

KINETIC ESR FOR SELF REACTIONS OF PERFLUOROALKYL ETHER PEROXYRADICALS

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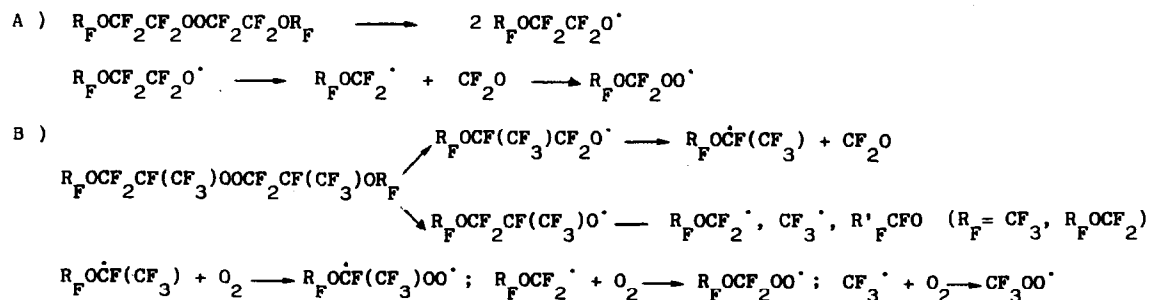
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ABSTRACT

The rate constants for self-reactions of perfluoroalkyl ether peroxy radicals are found to be several order of magnitude greater as compared to the rate constants for their not fluorinated analogues. This difference of reactivity is interpreted in terms of fluorine substituents effects.

Although an extensive literature on simple alkyl peroxy radicals exists (1), there is a paucity of data on the kinetics of self reactions of fluorine substituted analogues, despite the interest related to the key role that these species play in many important industrial oxidation processes in fluorine chemistry. The nature and distribution of products from the low temperature photooxidation of perfluoroolefins strongly suggest a decay behaviour similar to that of tertiary alkyl peroxy radicals, based on the disproportionations to dialkylperoxides and alkoxy radicals. In the absence of significant fluorine substituents effects, this mechanism is expected to yield $2k_t$ rate constants of $10^3 - 10^4 \text{ LM}^{-1}\text{s}^{-1}$ at room temperature with activation energies of 7-10 Kcal.mol^{-1} (1). In order to check this expectation and to investigate the effects of fluorine substitution, we have made kinetic ESR measurements on self reactions of primary and secondary perfluoroalkyl ether peroxy radical of formula $\text{R}_1\text{OCF}_2\text{OO}$ and $\text{R}_1\text{OCF}(\text{CF}_3)\text{OO}$ which were obtained by photolysis in air of the peroxidic perfluoropolyethers A and B according to the following scheme (2,3):



The precursor radicals R_1OCF_2 , $\text{R}_1\text{OCF}(\text{CF}_3)$, CF_3 (4) were directly identified from their steady state ESR spectra recorded during the photolysis under vacuum. The corresponding peroxyradicals signals, consisting of singlets centred at $g = 2.014$ appear immediately after the admission of air. The alkoxy radicals escaping the immediate beta-scission caused by the excess photon energy cannot be detected because of their large g anisotropy arising from the degeneracy of oxygen p orbitals (5). As shown by the reaction scheme, the photolysis of peroxide B leads to a mixture of peroxy species; nevertheless, specific kinetic measurements on the species $\text{R}_1\text{OCF}(\text{CF}_3)\text{OO}$ could be made because of their much slower decay

rate which caused their steady state concentration to be about 10 times greater than the accompanying species. The experiments were performed between -120 C and +20 C by using samples of peroxidic perfluoropolyethers of variable average molecular weight and viscosities. Radicals were generated by irradiation with a 100 W high pressure Mercury lamp and the decay curves were recorded on a Varian E-109 spectrometer equipped with a variable temperature accessory and a standard kinetic ESR equipment. The decay curves of both the primary and secondary peroxy radicals were found to follow second order kinetics with the termination rate constants reported in table 1, 2 (Fig. 1).

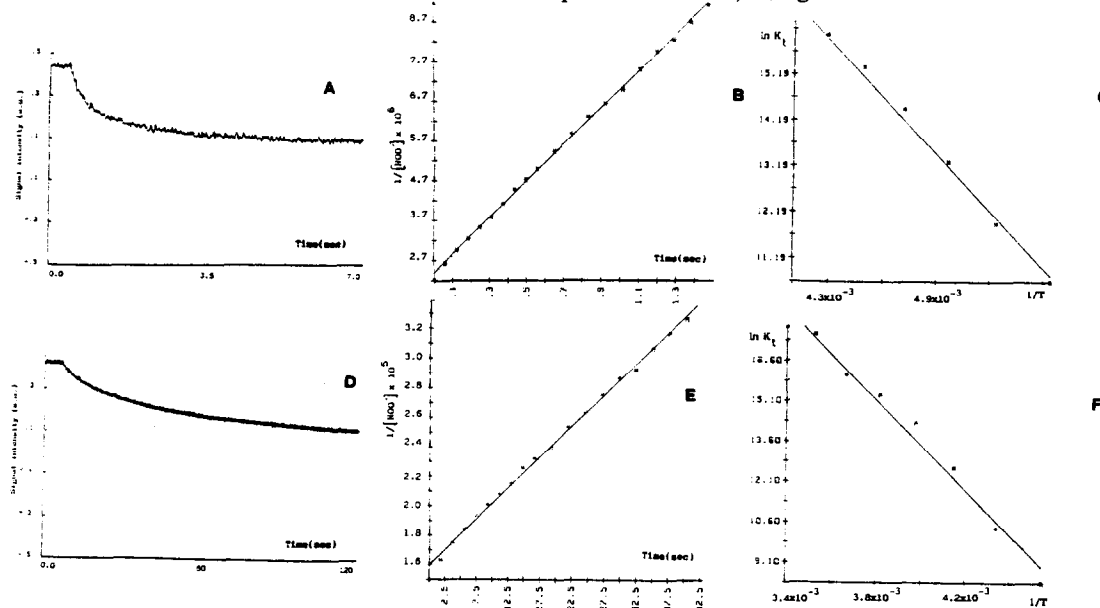
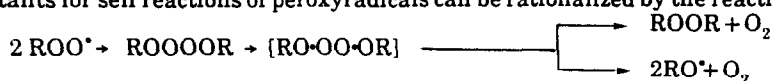


Fig. 1 - Sample curves showing the 2th order decay and the Arrhenius fit for self reactions of R_fOCF_2OO (a, b, c) and $R_fOCF(CF_3)OO$ (d, e, f) $T = -50^\circ C$.

Below $-80^\circ C$ t-Butyl peroxy radicals show two step kinetics and reversible temperature effect which were interpreted by an equilibrium between peroxy radicals and tetroxide intermediate (6). No clear evidence of a similar process could be detected with the F-analogues down to $-120^\circ C$. Kinetic data analysis reveals that the decay rates are diffusion controlled in the all range of temperatures and viscosities explored. As a consequence the measured $2k_t$ constants must be considered lower limit values and the activation energies are, at least partially, related to the diffusion process. A comparison with the reported $2k_t$ values of t-butyl peroxy radicals (table 1) and other tertiary alkylperoxy radicals (1) show that the self reactions of R_fOCF_2OO and $R_fOCF(CF_3)OO$ species are faster by factors of 10^3 , 10^5 . This dramatic increase of decay rate together with the lack of direct evidence of the equilibrium with the tetroxide are major differences which can be attributed to the effects of fluorine substitution. Second order rate constants for self reactions of peroxy radicals can be rationalized by the reaction scheme:



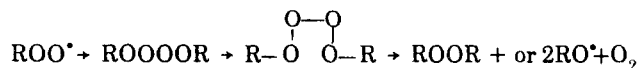
The alkoxy radicals resulting from the above scheme are of the type R_fOCF_2O and $R_fCF(CF_3)O$. The former species do not decompose by beta scission in the range of temperatures explored (7). Therefore if their fate is to undergo self reactions to dialkyl peroxides the following equation apply in condition of fast equilibrium:

$$-d[ROO^*]/dt = K k_2 [ROO^*]^2$$

where K is the association constant for the tetroxide $K = k_1/k_{-1}$

The secondary alkyl peroxy radicals are expected to undergo beta scission by cleavage of the C-C bonds yielding CF_3OO after reaction with oxygen as in equation B. If, as expected, these radicals react faster with the more abundant secondary peroxy radicals, the decay behaviour of the latter species would still be represented by the above second order equation but with a constant: $2k_1 = K k_2 (1+f)$, where f is fraction of perfluoromethylperoxy radicals undergoing cross coupling.

In both cases, the enhancement of decay rates induced by fluorine substituents can be related to the increase of the association constant K and/or to the increase of the rate of the irreversible decomposition to products (k_2). The tetroxide from *t*-butyl peroxy radicals does not decompose appreciably below -80 ; as a consequence, the intensity of the ESR signal changes reversibly with the temperature driven by the shift of the equilibrium. The fact that such phenomenon is not detected for the perfluorinated peroxy radicals, down to -120 C, implies that either the K constant has increased to such an extent that, at the equilibrium, the concentration of peroxy radicals does not reach the limit of detection, or that the activation energy for the irreversible decomposition of the tetroxide is significantly lowered. Fluorine substituents, being electron withdrawing, are expected to stabilize the polyoxide system by lowering the interaction energy between the oxygen lone pairs. In M.O. language, this stabilization arises from the interaction of the HOMO of the tetroxide system with the σ antibonding orbitals of C-F bonds (8). In agreement with this expectation, the strength of peroxidic bonds is reported to be enhanced by fluorine substituents ($D_{O-O} = 48.6$ Kcal/mol for CF_3OOCF_3 and $D_{O-O} = 38.6$ for CH_3OOCH_3 (9)). This effect is expected to lower the rate for the back dissociation of the tetroxide because of the increase of the activation energy which essentially corresponds to the strength of the intermediate O-O bond. The effect of fluorine substitution on k_2 is less straightforward since both O-O bond forming and O-O bond breaking take place in the route to the activated complex. However, accelerated decomposition of the fluorinated over the hydrocarbon tetroxide should be driven by the greater stability of the fluorinated reactive intermediate products, i.e. alkoxy radicals or dialkyl peroxides, for reasons previously noted. Transition states affording such products bear their resemblance and consequently are of lower energy. Furthermore significant stabilization of transition state (reaction 2) may be predicted to arise from synperiplanar conformations where P-P oxygen orbitals interactions are strongly enhanced.



Preference in anti or syn conformation about the central O_2 portion of the transition state could direct reaction to alkoxy radicals or peroxides respectively. Experimental evidence supporting preference for the former during F-olefin photooxidation reactions will be considered in a subsequent communication. We are at present inclined to favour the interpretation based on the enhancement by fluorine substituents of the dissociation of the tetroxide affording molecular products since it seems conceivable that if a 'stable' tetroxide was formed we should have observed the inherent two stage kinetic effects, over the wide range of temperatures explored. Further work is in progress in order to obtain more direct information about this problem. The rate data reported in table 1,2 show that self reactions of $R_pOCF(CF_3)OO$ peroxy radicals are at least two orders of magnitude slower as compared to R_pO-CF_2OO . A major part of this difference disappears when the comparison is made at R.T. for samples having approximately the same viscosity. This strongly suggests that the observed rate effects mainly arise from differences in diffusivities and their corresponding activation energies. In addition an explanation consistent with the above interpretation of the fluorine substituent effect may be based on the σ -p interaction which is enhanced in the primary species because of the greater number of C-F bonds.

Alternatively the increase of steric hindrance in the formation of the branched tetroxide can lead to a decrease in the association constant.

TABLE 1 - Second order rate constants for self termination of oligomeric RCF((CF₃)OO radicals.

Temperature (C)	$2k_t$ (l mol ⁻¹ s ⁻¹)	$2k_t$ *
-50	4.2×10^3	7.3
-40	3.2×10^4	
-30	3.9×10^5	360
-20	1.6×10^6	
-10	4.5×10^6	1.3×10^2
0	9.5×10^6	
+10	4.2×10^7	
+20	5.4×10^7	9.2×10^2

E(Kcal/mol.) 17.9

* $2k_t$ values for termination of t-butyl peroxyradicals (ref. 1)

**Kinematic viscosity at R.T. = 496/c.st.

TABLE 2 - Second order rate constants for self terminations of oligomeric R_rCF₂OO radicals measured as a function of the temperature and viscosity.

Kin. viscosity (C.St at R.T.)	17.6*	47.7*	552	4553	20000
Temperature (C)	$2k_t$	$2k_t$ (l/mol.s)	$2k_t$	$2k_t$	$2k_t$
-120	2.7×10^5	4.1×10^4			
-110	1.6×10^6	1.8×10^5			
-100	5.0×10^6	1.5×10^6			
-90	2.0×10^7	3.7×10^6	4.4×10^4	2.5×10^4	
-80	3.5×10^7	1.3×10^7	1.5×10^5	6.9×10^4	
-70	5.2×10^7	1.4×10^7	5.8×10^5	3.2×10^5	
-60		2.4×10^7	1.8×10^6	1.9×10^6	9.0×10^4
-50	6.7×10^7	4.6×10^7	4.6×10^6	1.9×10^6	3.5×10^5
-40		8.9×10^7	9.4×10^6	3.7×10^6	6.1×10^5
-30			1.3×10^7	8.4×10^6	1.3×10^6
20**			2.8×10^8		

E(Kcal/mol)

6.6

6.6

8.7

8.7

8.8

*solutions in n-perfluohexane

**extrapolated by using the activation energy of 8.7 kcal/mol

BIBLIOGRAPHY

1. J.A. Howard; Israel J. of Chem., **24**, 33 (1984) and references therein.
2. D. Sianesi, A. Pasetti, R. Fontanelli, G.C. Bernardi, G. Caporiccio: La Chimica e l'Industria, **55**, 208 (1973).
3. A. Faucitano, A. Buttafava, F. Martinotti, G. Caporiccio, C.T. Viola: J. Am. Chem. Soc., **106**, 4173 (1974).
4. A. Faucitano, A. Buttafava, F. Martinotti, A. Staccione, G. Marchionni: Proceedings 13th International Conference on photochemistry Budapest, August 1987
5. M.C.R. Symons: J. Amer. Chem. Soc. **91**, 5924, (1969).
6. J.E. Bennett, D.M. Brown, D. Mile: Chem. Com., 509 (1969).
7. A. Staccione, G.T. Viola, G. Marchionni; to be published.
8. P.V. Raguè Schleyer, A.J. Kos: Tetrahedron, **39** 1141 (1983).
9. L. Batt, R. Walsh: Int J. Chem. Kim., **14**, 933 (1982).

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