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# Formation of Radical Anions on the Reduction of Carbonyl-Containing Perfluoroaromatic Compounds in Aqueous Solution: A Pulse Radiolysis Study

## Lian C. T. Shoute* and Jai P. Mittal*,†

*Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India*

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Radical anions are formed on addition of hydrated electrons to pentafluoroacetophenone (PFA) and pentafluorobenzaldehyde (PFB) in aqueous solutions. On the other hand, addition of hydrated electrons to pentafluorobenzoic acid (PFBA) leads to rapid fluoride elimination. The spectrum of the radical anion of PFA has $\lambda_{max}$ at 300 and 440 nm with absorption coefficient at 440 nm $\epsilon_{440} = 2100$ L mol$^{-1}$ cm$^{-1}$. PFA$^{\bullet-}$ decays with a rate constant of $(7 \pm 3.0) \times 10^3$ s$^{-1}$. It has a p$K_a = 7.5$ and the spectrum of the conjugate acid has $\lambda_{max}$ at 270 and 460 nm with $\epsilon_{460} = 900$ L mol$^{-1}$ cm$^{-1}$. The spectrum of the radical anion of PFB has $\lambda_{max}$ at 285 and 430 nm with $\epsilon_{430} = 800$ L mol$^{-1}$ cm$^{-1}$. PFB$^{\bullet-}$ decays with a rate of $(4 \pm 2) \times 10^3$ s$^{-1}$. It has a p$K_a = 7.2$ and the spectrum of the conjugate acid has weak absorption at 330 nm. Evidence for the formation of the radical anion was obtained from intermolecular electron transfer from the radical anions of PFA and PFB to *p*-benzoquinone (Q), methyl viologen (MV$^{2+}$), and 9,10-anthraquinone-2-sulfonate (AQS$^-$). Strong reductants derived from reduction of 2,2-bipyridine (BpyH$^{\bullet}$) and 1,10-phenanthroline (PhenH$^{\bullet}$) can reduce both PFA and PFB. From the kinetics of these electron transfer reactions the reduction potentials of PFA and PFB have been determined to be $-0.86 \pm 0.1$ and $-0.75 \pm 0.1$ V vs NHE at pH 9.4. Addition of OH$^{\bullet}$ radical to the aromatic ring of these fluorinated compounds led to rapid HF elimination and the formation of phenoxyl radicals, and addition of H$^{\bullet}$ atoms led to the formation of cyclohexadienyl radical.

## Introduction

Due to their chemical inertness, there is increasing concern for accumulation of perfluorinated compounds in the environment.[1,2] As expected for compounds containing highly electronegative fluorine atoms, a chemical reaction to which they are most susceptible is reduction. Electrochemical technique has been increasingly used for the preparation of perfluorinated derivatives.[3] A serious problem encountered in this method is the ease with which fluoride is lost on reduction. Strong reductants led to complete mineralization of fluorine.[4] Using the photopolarographic technique, Konovalov et al.[5] have estimated a rate constant of ca. $10^9$ s$^{-1}$ for fluoride elimination from the radical anion of pentafluorobenzoate. Rapid fluoride elimination has been reported on reduction of perfluorobenzene.[6] Recently, we have reported[7] that the addition of hydrated electrons to pentafluorophenol and pentafluoraniline led to rapid fluoride elimination and the initially formed electron adducts could not be detected. The rate constants for fluoride elimination from these compounds were estimated to be $>10^7$ s$^{-1}$. This is in contrast to the radical anion of tetrafluoro-1,4-benzoquinone which does not lose fluoride.[8]

Due to the high C−F bond strength, it was speculated that addition of an electron to a perfluorocarbon may not lead to heterolytic breaking of the bond to form fluoride ion. In the gas phase[9] or in the rigid organic glassy matrices at low temperature,[10,11] the radical anions of perfluorocarbons were observed to be stable with respect to fluoride elimination. The difference in the dynamics of the radical anion in the gas phase and in the rigid low-temperature matrices on the one hand and aqueous solution at room temperature on the other can be traced to the solvation of fluoride in aqueous solution. In aqueous solution, fluoride ion is very strongly solvated and drives the release of fluoride from the radical anion.

The rate of fluoride elimination from the radical anions of a perfluorinated compound depends on several factors. If the unpaired electron occupies a $\sigma$ or a mixture of $\sigma$ and $\pi$ orbitals,[11,12] the rate is expected to be very fast. The rate is expected to be relatively slow for a $\pi$ radical anion as the rate of fluoride elimination in this case can be visualized as electron transfer from $\pi$ to the orthogonal $\sigma$ orbital of the C−F bond.[13] The rate also depends strongly on the electron affinity of the other substituent present in the ring, because in the presence of such substituents, fluoride elimination can be visualized as an intramolecular electron transfer from the substituent to the C−F bond.[13] In this study, we have investigated the formation of the radical anion of carbonyl containing perfluoroaromatic compounds $C_6F_5COX$ (X = COOH, CHO, COCH$_3$) on reduction and their intermolecular electron transfer reactions in aqueous solution.

## Experimental Section

The kinetic spectrophotometric pulse radiolysis system consists of a linear accelerator which delivers 7 MeV electrons of 50 ns, 500 ns and 2 $\mu$s pulse width and with doses in the range of 5−100 Gy per pulse. The dose absorbed was determined in an aerated 0.05 mol L$^{-1}$ KSCN solution assuming $G\epsilon = 2.5 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ per 100 eV ($G$ is radical formed per 100 eV). Details of the experimental setup are described elsewhere.[7,8] The bimolecular rate constants ($k$) reported here were obtained from the slope of the plots of the observed rate $k_{obs}$ vs [S], the substrate (S) concentration, using the equation $k_{obs} = k_0 + k[S]$. The uncertainties in the values of $k$ are estimated to be 10−20%.[7] 2,3,4,5,6-Pentafluoroacetophenone (PFA), 2,3,4,5,6-pentafluorobenzaldehyde (PFB), and 2,3,4,5,6-pentafluorobenzoic acid (PFBA) obtained from PCR Research Chemicals were used as received. All the chemicals used are either analytical or spectroscopic grade purity. A flow cell of 1.55 cm path length was used for spectral recording. The solutions for pulse radiolysis were adjusted to the desired pH by using HClO$_4$, H$_2$-

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Reduction of Carbonyl-Containing Perfluoroaromatic Compounds
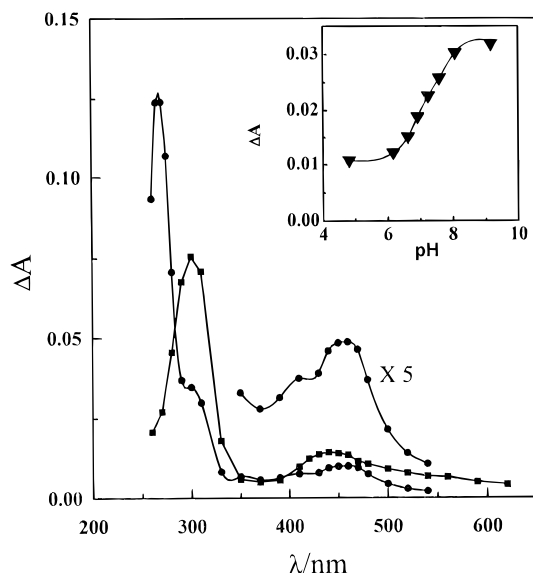
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**Figure 1.** Transient absorption spectra obtained on pulse radiolysis of deoxygenated solution of $(2.7–8) \times 10^{-4}$ mol L$^{-1}$ PFA containing 0.9 mol L$^{-1}$ *t*-BuOH (■) at pH 9.5 (20.3 Gy), and (●) at pH 4.8 (24.6 Gy). Inset: Dependence of the absorbance at 460 nm on pH of the solution (42 Gy).

**TABLE 1: Rate Constants of Reactions of e$^-_{aq}$, H, and OH with C$_6$F$_5$COX**

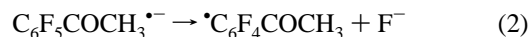| radical | substrate | pH | $k$/(L mol$^{-1}$ s$^{-1}$) |
|---------|-----------|----|-----------------------------|
| e$^-_{aq}$ | PFA | 7 | $(1.9 \pm 0.3) \times 10^{10}$ |
| e$^-_{aq}$ | PFB | 7 | $(2.4 \pm 0.4) \times 10^{10}$ |
| e$^-_{aq}$ | PFBA | 12 | $(9.6 \pm 1.5) \times 10^{9}$ |
| H$^•$ | PFBA | 0.6 | $(5.5 \pm 1.0) \times 10^{7}$ |
| OH$^•$ | PFA | 7 | $(1.5 \pm 0.3) \times 10^{9}$ |
| OH$^•$ | PFB | 7 | $(2.0 \pm 0.3) \times 10^{9}$ |
| OH$^•$ | PFBA | 0.6 | $(1.1 \pm 0.2) \times 10^{9}$ |
| OH$^•$ | PFBA | 9 | $(1.1 \pm 0.2) \times 10^{10}$ |
| O$^{•-}$ | PFBA | 13.3 | $(1.2 \pm 0.2) \times 10^{8}$ |

KPO$_4$, Na$_2$HPO$_4$, Na$_2$B$_2$O$_7$, and NaOH and were saturated with high-purity N$_2$, O$_2$, or N$_2$O gas prior to the introduction of volatile compounds such as PFA, PFB, etc. Distilled water was further purified in a Millipore Milli-Q system.

## Results and Discussion

**Reduction of Pentafluoroacetophenone.** Radiolysis of water produces e$^-_{aq}$, H$^•$, and OH$^•$ as primary reactive radicals. The reaction of PFA with hydrated electrons was studied under condition where OH$^•$ was scavenged by 2-methyl-2-propanol (*t*-BuOH), which transforms it to a relatively unreactive radical. Hydrated electrons react with PFA with a rate constant of $k_1 = (1.9 \pm 0.4) \times 10^{10}$ L mol$^{-1}$ s$^{-1}$ at pH 7, as determined from the dependence of the rate of e$^-_{aq}$ decay monitored at 700 nm as a function of PFA concentration in the pulse radiolysis of deoxygenated solutions containing 1 mol L$^{-1}$ *t*-BuOH. The rate constants of the reactions of PFA with the primary radicals of water radiolysis are summarized in Table 1.

The transient absorption spectrum recorded at 5 $\mu$s after pulse radiolysis of deoxygenated solution of $3 \times 10^{-4}$ mol L$^{-1}$ PFA containing 0.9 mol L$^{-1}$ *t*-BuOH at pH 9.5 has absorption maxima at 300 and 440 nm (Figure 1) with $\epsilon_{440} = 2100$ L mol$^{-1}$ cm$^{-1}$. The spectrum is similar to the spectrum of the radical anion of acetophenone.[14] At low concentration of PFA ($10^{-5}$ mol L$^{-1}$), the rate of e$^-_{aq}$ decay at 700 nm was concomitant with the formation of PFA$^{•-}$ absorption at 300 nm. This indicates that the spectrum can be assigned to the radical anion PFA$^{•-}$. The spectrum cannot be due to the phenyl radicals

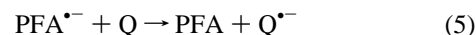produced by rapid loss of fluoride (reaction 2), because such radicals are known to have

$$e_{aq}^- + \text{PFA} \rightarrow \text{PFA}^{•-} \tag{1}$$

$$\text{C}_6\text{F}_5\text{COCH}_3^{•-} \rightarrow {}^{•}\text{C}_6\text{F}_4\text{COCH}_3 + \text{F}^- \tag{2}$$

weak absorption below 350 nm and rapidly abstract hydrogen from alcohol.[15] Since the radicals produced by fluoride elimination from PFA are not expected to have reducing properties, a direct evidence for the formation of the radical anion can be obtained from intermolecular electron transfer from PFA$^{•-}$ to a suitable acceptor discussed below. PFA$^{•-}$ decays with a rate constants of $(7 \pm 3) \times 10^3$ s$^{-1}$ presumably by fluoride elimination.

PFA$^{•-}$ protonates at lower pH and the spectrum exhibits a new absorption peaks at 270 and 460 nm ($\epsilon_{460} = 900$ L mol$^{-1}$ cm$^{-1}$). The spectrum (Figure 1) was recorded at 2 $\mu$s after pulse radiolysis of a deoxygenated solution of $7.8 \times 10^{-4}$ mol L$^{-1}$ PFA containing 0.5 mol L$^{-1}$ *t*-BuOH at pH 4.8. The spectrum is different from that of cyclohexadienyl radical obtained by addition of H$^•$ atom to PFA,

$$\text{H}^+ + \text{PFA}^{•-} \rightleftharpoons \text{PFAH}^{•} \tag{3}$$

indicating that the site of protonation and the localization of the unpaired electron spin density is on the oxygen atom of the carbonyl group. The p$K_a$ of the radical anion was determined from the dependence of the PFA$^{•-}$ absorbance at 440 nm as a function of pH in the pulse radiolysis of deoxygenated solutions of $1.3 \times 10^{-3}$ mol L$^{-1}$ PFA containing 0.2 mol L$^{-1}$ *t*-BuOH (insert of Figure 1). The p$K_a = 7.5$ of PFAH$^{•}$ obtained is 2.5 p$K_a$ unit more acidic than that of the p$K_a = 10$ of acetophenone anion,[14] as expected for the effect of perfluorination.[16]

Direct evidence that the spectrum is due to the radical anion PFA$^{•-}$ was obtained from the observation of intermolecular electron transfer from PFA$^{•-}$ to *p*-benzoquinone (Q) and methyl

$$\text{PFA}^{•-} + \text{MV}^{2+} \rightarrow \text{PFA} + \text{MV}^{•+} \tag{4}$$

$$\text{PFA}^{•-} + \text{Q} \rightarrow \text{PFA} + \text{Q}^{•-} \tag{5}$$

viologen (MV$^{2+}$) to yield the radical Q$^{•-}$ and MV$^{•+}$, respectively. The formation of MV$^{•+}$ and Q$^{•-}$ in reactions 4 and 5 were confirmed from their absorption spectra.[17,18]

Figure 2 presents time-resolved spectra obtained on pulse radiolysis of deoxygenated solution of $8.3 \times 10^{-4}$ mol L$^{-1}$ PFA containing $2.1 \times 10^{-5}$ mol L$^{-1}$ MV$^{2+}$ and 0.8 mol L$^{-1}$ *t*-BuOH at pH 9.4. In this solution 91% of the hydrated electrons produced on radiolysis react with PFA and the remaining 9% react with MV$^{2+}$. The spectrum recorded at 1 $\mu$s after the pulse shows absorption bands at 440 nm due to PFA$^{•-}$ and an intense band at 605 nm due to MV$^{•+}$ formed directly by reaction of MV$^{2+}$ with hydrated electrons. The decay of PFA$^{•-}$ absorption at 440 nm is accompanied by concurrent increase in the MV$^{•+}$ absorption at 605 nm due to electron transfer from PFA$^{•-}$ to MV$^{2+}$. At 15 $\mu$s after the pulse, the spectrum obtained is entirely due to the radical cation MV$^{•+}$ absorption. This shows that the decay of 440 nm absorption led to the formation of MV$^{•+}$. The rate constant $k_4 = (2.5 \pm 0.4) \times 10^9$ M$^{-1}$ s$^{-1}$ was determined by monitoring the rate of formation of MV$^{•+}$ at 605 nm as a function of MV$^{2+}$ concentration in the pulse radiolysis of deoxygenated solutions containing $1.4 \times 10^{-3}$ mol L$^{-1}$ PFA and 1 mol L$^{-1}$ *t*-BuOH at pH 9.6. The rate constant $k_5 = (3.3 \pm 0.5) \times 10^9$ L mol$^{-1}$ s$^{-1}$ was determined by monitoring the rate of formation of benzosemiquinone absorption at 430 nm
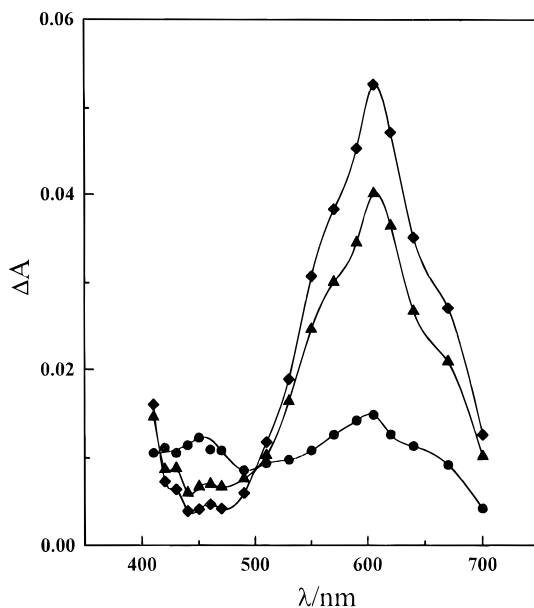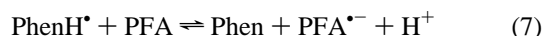
**Figure 2.** Time-resolved absorption spectra recorded at (●) 1, (▲) 5, and (◆) 15 $\mu$s after pulse radiolysis of deoxygenated solution of $8.3 \times 10^{-4}$ mol $L^{-1}$ PFA and $2.1 \times 10^{-5}$ mol $L^{-1}$ $MV^{2+}$ containing 0.8 mol $L^{-1}$ $t$-BuOH at pH 9.4. Dose = 15.2 Gy.

**TABLE 2: Rate Constants of Electron Transfer Reactions Involving PFA**

| radical | substrate | pH | $k$/(L mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|
| BpyH$^\bullet$ | PFA | 9.5 | $(1.1 \pm 0.2) \times 10^7$ |
| PhenH$^\bullet$ | PFA | 9.4 | $(3.3 \pm 2.0) \times 10^6$ |
| PFA$^{\bullet-}$ | Phen | 9.4 | $(4.2 \pm 2.0) \times 10^6$ |
| PFA$^{\bullet-}$ | Q | 9.5 | $(3.3 \pm 0.5) \times 10^9$ |
| PFA$^{\bullet-}$ | MV$^{2+}$ | 9.6 | $(2.5 \pm 0.4) \times 10^9$ |
| PFA$^{\bullet-}$ | AQS$^-$ | 9.4 | $(2.5 \pm 0.4) \times 10^9$ |
| PFAH$^\bullet$ | MV$^{2+}$ | 4.7 | $(8.0 \pm 2.0) \times 10^8$ |
| PFAH$^\bullet$ | AQS$^-$ | 4.8 | $(2.9 \pm 0.4) \times 10^9$ |
| PFAH$^\bullet$ | Q | 4.7 | $(5.0 \pm 0.8) \times 10^9$ |

as a function of Q concentration in the pulse radiolysis of deoxygenated solutions of $4 \times 10^{-3}$ mol $L^{-1}$ PFA containing 0.5 mol $L^{-1}$ $t$-BuOH at pH 9.5. The rate constants of electron transfer reactions are summarized in Table 2.

With the reducing radical (PhenH$^\bullet$), derived from reduction of 1,10-phenanthroline (Phen) in reaction 6

$$e_{aq}^- + Phen/Bpy \rightarrow PhenH^\bullet/BpyH^\bullet + OH^- \qquad (6)$$

$$PhenH^\bullet + PFA \rightleftharpoons Phen + PFA^{\bullet-} + H^+ \qquad (7)$$

the reduction potential of the PFA/PFA$^{\bullet-}$ couple was determined from the kinetics of the electron transfer reaction between PFA$^{\bullet-}$ and Phen with phenanthroline (Phen) as reference couple (E(Phen/PhenH$^\bullet$) = $-0.85$ V vs NHE).[19] The rate constants of the forward ($k_7$) and the backward ($k_{-7}$) reactions were determined from the dependence of the observed rate, $k_{obs}$, monitored at 350 nm, on PFA concentration in the pulse radiolysis of deoxygenated solutions of $1.3 \times 10^{-3}$ mol $L^{-1}$ Phen containing 1 mol $L^{-1}$ $t$-BuOH at pH 9.4. From the linear plot of $k_{obs}$/[PFA] vs [Phen]/[PFA] as in eq I,[20] $k_7 = (3.3 \pm 2.0) \times 10^6$ L mol$^{-1}$ s$^{-1}$

$$k_{obs} = k_7[PFA] + k_{-7}[Phen] \qquad (I)$$

and $k_{-7} = (4.2 \pm 2.0) \times 10^6$ L mol$^{-1}$ s$^{-1}$ were obtained from the intercept and the slope, respectively. A reduction potential of E(PFA/PFA$^{\bullet-}$) = $-0.86 \pm 0.1$ V vs NHE at pH 9.4 was obtained from the equilibrium constant $K = 0.8$, using eqs II

**TABLE 3: Comparison of the Rate Constants of Electron Transfer Reactions from the Radical Anion of PFA and Ac to Different Acceptors**

| acceptor | product | donor | |
|---|---|---|---|
| | | PFA$^{\bullet-}$ | Ac$^{\bullet-}$ |
| MV$^{2+}$ | MV$^{\bullet+}$ | $(2.5 \pm 0.4) \times 10^{9a}$ | $(7.5 \pm 1.1) \times 10^{9b}$ |
| AQS$^-$ | AQS$^{\bullet 2-}$ | $(2.5 \pm 0.4) \times 10^{9a}$ | $(3.0 \pm 0.4) \times 10^{9b}$ |
| Q | Q$^{\bullet-}$ | $(3.3 \pm 0.5) \times 10^{9a}$ | $(3.1 \pm 0.6) \times 10^{9c}$ |

[a] Rate constant in L mol$^{-1}$ s$^{-1}$ determined at pH 9.4−9.6. [b] Rate constant determined at pH 12. [c] Rate constant determined at pH 9.4.

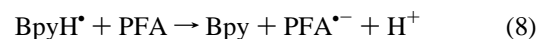and III.

$$\Delta E = 0.0591 \log K \qquad (II)$$

and

$$\Delta E = E(PFA/PFA^{\bullet-}) - E(Phen/PhenH^\bullet) \qquad (III)$$

Bipyridinium radical (p$K_a$ = 14)[19] produced by reduction of 2,2′-bipyridine (Bpy) also reduced PFA.

$$BpyH^\bullet + PFA \rightarrow Bpy + PFA^{\bullet-} + H^+ \qquad (8)$$

An increase in the rate constant $k_8 = (1.1 \pm 0.2) \times 10^7$ L mol$^{-1}$ s$^{-1}$ reflects the higher E(Bpy/BpyH$^\bullet$) = $-0.97$ V of Bpy. The rate was determined by monitoring the decay of BpyH$^\bullet$ at 365 nm in deoxygenated solutions of $1.2 \times 10^{-3}$ mol $L^{-1}$ Bpy containing 1 mol $L^{-1}$ $t$-BuOH at pH 9.5.

The protonated radical PFAH$^\bullet$ is a weaker reductant. The rate constant

$$PFAH^\bullet + MV^{2+} \rightarrow PFA + MV^{\bullet+} + H^+ \qquad (9)$$

$k_9 = (8.0 \pm 2.0) \times 10^8$ L mol$^{-1}$ s$^{-1}$ was determined from the buildup of MV$^{\bullet+}$ at 605 nm as a function of MV$^{2+}$ concentration in deoxygenated solutions of $1.1 \times 10^{-3}$ mol $L^{-1}$ PFA containing 0.7 mol $L^{-1}$ $t$-BuOH at pH 4.7. The rate constant $k_{10} = (5.0 \pm 0.8) \times 10^9$ L mol$^{-1}$ s$^{-1}$ for reduction of Q was

$$PFAH^\bullet + Q \rightarrow PFA + QH^\bullet \qquad (10)$$
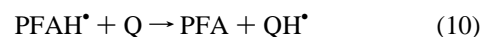
obtained from the dependence of the rate of build-up of Q$^{\bullet-}$/QH$^\bullet$ (p$K_a$ = 4.2)[18] absorption at 430 nm in deoxygenated solutions of $1.1 \times 10^{-3}$ mol $L^{-1}$ PFA containing 0.7 mol $L^{-1}$ $t$-BuOH at pH 4.7.

Electron transfer from the radical anion of a perfluorinated compound to an acceptor is a topic of considerable interest because the rate has been reported to be much less than that would normally be expected from their reduction potentials.[21] This is because of the drastic change in the geometry with the formation of the radical anion. In order to see whether the radical anions of pentafluoroarmatic compounds in aqueous solution exhibit this property, we compare the rate constants for electron transfer from PFA$^{\bullet-}$ to several acceptors with that of the corresponding rates of the radical anion of acetophenone (Ac$^{\bullet-}$). The rate constants for electron transfer reactions from Ac$^{\bullet-}$ to different acceptors were determined by monitoring the formation of the product absorption as a function of acceptor concentration in the pulse radiolysis of deoxygenated $3 \times 10^{-3}$ mol $L^{-1}$ Ac and 0.7 mol $L^{-1}$ $t$-BuOH solution at pH 12. The rate constants listed in Table 3 indicate that there is no significant difference in their rates. This indicates that both PFA$^{\bullet-}$ and AC$^{\bullet-}$ have similar geometry, and this conclusion is in agreement with the theoretical calculation which shows that the radical anions of perfluoroaromatic compounds which have electron affinic substituent such as CO group are normal $\pi$ radicals.[12]
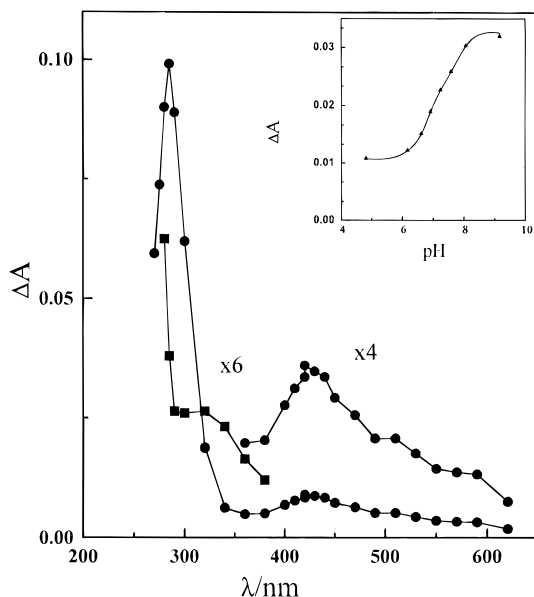
Reduction of Carbonyl-Containing Perfluoroaromatic Compounds

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**Figure 3.** Transient absorption spectra obtained on pulse radiolysis of deoxygenated solution of $9 \times 10^{-4}$ mol L$^{-1}$ PFB containing 0.5 mol L$^{-1}$ $t$-BuOH (●) in solution at pH 9.4 recorded at 2 $\mu$s and (■) in solution at pH 4.7 recorded at 4 $\mu$s after the pulse (25 Gy). Inset: Dependence of the transient absorption at 420 nm on pH of the solution (123 Gy).

**Reduction of Pentafluorobenzaldehyde.** Hydrated electrons react with PFB with a rate constant of $k_{11} = (2.4 \pm 0.4) \times 10^{10}$ L mol$^{-1}$ s$^{-1}$ at pH 7. It was determined by monitoring the decay rate of $e_{aq}^-$ at 700 nm as a function of PFB concentration in the pulse radiolysis of deoxygenated solutions of 1 mol L$^{-1}$ $t$-BuOH at pH 7.

$$e_{aq}^- + PFB \rightarrow PFB^{\bullet-} \qquad (11)$$
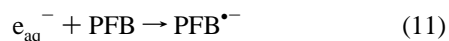
The spectrum of the radical anion PFB$^{\bullet-}$ formed on addition of $e_{aq}^-$ recorded at 2 $\mu$s after pulse radiolysis of deoxygenated solution of $9 \times 10^{-4}$ mol L$^{-1}$ PFB containing 0.5 mol L$^{-1}$ $t$-BuOH at pH 9.4, has bands at 285 and 430 nm (Figure 3) with $\epsilon_{430} = 800$ L mol$^{-1}$ cm$^{-1}$. The spectrum is similar to that of the benzaldehyde radical anion ($\lambda_{max}$ 300 and 435 nm).[22] PFB$^{\bullet-}$ decays with a rate constant of $(4 \pm 2) \times 10^3$ s$^{-1}$, presumably by fluoride elimination. The radical anion has a p$K_a$ = 7.2, which is 1.2 p$K_a$ unit more acidic than that of the radical anion of benzaldehyde (p$K_a$ = 8.4).[22] The p$K_a$ was determined from the dependence of

$$C_6F_5CHO^{\bullet-} + H^+ \rightleftharpoons C_6F_5C^{\bullet}HOH \qquad (12)$$

the PFB$^{\bullet-}$ absorbance at 430 nm on the pH of the solution in the pulse radiolysis of deoxygenated solutions of $1.7 \times 10^{-3}$ mol L$^{-1}$ PFB containing 0.2 mol L$^{-1}$ $t$-BuOH. (insert of Figure 3). The spectrum of the conjugate acid (PFBH$^{\bullet}$) recorded at 4 $\mu$s after pulse radiolysis of deoxygenated $9 \times 10^{-4}$ mol L$^{-1}$ PFB solution containing 0.5 mol L$^{-1}$ $t$-BuOH at pH 4.7 showed a weak absorption band at 330 nm (Figure 3) as in the case of benzaldehyde ketyl radical.[22]

The radical anion PFB$^{\bullet-}$ was observed to transfer electron to a number of compounds to form their radical anions (Table 4). These reactions are direct evidence that the species formed on addition of $e_{aq}^-$ to PFB is a radical anion. Reaction of PFB$^{\bullet-}$ with MV$^{2+}$ led to electron transfer and formation of MV$^{\bullet+}$. The rate constant $k_{13} = (5.4 \pm 0.8) \times 10^9$ L mol$^{-1}$ s$^{-1}$ was obtained from the dependence of the

**TABLE 4: Rate Constants for Electron Transfer Reactions Involving PFB**

| radical | substrate | pH | $k$/L mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| (CH$_3$)$_2$C$^{\bullet}$OH | PFB | 9 | $(5.9 \pm 0.9) \times 10^8$ |
| PFB$^{\bullet-}$ | Q | 9.5 | $(3.2 \pm 0.5) \times 10^9$ |
| PFB$^{\bullet-}$ | MV$^{2+}$ | 9.2 | $(5.4 \pm 0.8) \times 10^9$ |
| MV$^{\bullet+}$ | PFB | 4.8 | $(3.5 \pm 0.5) \times 10^5$ |
| PFBH$^{\bullet}$ | MV$^{2+}$ | 4.8 | $(9.0 \pm 1.4) \times 10^8$ |
| PFB$^{\bullet-}$ | AQS$^-$ | 9.4 | $(2.5 \pm 0.4) \times 10^9$ |
| PFBH$^{\bullet}$ | AQS$^-$ | 4.8 | $(2.7 \pm 0.4) \times 10^9$ |
| BpyH$^{\bullet}$ | PFB | 9.3 | $(1.9 \pm 0.3) \times 10^9$ |
| PhenH$^{\bullet}$ | PFB | 9.3 | $(2.2 \pm 0.3) \times 10^9$ |
| PFB$^{\bullet-}$ | Phen | 9.3 | $(3.6 \pm 0.5) \times 10^7$ |

$$PFB^{\bullet-} + MV^{2+} \rightarrow PFB + MV^{\bullet+} \qquad (13)$$

formation rate of MV$^{\bullet+}$ monitored at 605 nm as a function of MV$^{2+}$ concentration in deoxygenated solution of $1.1 \times 10^{-3}$ mol L$^{-1}$ PFB containing 0.5 mol L$^{-1}$ $t$-BuOH at pH 9.2. The rate constant of electron transfer from PFB$^{\bullet-}$ to Q of $k_{14} = (3.2 \pm 0.5) \times 10^9$ L mol$^{-1}$ s$^{-1}$ was obtained by monitoring the formation of benzosemiquinone Q$^{\bullet-}$

$$PFB^{\bullet-} + Q \rightarrow PFB + Q^{\bullet-} \qquad (14)$$

absorption at 430 nm as a function of Q concentration in deoxygenated solutions of $4 \times 10^{-3}$ mol L$^{-1}$ PFB containing 0.5 mol L$^{-1}$ $t$-BuOH at pH 9.5.

A number of radiolytically generated reducing radicals also reduce PFB to the radical anion. 2-Hydroxyl-2-propyl radical derived from 2-propanol reduces PFB with a rate constant $k_{15} = (5.9 \pm 0.9) \times 10^8$ L mol$^{-1}$ s$^{-1}$ at pH 9.

$$(CH_3)_2C^{\bullet}OH + PFB \rightarrow (CH_3)_2CO + PFB^{\bullet-} + H^+ \quad (15)$$
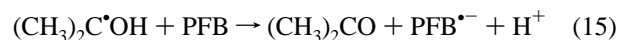
The rate constant was determined by monitoring the formation of PFB$^{\bullet-}$ at 420 nm as a function of PFB concentration in the pulse radiolysis of N$_2$O saturated solutions of 0.5 mol L$^{-1}$ 2-propanol at pH 9. In these solutions $e_{aq}^-$ produced on radiolysis reacts with N$_2$O to form OH$^{\bullet}$ which subsequently abstracts hydrogen from 2-propanol to form 2-hydroxyl-2-propyl radical. The rate constant $k_{16} = (1.9 \pm 0.3)10^9$ L mol$^{-1}$ s$^{-1}$ for reduction of PFB by bipyridyl radical (BpyH$^{\bullet}$) was determined by monitoring the decay of BpyH$^{\bullet}$ at 365 nm as a function of Bpy

$$BpyH^{\bullet} + PFB \rightarrow Bpy + PFB^{\bullet-} + H^+ \qquad (16)$$
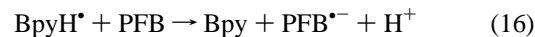
concentration in deoxygenated solutions of $7.2 \times 10^{-4}$ mol L$^{-1}$ Bpy containing 0.5 mol L$^{-1}$ $t$-BuOH at pH 9.3.

The reduction potential of the PFB/PFB$^{\bullet-}$ couple was determined from the kinetics of the electron transfer reaction using Phen/PhenH$^{\bullet}$ as reference couple. The overall electron transfer rate $k_{obs}$ for reaction 17 was

$$PhenH^{\bullet} + PFB \rightleftharpoons Phen + PFB^{\bullet-} + H^+ \qquad (17)$$
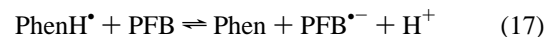
determined from the dependence of PhenH$^{\bullet}$ decay at 350 nm as a function of PFB concentration in deoxygenated solutions of $6.2 \times 10^{-4}$ mol L$^{-1}$ Phen containing 0.5 mol L$^{-1}$ $t$-BuOH at pH 9.3. From the linear plot of $k_{obs}$/[PFB] vs [Phen]/[PFB] and using eq I, the rate constants $k_{17} = (2.2 \pm 0.3) \times 10^9$ L mol$^{-1}$ s$^{-1}$, $k_{-17} = (3.6 \pm 0.5) \times 10^7$ L mol$^{-1}$ s$^{-1}$, and the equilibrium constant $K = 60$ were obtained. This yields a reduction potential E(PFB/PFB$^{\bullet-}$) = $-0.75 \pm 0.1$ V vs NHE at pH 9.3 using eqs II and III.

**Reduction of Pentafluorobenzoate.** Hydrated electrons react with pentafluorobenzoate (PFBA) with a rate constant of
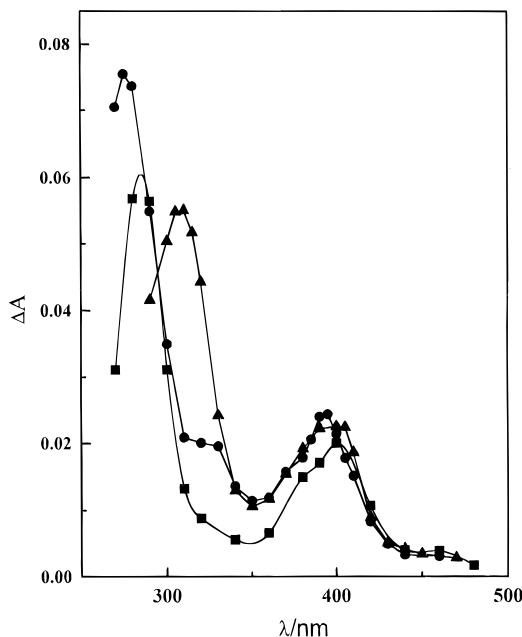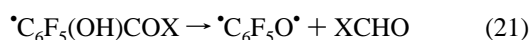
**Figure 4.** Transient absorption spectra of phenoxyl radicals obtained on pulse radiolysis of $N_2O$-saturated solutions of (■) $2.8 \times 10^{-3}$ mol $L^{-1}$ PFBA (24 Gy), (▲) $1 \times 10^{-3}$ mol $L^{-1}$ PFA (27 Gy), and (●) $1 \times 10^{-3}$ mol $L^{-1}$ PFB (27 Gy).

(9.6 ± 1.5) × $10^9$ L $mol^{-1}$ $s^{-1}$ at pH 12 (Table 1). This reaction does not lead to the formation of absorbing species which can be attributed to the formation of radical anion and was not observed to transfer electron to Q, in contrast to the radical anions of PFA and PFB. In low-temperature glassy 2-methyltetrahydrofuran matrix,[10] the radical anion formed on addition of electron to pentafluorobenzoic acid has absorption peaks at 330 and 540 nm. The radical anion of benzoic acid ($C_6H_5C^\bullet$ $(OH)O^-$) has absorption peaks at 310 and 435 nm at pH 9.1.[23] This indicates that in aqueous solution, the radical anion $PFBA^{\bullet-}$ formed rapidly loses fluoride.[5] This is in agreement with fluoride yield $G(F^-) = 3.6$ measured in the steady state $\gamma$-radiolysis of deoxygenated $1 \times 10^{-3}$ mol $L^{-1}$ PFBA containing $2 \times 10^{-3}$ mol $L^{-1}$ carbonate and 1 mol $L^{-1}$ t-BuOH solution at pH 11. In $N_2O$-saturated carbonate solution of $1 \times 10^{-3}$ PFBA at pH 11, a fluoride yield of $G(F^-) = 14$ was obtained.

**Reactions of $C_6F_5COX$ with $OH^\bullet$ Radicals.** Reaction of $OH^\bullet$ radical was carried out in $N_2O$-saturated solution where $e_{aq}^-$ was converted into OH by reaction with $N_2O$. Addition of $OH^\bullet$ to pentafluoroaromatic ring would lead to the formation of isomers of hydroxycyclohexadienyl radical[24] with the predominant addition at the ortho and the para positions. The formation of HO bond to a carbon where F is attached is unstable[25] and it rapidly undergoes HF elimination to yield phenoxyl radical.[6,7]

$$OH^\bullet + C_6F_5COX \rightarrow HO^\bullet C_6F_5COX \qquad (18)$$

$$HO^\bullet C_6F_5COX \rightarrow {}^\bullet OC_6F_4COX + H^+ + F^- \qquad (19)$$

Addition of $OH^\bullet$ to the ipso position may lead to the elimination of carbonyl group and formation of pentafluorophenoxyl radical.

$$OH^\bullet + C_6F_5COX \rightarrow {}^\bullet C_6F_5(OH)COX \qquad (20)$$

$${}^\bullet C_6F_5(OH)COX \rightarrow {}^\bullet C_6F_5O^\bullet + XCHO \qquad (21)$$

The spectrum of the phenoxyl radical (Figure 4) formed on addition of $OH^\bullet$ to pentafluorobenzoic acid (PFBA) by reactions
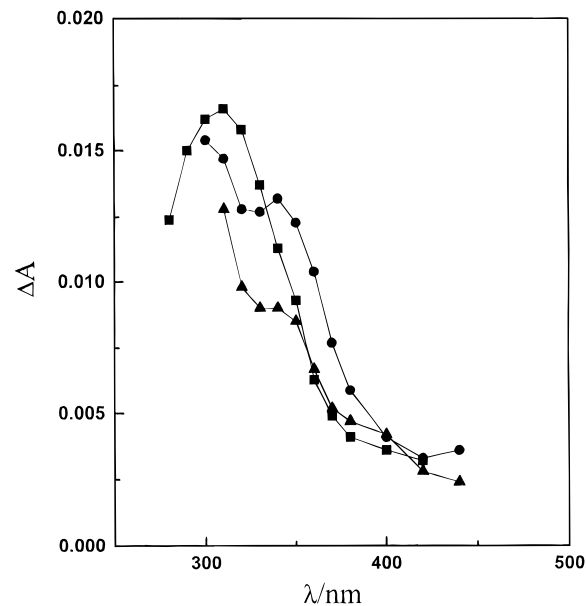


**Figure 5.** Transient absorption spectra of cyclohexadienyl radicals obtained on pulse radiolysis of deoxygenated 0.3 mol $L^{-1}$ t-BuOH solution at pH 7 containing (■) $1.8 \times 10^{-3}$ mol $L^{-1}$ PFBA, (●) $1.8 \times 10^{-3}$ mol$^{-1}$ PFA, and (▲) $2 \times 10^{-3}$ mol $L^{-1}$ PFB (dose = 40 Gy).

**TABLE 5: Rate Constants for Oxidation of Ascorbate by Substituted Tetrafluorophenoxyl radicals**

| radical | substrate | pH | $k/(L\ mol^{-1}\ s^{-1})$ |
|---|---|---|---|
| $^\bullet OC_6F_4COCH_3$ | $AH^-$ | 9.3 | $(1.5 \pm 0.3) \times 10^9$ |
| $^\bullet OC_6F_4CHO$ | $AH^-$ | 9.3 | $(7.6 \pm 1.0) \times 10^8$ |
| $^\bullet OC_6F_4COO^-$ | $AH^-$ | 9.4 | $(5.0 \pm 0.8) \times 10^8$ |

18 and 19 was recorded at 1 $\mu$s after pulse radiolysis of $N_2O$-saturated $3 \times 10^{-3}$ mol $L^{-1}$ PFBA solution at pH 6.5. It has $\lambda_{max}$ at 285 and 405 nm. Figure 4 also shows the spectrum of the phenoxyl radical obtained on $OH^\bullet$ addition to PFA ($\lambda_{max}$ 310 and 400 nm) recorded at 3 $\mu$s after pulse radiolysis of $N_2O$-saturated $1 \times 10^{-3}$ mol $L^{-1}$ PFA solution at pH 7. The phenoxyl radical produced on addition of $OH^\bullet$ to PFB recorded at 2 $\mu$s after pulse radiolysis of $N_2O$-saturated $1 \times 10^{-3}$ mol $L^{-1}$ PFB solution at pH 7 has $\lambda_{max}$ at 275 and 395 nm. The absorption spectra of tetrafluorophenoxyl radicals obtained are similar to that of the pentafluorophenoxyl[6,7] and other phenoxyl radicals.[26]

The rate constants of $OH^\bullet$ attack on $C_6F_5COX$ (reaction 18) were determined from competition kinetics using $OH^\bullet + SCN^-$ reaction as reference by monitoring the change in the absorbance $(A)$ of $(SCN)_2^{\bullet-}$ as a function of $C_6F_5COX$ concentration in the pulse radiolysis of $N_2O$-saturated $4 \times 10^{-4}$ mol $L^{-1}$ KSCN solutions at pH 7. The rate constants obtained from the slope of the plot of $A_0/A$ vs $[C_6F_5COX]/[SCN^-]$[27] are summarized in Table 1.

As in the case of other phenoxyl radicals,[7,28] substituted tetrafluorophenoxyl radicals oxidized ascorbate ($AH^-$) to ascorbate radical.

$${}^\bullet OC_6F_4COX + AH^- \rightarrow {}^- OC_6F_4COX + AH^\bullet \qquad (22)$$

The rate constants for reaction 22 were determined by monitoring the formation of ascorbate radical at 360 nm as a function of ascorbate concentration in the pulse radiolysis of $N_2O$-saturated solutions of ca. $10^{-3}$ mol $L^{-1}$ substrate at pH 9.3. The rate constants obtained are summarized in Table 5.

**Reactions C₆F₅COX with H• Radical.** H• atoms normally add to the benzene ring of aromatic compounds to form adduct, cyclohexadienyl radical, which have absorption in the 300–360 nm region.[24] The adduct formed on H• addition to PFBA has $\lambda_{max}$ at 310 nm. The spectrum (Figure 5) was recorded at 10 $\mu$s after pulse radiolysis of $1.8 \times 10^{-3}$ mol L$^{-1}$ PFBA containing 0.3 mol L$^{-1}$ t-BuOH at pH 2.2. The spectra of H• atom adducts of PFA and PFB have $\lambda_{max}$ at 340 and 310 nm, respectively. The rate constant (Table 1) for reaction of H• atoms with PFBA was determined by monitoring the adduct absorption at 310 nm as a function of PFBA concentration in deaerated 0.3 mol L$^{-1}$ *t*-BuOH solutions at pH 2.0.

## Conclusion

Addition of hydrated electrons to hexafluorobenzene,[6] pentafluorophenol,[7a] and pentafluoroaniline[7b] in aqueous solution led to rapid fluoride elimination because the unpaired electron in these radical anions has significant $\sigma$ character. Increasing the electron affinity of the carbonyl substituents in going from $-COO^-$ to $-CHO$ and $-COCH_3$ led to increase stability of the radical anion of perfluorinated compounds due to the delocalization of the unpaired electron into the $\pi$ orbital of the C=O moiety which reduces the spin density on the C–F bond and hence the rate of fluoride elimination. This leads to significant increase in the lifetimes of these radical anions and hence opens a window for observing reactions of the radical anion with other solute present in the solution.

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