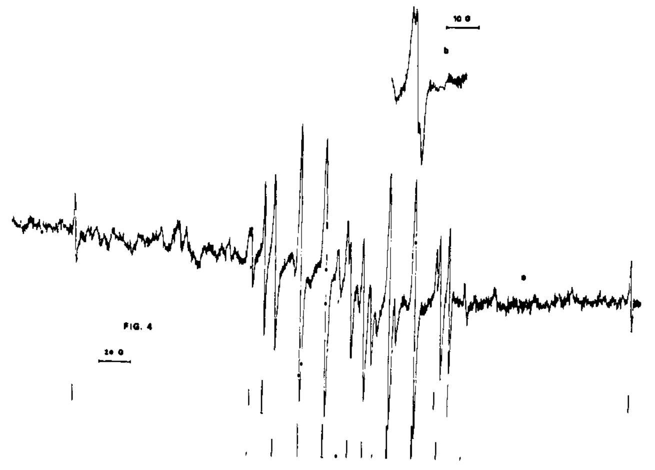


Figure 4. ESR spectrum of UV-irradiated peroxidic C3P at high temperature: (a) recorded at 190 °C; (b) details showing the triplet structure due to the interaction of a γ-CF_2 group in the $CF_2CF_2\dot{C}F(CF_3)$ radical.

to undergo β scission yielding alkoxyfluoroalkyl radicals of type I_A and I_B.

$$ROCF_2OCF_2CF_2OCF_2O\cdot \rightarrow ROCF_2OCF_2CF_2O\cdot + CF_2O \quad (1)$$

$$ROCF_2CF_2OCF_2CF_2O\cdot \rightarrow ROCF_2CF_2OCF_2\cdot + CF_2O \quad (2)$$

$$ROCF_2OCF_2CF_2O\cdot \rightarrow ROCF_2OCF_2\cdot + CF_2O \quad (3)$$

The signal of radicals II, appearing above 100 °C, is diagnostic of the intervention of thermal reactions of type (4)–(7), where

$$ROCF_2OCF_2CF_2OCF_2\cdot \rightarrow ROCF_2OCF_2CF_2\cdot + CF_2O \quad (4)$$

$$ROCF_2OCF_2CF_2\cdot \rightarrow ROCF_2O\cdot + CF_2{=}CF_2 \quad (5)$$

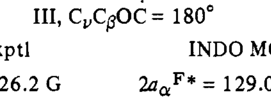
$$ROCF_2\cdot + CF_2{=}CF_2 \rightarrow ROCF_2CF_2CF_2\cdot \quad (6)$$

$$ROCF_2O\cdot \rightarrow CF_2O + RO\cdot \quad (7)$$

$RO\cdot$ are alkoxy radicals which propagate the chains through the reactions 1–3.

Photothermolysis of C3P. The photothermolysis of C3P at 60 °C yields a complex spectrum that arises from the superimposition of three hf patterns (Figure 3); the signal due to CF_3 radicals ($3a^F = 144.6$ G), a doublet of quartets 1:3:3:1 with splitting 88.7 and 12.2 G, respectively, and a triplet 1:2:1 of 126.2 G with the $M \pm 1$ lines showing a quintet structure of 2.3 G. Above 100 °C a new spectrum is recorded in quasi-stationary conditions having, as a major component, a doublet of binomial sextets with splittings 69.7 and 19.4 G and each line showing a fine structure 1:2:1 of 0.5 G (Figure 4); a second component is the signal of CF_3 radicals. The change from the low- to high-temperature spectrum is reversible, provided the irradiation times are not too long.

By analogy with the radical I_A and on the basis of INDO calculations on the model $CF_3CF(CF_3)OCF_2\cdot$, the triplet of 126.2 G is assigned to the primary perfluoroalkoxyalkyl radical $RCF_2CF(CF_3)OCF_2\cdot$ (III):

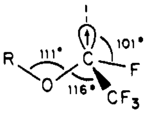


III, $C_\nu C_\beta O\dot{C} = 180°$

exptl	INDO MO
$2a_\alpha{}^F = 126.2$ G	$2a_\alpha{}^{F*} = 129.0$ G
$a_\gamma{}^F(CF) = 2.3$ G	$a_\gamma{}^F(CF) = 4.4$ G
$3a_\delta{}^F(CF_3) = 2.3$ G	$3a_\delta{}^F(CF_3)^* = 7.1$ G
$2a_\delta{}^F(CF_2) < 0.5$ G	$2a_\delta{}^F(CF_2)^* = 0.28$ G

*average values

The doublet of quartets is diagnostic of a species bearing one α-fluorine and three equivalent β-fluorines. Furthermore the magnitude of the α-F splitting is about 30% larger as compared to normal secondary perfluoroalkyl radicals, thus suggesting the presence of an alkoxy substituent;[4] a most reasonable hypothesis is therefore a radical of type $RO\dot{C}F(CF_3)$ (IV). This conclusion is supported also by INDO calculations which yield a satisfactory fit between experimental and calculated α-fluorine splittings in coincidence with the energy minimum.



IV

exptl	INDO MO
$a_\alpha{}^F = 88.75$ G	$a_\alpha{}^F = 92.0$ G
$3a_\beta{}^F(CF_3) = 12.2$ G	$3a_\beta{}^F(CF_3)_{av} = 35.0$ G

The number and magnitude of the main splittings in the doublet of sextet, which is observed above 60 °C, are diagnostic of a secondary perfluoroalkyl radical, without oxygen substituent at the radical center and bearing one α-fluorine and five equivalent β-fluorine atoms; furthermore the fine structure of 0.5 G reveals the presence of two additional F atoms in γ positions; the most likely species is therefore $CF_2CF_2\dot{C}F(CF_3)$ (V):

$$a_\alpha{}^F = 69.7 \text{ G} \qquad 2a_\beta{}^F(CF_2) = 19.4 \text{ G}$$

$$3a_\beta{}^F(CF_3) = 19.4 \text{ G} \qquad 2a_\gamma{}^F = 0.5 \text{ G}$$

Reaction Mechanism. The rationalization of the radical species, identified during the photothermolysis of C3P at different temperatures is achieved on the basis of a mechanism that is very similar to that of C2P.

The initial cleavage of peroxy bonds yields alkoxy radicals of type $ROCF_2CF(CF_3)O\cdot$ and $ROCF(CF_3)CF_2O\cdot$, which decompose by β scission according to the following scheme:

$$ROCF_2CF(CF_3)OCF_2CF(CF_3)O\cdot \rightarrow ROCF_2CF(CF_3)OCF_2\cdot + CF_3CFO$$

$$ROCF_2CF(CF_3)OCF_2CF(CF_3)O\cdot \rightarrow ROCF_2CF(CF_3)OCF_2CFO + CF_3\cdot \quad (8)$$

$$ROCF(CF_3)CF_2O\cdot \rightarrow RO\dot{C}F(CF_3) + CF_2O \quad (9)$$

These reactions account for the ESR observations at 60 °C; above 100 °C the alkoxyfluoroalkyl radicals decompose initiating the "unzipping" mechanism, which leads to formation of perfluoropropylene monomer and of radicals V.

$$ROCF_2CF(CF_3)OCF_2\cdot \rightarrow ROCF_2\dot{C}F(CF_3) + CF_2O \quad (10)$$

$$ROCF(CF_3)CF_2O\dot{C}F(CF_3) \rightarrow ROCF(CF_3)CF_2\cdot + CF_3CFO \quad (11)$$

$$ROCF_2\dot{C}F(CF_3) \rightarrow CF_2{=}CF(CF_3) + RO\cdot \quad (12)$$

$$ROCF(CF_3)CF_2\cdot \rightarrow CF_2{=}CF(CF_3) + RO\cdot \quad (13)$$

$$ROCF_2\cdot + CF_2{=}CF(CF_3) \rightarrow ROCF_2CF_2\dot{C}F(CF_3) \quad (14)$$

Conclusions

The UV-assisted vacuum thermolysis between 100 and 250 °C of C2P and C3P perfluoro polyethers, containing about 1% of peroxide units as photoactive initiators, proceeds by a complex "unzipping" mechanism based on the β scission at the C–O bonds of intermediates fluoroalkyl radicals with production of C_2F_4 and C_3F_6 monomers (reactions 4–7 and 10–14 in the text); the $RCF_2\cdot$ species add to the monomers yielding $-CF_2CF_2CF_2-$ and $-CF_2CF_2CF(CF_3)-$ units. The persistence in the high-temperature spectra of the signal of radicals $ROCF_2OCF_2\cdot$ is interpreted in terms of a greater thermal stability of the $-(OCF_2)_n-$ structures as compared to the $-(OCF_2CF_2)_n-$ ones. By generalization of these results, it is inferred that the unzipping mechanism be of major importance in the high-temperature pyrolysis of polymers with perfluorooxymethylene, perfluorooxyethylene, and perfluorooxypropylene structures. Among the intermediates of the C2P and C3P photothermolysis, of special interest are some novel primary alkoxyfluoroalkyl radicals with strongly bent structures at the radical centers and showing unusually large long-range interactions with γ- and δ-fluorine atoms, which are actually being investigated by MO methods.