Perfluorobutylperoxyl Radical as an Oxidant in Various Solvents

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Perfluorobutylperoxyl radicals were produced by pulse radiolysis of aerated solutions of perfluorobutyl iodide. The rate constants for reaction of this radical with several organic reductants, chlorpromazine, trolox, hydroquinone, and several other phenols, were determined in various solvents and were found to be in the range of 10^5-10^9 M⁻¹ s⁻¹. By comparison with other haloalkylperoxyl radicals, C4F9OO* was found to be a much more powerful oxidant, whose reactions took place more rapidly and were less sensitive to solvent and substituent effects. The rate constants (k) for oxidation of a series of para-substituted phenols by $C_4F_9OO^*$ gave a good linear correlation between log k and the electrophilic substituent constant σ^+ , with a slope of $\rho^+ = -2.3$, indicating formation of a positively charged transition state. Parallel experiments with CCl₃OO[•] were limited to the most reactive phenols and gave a higher slope, $\rho^+ = -3.3$. The rates of reaction of C₄F₉OO[•] with trolox and chlorpromazine were found to depend on solvent viscosity, but much less on solvent polarity and acid-base properties, probably because they were closer to the diffusion-controlled limit. The longer chain $C_{10}F_{21}OO^{\circ}$ was somewhat less reactive than $C_4F_9OO^{\circ}$ because of geometric factors.

Introduction

Perfluoroalkyl radicals are of interest as they may be produced during radiolytic or pyrolytic degradation of poly(tetrafluoroethylene) and from certain halocarbons in the atmosphere. Under aerobic conditions, alkyl radicals react rapidly with oxygen to form peroxyl radicals.

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$
 (1)

These radicals may react with a variety of compounds by hydrogen abstraction, addition, or electron-transfer oxidation.² Reactions of peroxyl radicals with biological materials have been associated with the toxicity of several halocarbons.³ In this study we examine the reactivities of several compounds with perfluorobutylperoxyl radicals and compare them with those determined previously for CF_3OO^{4} and CCl_3OO^{5-7} We find that $C_4F_9OO^{4}$ in general is more reactive than the other radicals and the solvent effect on its rate constants less pronounced. The effect of chain length indicates the order of reactivity to be $CF_3OO^{\bullet} < C_{10}F_{21}OO^{\bullet} <$ C₄F₉OO[•].

Experimental Section⁸

Perfluorobutyl iodide (Aldrich) was purified by passing through a column of activated neutral alumina (Aldrich), kept refrigerated in the dark, and used within several days. Perfluorodecyl iodide (Aldrich) was used as received (white crystals). Chloropromazine (2-chloro-10-(3-dimethylaminopropyl)phenothiazine), phenol, and 4-methoxyphenol were obtained from Sigma, 4-tert-butylphenol was from Fluka, and trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), hydroquinone, and the other phenols were from Aldrich, and were used as received. The organic solvents were analytical or spectrophotometric grade reagents. Water was purified with a Millipore Super-Q system.

Solutions were prepared just before irradiation and were protected from unnecessary illumination. Perfluorobutyl iodide was

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(8) The identification of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

dissolved in most solvents at a concentration of 30-120 mM (0.5-2% v/v). In aqueous solutions, however, it was necessary to add an organic cosolvent, generally an alcohol, to dissolve sufficient concentrations of the halide ($\sim 2 \text{ mM}$) to produce a substantial concentration of the radicals. In most experiments, aerated solutions containing perfluorobutyl iodide and various concentrations of the organic reductant were fed into the irradiation cell by a syringe and a new sample was introduced for each pulse. All experiments were carried out at room temperature, 22 ± 2 °C.

Pulse radiolysis experiments were carried out with a Febetron Model 705 accelerator, producing 2-MeV electron pulses of 50 ns duration. The radiation dose ranged from 9 to 20 Gy per pulse. The detection system consisted of a 300-W Xe lamp, a Kratos monochromator, a RCA 4840 photomultiplier and associated optical components. The signals were transferred through a Tektronix 7612 digitizer to a PC Designs GV 386 computer for analysis. Other details of the experiments were as described before 5-7

Results and Discussion

Formation and Reactions of Perfluorobutylperoxyl Radicals. The peroxyl radicals, $C_4F_9OO^*$, were produced by reduction of C_4F_9I with solvated electrons or with organic radicals in the presence of oxygen, as discussed in detail for similar radicals studied previously.5-

$$C_4F_9I + e^- \rightarrow C_4F_9^* + I^-$$
 (2)

$$C_4F_9^{\bullet} + O_2 \rightarrow C_4F_9OO^{\bullet} \tag{3}$$

In the absence of other substrates, $C_4F_9OO^{\bullet}$ decays by radicalradical reactions. It may also abstract H from certain solvents

$$C_4F_9OO^{\bullet} + RH \rightarrow C_4F_9OOH + R^{\bullet}$$
 (4)

and may thus propagate a chain reaction if the radical R* reduces C_4F_9I . However, in the presence of organic reductants, such as chlorpromazine, trolox, or phenols, $C_4F_9OO^*$ will oxidize these compounds to form radical cations, e.g., with chlorpromazine (Pz)

$$C_4F_9OO^{\bullet} + Pz + H^+ \rightarrow C_4F_9OOH + Pz^{\bullet+}$$
(5)

or the neutral radicals, e.g., with phenols (see mechanism below).

$$C_4F_9OO^{\bullet} + ArOH \rightarrow C_4F_9OOH + ArO^{\bullet}$$
 (6)

We have monitored the appearance of the optical absorption spectra of the product radicals under various conditions to confirm the oxidation process. No reaction was observed in the absence of C_4F_9I , O_2 , or the organic reductants. The yield and kinetics of oxidation of hydroquinone in methanolic solution was found to be the same in the absence or presence of 5% acetone. As

TABLE I: Rate Constants for Oxidation of Substituted Phenols by $C_4F_9OO^*$ and CCl_9OO^* in Methanol

	k, M ⁻¹ s ⁻¹		
compound	C4F900*	CCl ₃ OO*	σ^{+a}
phenol	$(7.0 \pm 1.1) \times 10^{5}$	<1 × 10 ⁵	0.00
4-fluorophenol	$(4.5 \pm 1.3) \times 10^{5}$		-0.07
4-tert-butylphenol	$(2.4 \pm 0.4) \times 10^{6}$	<3 × 10 ⁵	-0.26
4-methylphenol	$(4.2 \pm 0.6) \times 10^{6}$	<1 × 10 ⁵	-0.31
4-phenoxyphenol	$(4.0 \pm 1.2) \times 10^6$		-0.5
4-methoxyphenol	$(6.9 \pm 1.1) \times 10^7$	$(7.8 \pm 1.5) \times 10^{5}$	-0.78
4-hydroxyphenol	$(1.1 \pm 0.2) \times 10^8$	$(3.0 \pm 0.6) \times 10^{6}$	-0.92
4-(N,N-dimethyl-	$(3.2 \pm 0.5) \times 10^9$	$(1.0 \pm 0.2) \times 10^9$	-1.7

amino)phenol

"Electrophilic substituent constants from ref 13.

acetone is an efficient electron scavenger, which transforms e^- to the ketyl radical $(CH_3)_2\dot{C}O^-$ or its protonated form $(CH_3)_2\dot{C}OH$, we conclude that the latter radicals also reduce C_4F_9I , e.g.

$$(CH_3)_2COH + C_4F_9I \rightarrow (CH_3)_2CO + H^+ + C_4F_9^* + I^-$$
 (7)

The rate of oxidation of the various substrates, which occurred over several tens of microseconds, was determined by following the buildup of absorption of their transient oxidation product (at 525 nm for chlorpromazine, 395–430 nm for trolox and most phenols, and 490 nm for (dimethylamino)phenol). From plots of first-order rates (k_{obs}) vs concentration, we derived the second-order rate constants summarized in the tables. The rate constants are found to vary between 10⁵ and 10⁹ M⁻¹ s⁻¹ and to depend on the nature of the organic reductants and also on solvent composition. In all cases, however, the rate constants for C₄F₉OO[•] are found to be considerably higher than those reported for CCl₃OO[•] or CF₃OO[•],² suggesting that C₄F₉OO[•] is a more powerful oxidant.

Mechanism of Reaction. Substituent Effects. The organic reductants examined here include chlorpromazine, which is oxidized to the radical cation by an electron-transfer mechanism,^{7,9} and various phenols, which form the neutral phenoxyl radicals either by electron transfer or by hydrogen abstraction.^{6,10,11} Previous studies concluded that phenols are oxidized by an electron-transfer mechanism, at least in the case of the fast reactions in polar solvents.^{6,10} It was suggested, however, that the electron transfer to peroxyl radicals is concerted with a proton transfer to form the neutral hydroperoxide product,⁶ as in reaction 5, with the proton being supplied by the solvent to the transition state $[C_4F_9OO^{\circ}Pz]$. In reaction 6 the solvent may also participate by deprotonating ArOH to ArO⁻ in the transition state to facilitate its oxidation to ArO. That the mechanism involves polar intermediates was also indicated by the finding that the rate constant for oxidation by peroxyl radicals increased with increasing electron affinity of the alkyl group of this radical.⁵ The perfluorobutyl group in C₄F₉OO[•] has a higher electron affinity $(3.2 \text{ eV})^{12}$ than CCl₃ and CF₃ ($\sim 2 \text{ eV}$)¹² and, therefore, it is not surprising that this radical reacts more rapidly than CCl₃OO[•] and CF₃OO[•].

To unravel more details on the mechanism of reaction of $C_4F_9OO^{\circ}$, we measured the rate constants for its reaction with a series of substituted phenols and compared them with those of CCl_3OO° (Table I). With $C_4F_9OO^{\circ}$, the rate constants varied from 4.5×10^5 M⁻¹ s⁻¹ for 4-fluorophenol to 3.2×10^9 M⁻¹ s⁻¹ for 4-(*N*,*N*-dimethylamino)phenol. CCl₃OO[•] was much less reactive and its rate constants could be determined only with the three most reactive phenols; for the less reactive phenols we obtained only upper limits. For both radicals, however, electron-donating substituents are found to increase the reactivity. Correlation of the rate constants for $C_4F_9OO^{\circ}$ with the electrophilic substituent constants¹³ σ^+ gives a good straight line (Figure 1)



Figure 1. Dependence of log k for oxidation of 4-substituted phenols on the electrophilic substituent constant σ^+ : (O) C₄F₉OO[•], (Δ) CCl₃OO[•].



Figure 2. Dependence of log k on solvent dielectric constant ϵ . Rate constants for oxidation of chlorpromazine (a) and hydroquinone (b) by C₄F₉OO[•] (O, results from Table II) and by CCl₃OO[•] (\oplus , from ref 7; \blacktriangle , Alfassi, Z. B., unpublished results; and \blacksquare , this work).

with a slope of $\rho^+ = -2.3$. This line has a somewhat better fit to the experimental points than that using Hammett σ . This result indicates that the transition state involves a partial positive charge on the phenolic oxygen, which supports the electron-transfer mechanism. The correlation for CCl₃OO[•] with the most reactive phenols gives a similar straight line (Figure 1) with a greater slope, $\rho^+ = -3.3$ (the line derived from the three points for the same phenols reacting with C₄F₉OO[•] gives $\rho^+ = -1.8$). This greater selectivity is associated with the lower rate constants of the CCl₃OO[•] radical.

Solvent Effects in Alcohol Mixtures. Rate constants for electron-transfer reactions of peroxyl radicals are known to depend on the solvent. The rate cosntants (k) for the reaction of chlorpromazine with CCl₃OO[•] in CCl₄/alcohol/water mixtures varied in the range of 10^7-10^9 M⁻¹ s⁻¹.⁷ A plot of log k vs the dielectric constant (ϵ) of the medium was found to give a good straight line (the results of ref 7 and more recent results are shown

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TABLE II: Rate Constants for Reactions of $C_4F_9OO^*$ in Various Media

compound	solvent	$k, M^{-1} s^{-1}$	ۻ
chlorpromazine	2-PrOH	$(2.8 \pm 0.6) \times 10^8$	18.3
•	3:2 2-PrOH:H ₂ O	$(6.7 \pm 1.1) \times 10^8$	43.2
	1:4 2-PrOH:H ₂ O	$(6.6 \pm 1.1) \times 10^8$	67.7
	МеОН	$(5.9 \pm 0.9) \times 10^8$	32.7
	1:1 MeOH:H ₂ O	$(1.9 \pm 0.3) \times 10^9$	57.5
	1:4 $MeOH:H_2O$	$(2.2 \pm 0.4) \times 10^8$	70.8
	2:1 MeOH:formamide	$(1.0 \pm 0.2) \times 10^9$	59.3
	1:3 MeOH:formamide	$(6.4 \pm 0.9) \times 10^8$	91.4
	formamide	$(2.1 \oplus 0.5) \times 10^8$	111.0
tolox	MeOH	$(6.4 \pm 1.1) \times 10^8$	32.7
	1:1 MeOH:H ₂ O	$(7.9 \pm 1.2) \times 10^8$	57.5
	1:4 MeOH: H_2O	$(3.6 \pm 0.5) \times 10^8$	70.8
hydroquinone	2-PrOH	$(1.2 \pm 0.2) \times 10^8$	18.3
-	MeOH	$(1.1 \triangleq 0.2) \times 10^8$	32.7
	1:1 MeOH:H ₂ O	$(1.0 \oplus 0.2) \times 10^8$	57.5
	1:4 2-PrOH:H ₂ O	$(1.8 \triangleq 0.5) \times 10^8$	67.7
	formamide	$(1.2 \triangleq 0.2) \times 10^8$	111.0
phenol	MeOH	$(7.0 \pm 1.1) \times 10^{5}$	32.7
-	1:1 MeOH:H ₂ O	$(1.7 \pm 0.8) \times 10^{6}$	57.5

^a The dielectric constant of the solvent, from: *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed., McGraw Hill: New York, 1985; pp 10–103. The values for mixtures were based on: Marcus Y. *Ion Solution*; Wiley: New York, 1986; p 186.

in Figure 2a). Therefore, we examined the dependence of log k for the reaction of C₄F₉OO[•] on dielectric constant by using alcohols and several alcohol mixtures with water and formamide (Table II).

The rate constants for chlorpromazine are found to be much higher with $C_4F_9OO^{\circ}$ than with CCl_3OO° in the less polar solvent mixtures ($\epsilon < 60$), but their dependence on solvent polarity is very weak (Figure 2a). Moreover, for mixtures of each pair of solvents, the values for $C_4F_9OO^{\bullet}$ are found to increase with polarity and then decrease, in contrast with the previous findings for CCl₃OO^{*}. The value determined in this work for CCl₃OO[•] reaction with chlorpromazine in formamide also shows a decreased reactivity at high polarity (see discussion below). The rate constants for the reaction of trolox with $C_4F_9OO^{\bullet}$ in aqueous methanol mixtures (Table II) are higher than the corresponding values for CCl₃OO[•]. The rate constants also show a decrease at higher solvent polarity, but unlike the chlorpromazine system, this finding is qualitatively in line with previous results on CCl₃OO[•] and CF₃OO[•] in the same solvents. For hydroquinone, the rate constants with $C_4F_9OO^{\circ}$ are considerably higher than the values reported for CCl₃OO[•] and CF_3OO^{\bullet} . The variations in k with the solvent are very small and practically within experimental error, unlike the case of CCl₃OO[•], where k increased with solvent polarity up to $\epsilon \sim 80$ and then decreased in the highly polar formamide (Table IV and Figure 2b).

These results suggest that the rate constants for $C_4F_9OO^{\bullet}$ may be dependent on other solvent parameters in addition to the dielectric constant. To examine this possibility we measured the rate constants for chlorpromazine and trolox in a series of pure solvents for which various physical constants and empirical parameters have been determined extensively. We carried out the measurements in the same solvents used before for the reaction of trolox with CCl₃OO[•].

Solvent Effects in Pure Solvents. The rate constants for reaction of trolox with $C_4F_9OO^{\circ}$ in a wide variety of solvents (Table III) are found to be much higher than those determined before for CCl₃OO^{•.6} However, a plot of log k for C₄F₉OO[•] vs log k for CCl₃OO^{•.6} However, a plot of log k for C₄F₉OO[•] vs log k for CCl₃OO[•] showed no correlation between the two sets of rate constants. To find the dependence of k on the various solvent parameters, we performed multiparameter correlations of the type used before for the reaction of trolox with CCl₃OO^{•.6} Correlations with ϵ and ξ (a measure of the proton-transfer basicity of the solvent¹⁴ important in enhancing deprotonation of trolox in the





Figure 3. Correlations of rate constants with solvent parameters. (a) Chlorpromazine, $\log k_{obs}$ vs $\log k_{calc}$, calculated from the solvent parameters according to eq 10. (b) Trolox, $\log k_{obs}$ vs $\log k_{calc}$, calculated from the solvent parameters according to eq 8. (c) Trolox, plot of $1/k_{obs}$ vs solvent viscosity (in cP).

transition state), which gave good results for the reactions of CCl₃OO[•] with trolox, gave very scattered results for the reaction of C₄F₉OO[•]. Because the results with *t*-BuOH, formamide, and ethylene glycol, the three solvents with the highest viscosities, showed the greatest deviations, we added the viscosity η as a third parameter. We also added a fourth parameter, α , which is a measure of the hydrogen-bonding acidity of the solvent¹⁵ and may be important in enhancing the protonation of the hydroperoxide anion in the transition state. Reasonable fits ($R^2 = 0.90$) were obtained (Figure 3b) with equations such as log $k = (8.60 \pm 0.15) - (0.53 \pm 0.13) \log \eta - (0.08 \pm 0.25)\alpha + (0.82 \pm 1.25)\xi + (0.002 \pm 0.003)\epsilon$. This shows, however, that η is the most important parameter. Indeed, correlation with viscosity alone fits ($R^2 = 0.88$) the equation

$$\log k = (8.73 \pm 0.11) - (0.47 \pm 0.07) \log \eta \tag{8}$$

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TABLE III: Rate Constants for Reactions of C₄F₉OO' with Chlorpromazine and Trolox in Various Solvents

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	K, IVI 5						
solvent	chlorpromazine	trolox	ۻ	η^b	Ę	ad	
dioxane	$(3.0 \pm 0.6) \times 10^8$	$(5.3 \pm 0.8) \times 10^8$	2.2	1.2	0.2	0.0	
pyridine	$(1.5 \pm 0.5) \times 10^8$	е	12.3	0.95	0.6	0.0	
tert-butyl alcohol	$(1.4 \pm 0.2) \times 10^8$	$(2.6 \pm 0.4) \times 10^8$	12.5	3.90	0.2	0.68	
2-propanol	$(2.8 \pm 0.6) \times 10^8$	$(6.0 \pm 1.0) \times 10^8$	18.3	2.22	0.2	0.76	
acetone	$(5.7 \pm 0.9) \times 10^8$	$(7.7 \pm 1.5) \times 10^8$	20.7	0.32	0.0	0.08	
methanol	$(5.9 \pm 0.9) \times 10^8$	$(6.4 \pm 1.1) \times 10^8$	32.7	0.58	0.2	0.93	
acetonitrile	$(7.9 \pm 1.0) \times 10^8$	$(8.0 \pm 1.2) \times 10^8$	37.5	0.37	0.0	0.19	
ethylene glycol	$(8.5 \pm 1.5) \times 10^7$	$(1.0 \pm 0.3) \times 10^8$	37.7	20	0.2	0.90	
formamide	$(2.1 \pm 0.5) \times 10^8$	$(3.5 \pm 0.5) \times 10^8$	111.0	3.64	0.0	0.71	

"The dielectric constant of the solvent, from: Lange's Handbook of Chemistry, 13th ed.; Dean, J. A., Ed.; McGraw Hill: New York, 1985; pp 10–103. "Viscosity in cP at ~ 22 °C based on: Viswanath, D. S.; Natarajan, G. Data Book on the Viscosity of Liquids; Hemisphere Publishing: New York, 1989. "Coordinate covalency parameter, a measure of the proton-transfer basicity of the solvent, from ref 14. "Hydrogen bond donors acidity of the solvent, from ref 15. "Could not be determined, apparently because it is very high and required small concentrations of trolox, which resulted in decreased yield due to competing reactions."

For the reaction of C₄F₉OO[•] with chlorpromazine, the best fit using all four parameters (Figure 3a) was better ($R^2 = 0.96$) than that for trolox and gave the equation

$$\log k = (8.58 \pm 0.09) - (0.55 \pm 0.08) \log \eta + (0.21 \pm 0.11)\alpha - (0.64 \pm 0.22)\xi - (0.001 \pm 0.001)\epsilon$$
(9)

Removing ϵ decreased the fit only slightly (to $R^2 = 0.95$), but removing ξ or α decreased the correlation coefficient to $R^2 = 0.86$. Correlation with viscosity alone gave a poor fit ($R^2 = 0.77$) for log $k = 8.52 - 0.50 \log \eta$. Unlike the case of trolox, it seems that the acidity and basicity of the solvent play some role in the oxidation of chlorpromazine. This is perhaps because chlorpromazine, unlike trolox, has no labile protons and the solvent is the only source for protons necessary to neutralize the hydroperoxide anion (cf. reactions 5 and 6).

These correlations suggest that the most critical solvent parameter that influences the reaction of $C_4F_9OO^*$ is the viscosity. This is rationalized by assuming that the high rate constants observed, $(5-8) \times 10^8$ M⁻¹ s⁻¹, are very near the diffusion-controlled limit in these solvents and, therefore, are insensitive to solvent parameters other than viscosity. The rates of diffusion in the various solvents, estimated from the Debye equation, k_{dif} = $8kT/3\eta$ (assuming the radii of the two reactants to be similar), are found to be higher than the observed rate constants by a factor of $k_{\rm dif}/k_{\rm obs} = 3$ for ethylene glycol, 5–6 for 2-PrOH, t-BuOH, and formamide, and 10-20 for the other solvents. The rate constants measured in these solvents, however, may be the diffusion-controlled limit if geometric factors are taken into account.¹⁶ The active sites comprise only a small portion of the reactant surfaces in these reactions so that the reactants may need to rotate to bring the active sites together.¹⁶ Since the viscosity of the solvent affects the rate of rotation of the reactants,¹⁶ the observed rate constants may be indeed limited by translational and rotational diffusion and thus dependent mainly on solvent viscosity.

The above regression analyses gave best fits of log k vs -0.5 log η implying a dependence of k on $1/\eta^{1/2}$ rather than on $1/\eta$ as expected from the Debye equation. The actual reaction rate may depend on the diffusion rate, and through it on η , in a more complex way, due to geometric factors, as suggested before.¹⁶ We confirmed this by plotting 1/k vs η for the trolox system, where η was the only solvent parameter that had a significant effect. The results (Figure 3c) show a good correlation ($R^2 = 0.98$). A similar plot for chlorpromazine gave a poorer correlation ($R^2 = 0.72$), probably because it ignored the other solvent parameters.

Perfluorodecylperoxyl Radical. To investigate the behavior of longer perfluoroalkylperoxyl radicals, we measured the reactivity of perfluorodecylperoxyl with trolox and chlorpromazine in

TABLE IV: Rate Constants for Other Radicals

compound	radical	solvent	k, M ⁻¹ s ⁻¹
hydroquinone	CCl ₃ OO*	1:1 2-PrOH:CCl	$(2.9 \pm 0.1) \times 10^{6}$
	CCI.00	20:1:0.01 H,O:2-PrOH:CCl4	$(4.0 \pm 0.3) \times 10^7$
	CCI-00.	99:1 formamide:CCL	$(9 \pm 2) \times 10^{6}$
	CHCP00.	7:3 2-PrOH:CHCl	~106
chlorpromazine	CCI100	20:1 formamide:CCL	$(2.1 \pm 0.3) \times 10^8$
•	C10F2100*	MeOH	$(4.5 \pm 0.9) \times 10^8$
trolox	C10F2100'	MeOH	$(4.2 \pm 0.8) \times 10^8$

methanol. The rate constants (Table IV) were found to be slightly lower than those for $C_4F_9OO^{\bullet}$. Taking into account that the rate constants for CF_3OO^{\bullet} were lower than those for $C_4F_9OO^{\bullet}$, we find an increase and then a decrease in reactivity with chain length. This behavior results from the opposing effects of two parameters. Increasing the chain length of the perfluoroalkyl group increases its electron affinity,¹² which causes the longer perfluoroalkylperoxyl to have a higher reduction potential and thus to react more rapidly. With $C_4F_9OO^{\bullet}$ the reaction reaches the diffusion-controlled limit and its rate constant becomes limited by geometric factors (the fraction of active site on the radical surface). Further lengthening of the perfluoroalkyl chain decreases this geometric factor and thus lowers the rate constant.

Conclusion

Perfluoroalkylperoxyl radicals are found to be more powerful oxidants than other halogenated peroxyl radicals. All these radicals oxidize phenols, chlorpromazine, and other organic reductants most likely by an inner-sphere electron-transfer process in which the solvent plays a major role through its polarity and its acid-base properties. The rate constants for oxidation by $C_4F_9OO^{\circ}$ are found to be considerably higher than those of CCl_3OO^* and also than those of CF_3OO^* . This increase in reactivity is due to the higher electron affinity of the perfluorobutyl group which increases the driving force for electron acceptance by the peroxyl radical. In fact, the rate constants for reaction of $C_4F_9OO^{\circ}$ with trolox are diffusion-controlled. They are found to be strongly affected by solvent viscosity but not very sensitive to solvent dielectric constant or acid-base properties. The rate constants for chlorpromazine are somewhat lower than the diffusion-controlled limit and thus are affected by solvent viscosity as well as by its proton-transfer properties. The effect of chain length on the reactivity of perfluoroalkylperoxyl radicals is demonstrated by comparing CF₃OO[•], C₄F₉OO[•], and C₁₀F₂₁OO[•]. The rate constants are found to increase and then decrease with chain length, probably due to compensating effects of electron affinity and geometric factors.

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