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Kinetics and Absorption Spectra of Transients in the Radiolysis of Hexafluorobenzene in Aqueous Solution: A Pulse Radiolysis Study

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Hexafluorobenzene reacts with hydrated electrons with a rate constant of $8.5 \times 10^9\ M^{-1}\ s^{-1}$. In alkaline solution, the radical anion formed has absorption maxima at 280 and 390 nm. The radical anion decays with a rate constant $2k = 4.6 \times 10^9\ M^{-1}\ s^{-1}$ to form carbanion which has absorption maxima at 290, 345, and 410 nm. Below pH 11, $C_6F_6^{\bullet -}$, is rapidly protonated to form cyclohexadienyl radical which has bands at 260 and 350 nm. The pK_a of the $C_6F_6H^{\bullet} \rightleftharpoons C_6F_6^{\bullet -} + H^+$ equilibrium was estimated to be 12.4. The radical anion derived from ethanol also reduces C_6F_6 with a rate constant of $2.5 \times 10^6\ M^{-1}\ s^{-1}$, and the radical anion formed has absorption bands at 300 and 440 nm. It decays by radical recombination to yield a carbanion which has absorption bands at 310 and 580 nm. Both the radical anion and the carbanion formed display considerable inertness and have long lifetimes. The product spectrum shows evidence for the formation of long-chain molecules, indicating the involvement of anionic polymerization. Hydroxyl radical adds to hexafluorobenzene with a rate constant of $1.4 \times 10^9\ M^{-1}\ s^{-1}$ to form an adduct, hydroxycyclohexadienyl radical, which has absorption bands at 280 and 400 nm. $O^{\bullet -}$ adds to hexafluorobenzene with a rate constant of $9.4 \times 10^7\ M^{-1}\ s^{-1}$. The adduct undergoes base-catalyzed fluoride elimination to yield phenoxide radical which has absorption maxima at 300 and 430 nm. The adduct also undergoes acid-catalyzed water elimination at lower pH to yield $C_6F_6^{\bullet +}$, and the radical cation is also formed by electron-transfer reaction with $SO_4^{\bullet -}$.

Introduction

Investigation of the physicochemical properties of hexafluorobenzene is important in understanding the intrinsic nature of aromaticity as much as of benzene. It is also interesting in connection with the perfluoro effect. When all hydrogen atoms in benzene are replaced by fluorine, the physicochemical properties of hexafluorobenzene formed show little resemblance to the parent benzene.[1] These phenomena have been given the term perfluoro effect. Some aspects of the perfluoro effect can be explained on the basis of the well-known substituent effects. Since the fluorine atom is strongly electron withdrawing by field inductive effect and is weakly electron pair donating, fluorine substitution in benzene is expected to exert strong stabilizing effect on σ-type orbitals, while the combined field effect stabilization and opposing π donation have only moderately net stabilizing effect on π-type orbitals.[2] This effect leads to lowering of the σ orbital relative to the π orbitals on substitution of fluorine in benzene. Hence, in hexafluorobenzene, unoccupied σ^* and π^* orbitals have comparable energy.[3]

The radical anion and cation of hexafluorobenzene and benzene are of theoretical interest since addition/removal of electron in the molecule would lead to a typical Jahn–Teller situation. Benzene radical anion is of interest in experimental organic chemistry as the species formed in the first stage of the Birch reduction of benzene by solvated electrons in ammonia solution.[4] At low temperature, a broad band at 385 nm extending to the near-IR observed on γ-radiolysis of benzene in 2-methyltetrahydrofuran has been assigned to the benzene radical anion.[5] At room temperature, although electron adds to benzene with a rate constant of $1 \times 10^7\ M^{-1}\ s^{-1}$, the spectrum of the radical anion has never been unambiguously reported.[6]

Conventional methods for the preparation of radical anion, when applied to fluorinated compounds generally lead to the loss of fluoride ion.[7] Hexafluorobenzene anion was first prepared by Yim and Wood[8] using matrix isolation technique and radiolysis. On the basis of the large isotropic ESR coupling constants of $C_6F_6^{\bullet -}$, they suggested that the extra electron is located in the σ^* orbital and the anion retained planar D_{6h} symmetry.[8,9] Symons et al.,[10] on the basis of anisotropic ESR coupling constant magnitudes, suggested a highly distorted structure, the carbon skeleton being similar to the chair form of cyclohexane. However, a more detailed theoretical examination by Shchegoleva et al.[11] obtained a better agreement with the coupling constants if the carbon structure is planar containing out-of-plane C–F bonds. The extra electron occupies a π^*, σ^* combination orbital in which the π^* component prevails.

Till recently, there has been little information on the redox reactions of fluorinated compounds. In the pulse radiolysis of aqueous solution of hexafluorobenzene,[12] a rate constant $k = 2 \times 10^{10}\ M^{-1}\ s^{-1}$ was reported for the reaction $e_{aq}^- + C_6F_6$, but absorption due to the radical anion was not observed. Since F^- was produced with $G(F^-)$ of 2.7 and 4.8, in pulse and γ-radiolysis, respectively, the addition of electrons to hexafluorobenzene was believed to lead to efficient dissociative electron capture. The addition of $OH^{\bullet}$ also produced F^-, and the spectrum with a band at 400 nm was assigned to pentafluorophenoxide radical.

In highly polar methanol glass, electron attachment to C_6F_6 has been reported to lead to dissociation[10,13] yielding F^-. However, in less polar organic glasses, electron scavengers and conductivity studies have shown that the addition of electron to hexafluorobenzene is nondissociative.[14] The spectrum of the radical anion has bands at 370 and 460 nm. In 2-methyltetrahydrofuran at 77 K, $C_6F_6^{\bullet -}$ is stable for months.[15] In pulse radiolysis at ambient temperature, the spectrum of the radical anion $C_6F_6^{\bullet -}$ has been reported to have bands at 390 and 480 nm in isooctane solution, and in pure hexafluorobenzene the absorption is located at 550 nm.[16]

Unlike hydrocarbons, there are only very few studies on the radiation chemistry of perfluorocarbons.[17] Although such studies suggest that free radicals play an important role in the mechanism of radiolysis of perfluorocarbons, relatively little work has been done to establish this point. In the present study, we have investigated the transient species produced in the reaction between hexafluorobenzene and the primary species produced on radiolysis of water and its reaction with reducing/oxidizing radicals with the aim of understanding the mechanism of radiolytic degradation of perfluoroaromatic compounds.

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Experimental Section

Hexafluorobenzene (>99%), purchased from Fluka, AG (Puriss) was used as received. The pH of the solution was adjusted with KOH, Na_2HPO_4, KH_2PO_4, and $HClO_4$. To study reactions with hydrated electrons, *tert*-butyl alcohol was used to scavenge $^{\bullet}OH$ formed in the pulse radiolysis of the aqueous solution. Hexafluorobenzene has low solubility (3 mM) in water. Due to the noninteracting nature of perfluorinated compounds, special care was needed to avoid loss of C_6F_6 during bubbling and storing in aqueous solution. Hexafluorobenzene can easily be lost during bubbling because of high volatility. This is true even in 50 vol % aqueous alcohol solution where C_6F_6 has better solubility (<0.1 M). In order to minimize the loss, a 3–5-mL portion of the matrix solution was deaerated in a cell prior to the addition of C_6F_6 and a known concentration of C_6F_6 in alcohol solution, or neat C_6F_6 was injected through a microsyringe. The concentration of C_6F_6 was determined in some cases from the absorption measurements at an appropriate wavelength ϵ (231) = 654 M^{-1} cm^{-1}.

The pulse radiolysis system consists of an electron linear accelerator (Viritech Ltd. England) capable of delivering a single pulse of 7-MeV electrons having a pulse width of 5–2000 ns at a peak current of 1 A. The detailed instrumental setup was described earlier.[18] The dose per pulse was determined with N_2O-bubbled 0.06 M KSCN aqueous solution at 480 nm assuming $G((SCN)_2^{\bullet -}) = 6.1$ and $\epsilon_{480} = 7600$ M^{-1} cm^{-1}).

Results and Discussion

Reaction with e_{aq}^- and Reducing Radicals. The primary transient species produced in the pulse radiolysis of aqueous solution are e_{aq}^-, $OH^{\bullet}$, and $H^{\bullet}$. The rate constant for reaction of hexafluorobenzene with hydrated electrons was determined by monitoring the decay of the absorption at 700 nm due to e_{aq}^- following a 25-ns pulse in a solution containing 0.1 M *tert*-butyl alcohol at pH 7. In this solution $OH^{\bullet}$ is effectively scavenged by *tert*-butyl alcohol.

$$H_2O \rightsquigarrow e_{aq}^-, OH^{\bullet}, H^{\bullet}$$

$$OH^{\bullet} + t\text{-BuOH} \rightarrow {}^{\bullet}CH_2C(CH_3)_2OH + H_2O$$

$$e_{aq}^- + C_6F_6 \rightarrow C_6F_6^{\bullet -} \tag{1}$$

The bimolecular rate constant, k_1, was obtained from the slope of the plot k_{obs} versus $[C_6F_6]$, using the equation $k_{obs} = k_0 + k_1[C_6F_6]$. The slope of the plot yields a bimolecular rate constant $k_1 = 8.5 \times 10^9$ M^{-1} s^{-1}. This value is not very different from the rate constant reported earlier.[12] The rate constant is, however, lower than that for most of the monosubstituted pentafluorobenzenes,[19] although C_6F_6 has a high positive electron affinity of 0.52 eV[20] and in the gas phase it scavenges electrons with collision-controlled rate constant.[21] It might be assumed that C_6F_6 forms complexes with ions in aqueous solution, e.g., $HO^-(C_6F_6)$, much like its complexes with halogen in the gas phase, $X^-(C_6F_6)$ (where $X = F^-, Cl^-$, etc.),[22] and such complexes would react slower with e_{aq}^-. This possibility was ruled out because the rate constant determined at 1.0 M KOH solution has the same magnitude as in dilute solution.

Figure 1 shows time-resolved spectra obtained on pulse radiolysis of N_2-bubbled aqueous solution of 2 mM C_6F_6 containing 0.1 M *tert*-butyl alcohol and 0.94 M KOH. The spectrum obtained immediately after a 2-μs pulse has maxima at 280 and 390 nm and is assigned to the radical anion $C_6F_6^{\bullet -}$. The absorption is not due to cyclohexadienyl radical formed by rapid protonation of the radical anion as in the case of benzene radical anion, because the spectrum of the cyclohexadienyl radical determined at lower pH is quite different from that of the radical anion (discussed below). The extinction coefficient of the anion absorption at 390 nm was estimated to be $\epsilon(390) = 1480$ M^{-1} cm^{-1} (assuming $G(e_{aq}^-) = G_{e_{aq}^-} + G_{H^{\bullet}} = 3.28$ at pH 14). The formation and the decay of $C_6F_6^{\bullet -}$ is not much affected in aerated solution. The radical anion decay monitored at 390 nm was found to be independent of C_6F_6 concentration up to 3 mM, indicating that $C_6F_6^{\bullet -}$ either does not react or reacts very slowly with C_6F_6. The decay is fitted well by second-order kinetics with a rate constant $2k = 4.6 \times 10^9$ M^{-1} s^{-1} and is independent of the absorbed dose (2.1–16 krad). The fact that a new absorbing species is formed with the decay of $C_6F_6^{\bullet -}$ and the spectrum at the end of 80 μs is predominantly due to the new species showed that it is formed by dimerization of $C_6F_6^{\bullet -}$ ($C_6F_6^{\bullet -} + C_6F_6^{\bullet -} \rightarrow (C_6F_6)_2^{2-}$). The spectrum of the dimer carbanion recorded at 80 μs after the pulse, when the anion has decayed, exhibits bands at 290, 345, and 410 nm.

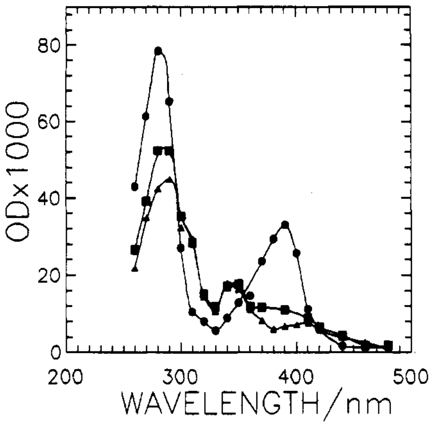

Figure 1. Time-resolved spectra obtained on pulse radiolysis of N_2-bubbled aqueous solution of 2 mM C_6F_6 at pH 14 containing 0.1 M *tert*-butyl alcohol at different times after a 2-μs electron pulse: (●) end of the pulse, (■) 30 μs, and (▲) 80 μs.

Earlier workers[12] did not observe absorption due to the radical anion probably because they worked at lower pH (<7). This led them to assume that fluoride ion is eliminated whenever e_{aq}^- adds to C–F bond in fluorinated benzene in aqueous solution and addition of e_{aq}^- to C_6F_6 is dissociative. This is contrary to our results which indicate that electron addition to C_6F_6 is nondissociative and the $C_6F_6^{\bullet -}$ formed is stable with respect to F^- ion elimination. The stability of $C_6F_6^{\bullet -}$ would mainly arise from the high C–F bond energy ($D_{C-F} = 6.3$ eV), in spite of the high electron affinity of the $F^{\bullet}$ atom ($EA(F^{\bullet}) = 3.45$ eV) and the strong solvation of F^- ion formed in aqueous solution. For the dissociative electron capture reaction to occur

$$e_{aq}^- + C_6F_6 \rightarrow C_6F_6^{\bullet -}$$

$$C_6F_6^{\bullet -} \rightarrow C_6F_5^{\bullet} + F^-$$

the following energy difference, ΔE, should be less than zero[14]

$$\Delta E = D(C\text{-}F) + EA(C_6F_6) - P(C_6F_6^{\bullet -}) - EA(F^{\bullet}) + P(F^-) \tag{I}$$

where P, the solvation energy of the ions, can be estimated from the Born expression[23]

$$P = -[(1 - (1/\epsilon))e^2]/2a \tag{II}$$

ϵ is the dielectric constant of the medium, a is the radius of the ion, and e is the electronic charge. Substituting the values of $a(F^-) = 1.33$ Å and $a(C_6F_6^{\bullet -}) = 2.999$ Å, eq II yields $P(F^-) = -5.4$ eV and $P(C_6F_6^{\bullet -}) = -2.4$ eV. Hence from eq I, the thermochemical estimates show that in aqueous solution fluoride elimination from $C_6F_6^{\bullet -}$ would be endothermic by as much as 0.37 eV, which is in agreement with the experimental observation for the formation of long-lived radical anion.

TABLE I: Rate Constants for Reactions of C_6F_6 with Various Reducing and Oxidizing Radicals

reactant	substrate	solvent	pH	rate const, $M^{-1}\,s^{-1}$	transient radical
e_{aq}^-	C_6F_6	water	7	$(8.5 \pm 0.9) \times 10^9$	$C_6F_6H^•$
e_{aq}^-	C_6F_6	water	14	$(8.5 \pm 0.9) \times 10^9$	$C_6F_6^{•-}$
$CH_2O^{•-}$	C_6F_6	60:40 MeOH:H_2O	14	$(4.4 \pm 0.5) \times 10^5$	$C_6F_6^{•-}$
$CH_3CHO^{•-}$	C_6F_6	50:50 EtOH:H_2O	14	$(2.5 \pm 0.3) \times 10^6$	$C_6F_6^{•-}$
$(CH_3)_2CO^{•-}$	C_6F_6	40:60 *i*-PrOH:H_2O	14	$(1.6 \pm 0.2) \times 10^6$	$C_6F_6^{•-}$
$OH^•$	C_6F_6	water	7	$(1.4 \pm 0.2) \times 10^9$	$C_6F_6OH^•$
$O^{•-}$	C_6F_6	water	14	$(9.4 \pm 1.4) \times 10^7$	$C_6F_5O^•$
$SO_4^{•-}$	C_6F_6	water	7	$(7.1 \pm 0.7) \times 10^8$	$C_6F_6^{•+}$

Due to the low solubility of hexafluorobenzene in water, its reactions with reducing radicals were studied in aqueous alcohol solutions. The rate constants for alcohol radicals were measured in N_2O-bubbled 60% methanol, 50% ethanol, and 40% 2-propanol aqueous solution containing 1.0 M KOH. The rate constants measured are 4.4×10^5, 2.5×10^6, and 1.6×10^6 $M^{-1}\,s^{-1}$ for reaction of C_6F_6 with $CH_2O^{•-}$, $CH_3CHO^{•-}$, and $(CH_3)_2CO^{•-}$, respectively, at pH 14. The first two were measured from the buildup at 310 nm and the latter from the decay kinetics at 350 nm due to $(CH_3)_2CO^{•-}$. The rate constants and the solvent compositions are listed in Table I. Reducing radicals such as those derived from methylviologen do not react with hexafluorobenzene (up to 0.2 M) in 2-propanol solution.

Figure 2 shows time-resolved spectra obtained on pulse radiolysis of N_2O-bubbled solution of 30 mM C_6F_6 in 1:1 ethanol:water (1:1 EtOH:H_2O) mixture at pH 14. Under this condition the radical anion ($CH_3CHO^{•-}$) derived from ethanol is the only major reactive species as follows:

$$H_2O \rightsquigarrow e_s^-,\ OH^•,\ H^•$$

$$CH_3CH_2OH \rightarrow CH_3CH_2OH^{•+} + e_s^-$$

$$CH_3CH_2OH^{•+} + H_2O/CH_3CH_2OH \rightarrow CH_3CHOH^• + H^+\ (H_2O/C_2H_5OH)$$

$$e_s^- + N_2O \rightarrow N_2 + OH^• + OH^-$$

$$OH^• \rightleftarrows O^{•-} + H^+ \qquad (pK_a = 11.9)$$

$$CH_3CH_2OH + O^{•-}/H^• \rightarrow CH_3CHOH^• + OH^-/H_2$$

$$CH_3CHOH^• \rightleftarrows CH_3CHO^{•-} + H^+ \qquad (pK_a = 11.6)$$

$$CH_3CHO^{•-} + C_6F_6 \rightarrow CH_3CHO + C_6F_6^{•-} \qquad (2)$$

The spectrum recorded at 40 μs after a 50-ns pulse when reaction 2 is completed ($k_2 = 2.5 \times 10^6\ M^{-1}\,s^{-1}$) has maxima at 300 and 440 nm. Similar spectra are observed in other alcohols. The formation of the radical anion is very sensitive to air due to the slow rate constant. The absorption maximum (of $C_6F_6^{•-}$) is red-shifted and the visible band is broadened in these solvents compared to that of 100% aqueous solution. This is not unexpected as the $C_6F_6^{•-}$ absorption maximum is observed at different wavelengths in different solvents.[14,16] The spectrum is unlikely to be due to dimer radical anion because the spectrum and the decay kinetics are independent of neutral C_6F_6 concentration. It is not due to radical (of alcohol) addition to C_6F_6 as no absorption was observed at pH <11 (discussed below). The radical anion decay is independent of C_6F_6 concentration and follows second-order kinetics, $2k/\epsilon = 3 \times 10^4$ cm s^{-1}, to yield a transient which has absorption maxima at 300, 350, and 580 nm. This indicates that $C_6F_6^{•-}$ decays by radical recombination and the species produced is not the dimer radical anion $C_6F_6^{•-}(C_6F_6)$ (which is reported to have a gas-phase binding energy of 10.4 kcal/mol[24]). The time-resolved spectra showed two isobestic point at 350 and 505 nm, indicating that the spectra have parent/daughter relationship. As in the case of 100% aqueous solution, the species produced by radical–radical reaction of $C_6F_6^{•-}$ would yield dimer dianion or dicarbanion. The carbanion would be expected to rapidly protonate;[25] however, the kinetics of its formation and decay indicate that it has a surprisingly long lifetime. In recent years, protonation dynamics has been an active area of research because of the discovery of unusually slow protonation rates measured in certain thermodynamically favorable reactions.[26] This behavior has been reported in the case of carbanions and their participation in polymerization reaction has been an active area of research in recent years. The most studied system is that of the anionic polymerization of styrene in polar aprotic solvents.[27] In the case of hexafluorobenzene, there is evidence that the carbanion formed can undergo further reaction as indicated by the absorption spectrum of the stable product produced in the γ-radiolysis at pH 14 as shown in Figure 3. The absorption spectrum of the stable product is at a longer wavelength than that of perfluorobiphenyl. Polymers have been reported to be the major products in the radiolysis of hexafluorobenzene and perfluoroaromatic compounds.[28] Since our results show that the radical–molecule reaction is too slow to compete with radical–radical reaction, the long-chain molecule and hence polymerization in this system is most probably propagated by carbanion. This suggests that anionic polymerization in hexafluorobenzene is possible even in aqueous solution.

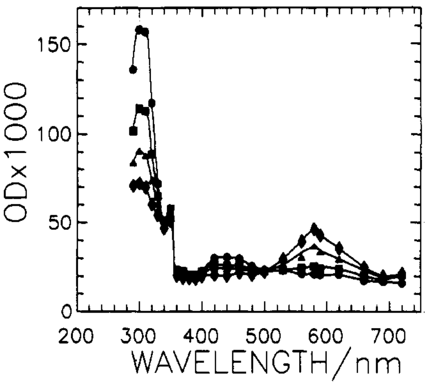

Figure 2. Time-resolved spectra obtained on pulse radiolysis of N_2O-bubbled aqueous ethanol (1:1 EtOH:H_2O) solution of 30 mM C_6F_6 containing 1.0 M KOH at different times after a 50-ns electron pulse: (●) 40, (■) 300, (▲) 700, and (♦) 1800 μs.

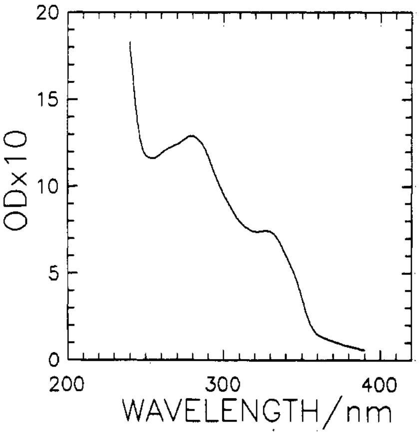

Figure 3. Absorption spectrum of stable product produced in the steady state γ-radiolysis of N_2-bubbled aqueous solution of 2 mM C_6F_6 containing 0.1 M *tert*-butyl alcohol at pH 14.

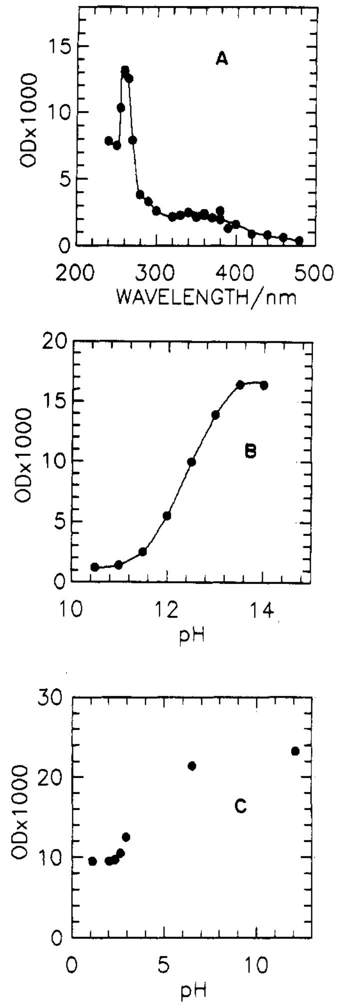

Figure 4. (A) Absorption spectrum obtained on pulse radiolysis of N_2-bubbled aqueous solution of 2 mM C_6F_6 at pH 7 containing 0.1 M *tert*-butyl alcohol recorded immediately after a 2-μs electron pulse. (B) Dependence of the absorbance at 390 nm due to $C_6F_6^{\bullet -}$ on pH in solution as above on pulse radiolysis. (C) Dependence of the absorbance at 260 nm due to $C_6F_6H^{\bullet}$ on pH in solution as above on pulse radiolysis.

Figure 4A shows the spectrum produced in the pulse radiolysis of 2 mM C_6F_6 in aqueous solution containing 0.1 M *t*-BuOH at pH 7. The spectrum has a weak band at 350 nm and a more intense one at 260 nm with low extinction coefficients. In this solution the rate constant for electron scavenging, $k_1 = 8.5 \times 10^9$ M^{-1} s^{-1}, is the same as in higher pH, but the radical anion spectrum was not observed. The spectrum is attributed to hexafluorocyclohexadienyl radical for the following reasons. It is different from the radical anion spectrum obtained at higher pH >13. It is known that benzene and fluorine-substituted benzene radical anions undergo rapid protonation to yield cyclohexadienyl radicals.[7] This means $C_6F_6H^{\bullet}$ is the acid form of the radical anion and the equilibrium exists in the pH region accessible in the aqueous solution. Figure 4B shows the plot of the absorbance of the radical anion measured at 390 nm, OD(390) versus pH, of the solution in aqueous solution containing 0.1 *t*-BuOH. In order to avoid the possible effects of ionic strength on pK_a, the ionic strength was kept constant at 2.0 M using Na_2SO_4 as the inert salt. The plot yielded $pK_a = 12.4$ for the equilibrium

$$C_6F_6H^{\bullet} \rightleftarrows C_6F_6^{\bullet -} + H^+ \qquad (3)$$

The low pK_a reflects the effects of fluorine substitution on acidity.[25,29]

A more direct confirmation for the formation of hexafluorocyclohexadienyl radical failed because pulse radiolysis of 2 mM C_6F_6 in acid (1–100 mM $HClO_4$) solution containing 0.1 M *t*-BuOH, where all e_{aq}^- are converted to $H^{\bullet}$ by reaction with H^+, yields absorption in the UV which is attributable to radical originating from *t*-BuOH.[30] Since *t*-BuOH scavenges $H^{\bullet}$ atom with a rate constant of 1×10^5 M^{-1} s^{-1},[31] the upper limit for the rate constant of $H^{\bullet}$ with C_6F_6 was estimated to be $<1 \times 10^7$ M^{-1} s^{-1}. When the absorbance at 260 nm was monitored as a function of pH (Figure 4C) of the solution, an increase in absorbance was observed at pH above 2.5 and reaching a plateau at higher pH. The increase in absorbance was as expected for a competition for e_{aq}^- between H^+ and C_6F_6, which have a rate constants of 2.3×10^{10} and 8.5×10^9 M^{-1} s^{-1}, respectively. In the steady-state study, the stable product absorption spectrum obtained after γ-radiolysis is similar to the spectrum of decafluorobiphenyl, indicating that F^- elimination occur at a longer time scale.

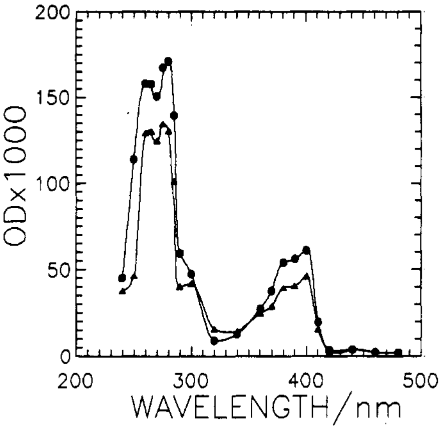

Figure 5. Time-resolved spectra obtained on pulse radiolysis of N_2O-bubbled aqueous solution of 2 mM C_6F_6 at pH 11: (●) end of the pulse and (▲) 12 μs after a 2-μs electron pulse.

Reaction with Oxidizing Radicals. Figure 5 shows the time-resolved spectrum obtained on pulse radiolysis of N_2O-bubbled aqueous solution of 2 mM C_6F_6 at pH 11. In this solution e_{aq}^- is effectively scavenged by N_2O to yield $OH^{\bullet}$.

$$H_2O \rightsquigarrow e_{aq}^-, OH^{\bullet}, H^{\bullet}$$

$$e_{aq}^- + N_2O \rightarrow N_2 + OH^{\bullet} + OH^-$$

$$OH^{\bullet} + C_6F_6 \rightarrow C_6F_6OH^{\bullet} \qquad (4)$$

The spectrum obtained at the end of 2 μs pulse was assigned to hydroxyhexafluorocyclohexadienyl radical. It has bands at 280 and 400 nm with extinction coefficient $\epsilon(400) = 1570$ M^{-1} cm^{-1} (assuming $G(OH^{\bullet}) = G_{OH^{\bullet}} + Ge_{aq}^- = 5.6$ at pH 11) at 400 nm. At longer time scale $H^{\bullet}$ atoms may also contribute to the formation of $C_6F_6OH^{\bullet}$ through reaction with OH^- and N_2O. The spectrum and the extinction coefficient are similar to those reported earlier,[12] but they assigned it to pentafluorophenoxide radical, a species formed by elimination of HF from the initial OH adduct. It was assumed that hydroxyhexafluorocyclohexadienyl radical has a short lifetime because of the formation of an OH bond on the same carbon where a fluorine is attached, and such structure has been reported to be unstable with respect to HF elimination.[32]

Direct evidence that the transient species is not the pentafluorophenoxide radical was obtained by pulse radiolysis of N_2O bubbled solution of 2 mM pentafluorophenol at pH 2 (10 mM $HClO_4$). Under this condition the OH adduct, $C_6F_5(OH)_2^{\bullet}$, initially formed would undergo rapid water elimination to yield pentafluorophenoxide radical[33] as follows:

$$C_6F_5OH + OH^{\bullet} \rightarrow [C_6F_5(OH)_2^{\bullet}]$$

$$[C_6F_5(OH)_2^{\bullet}] \xrightarrow{H^+} C_6F_5O^{\bullet} + H_2O$$

The spectrum of pentafluorophenoxide radical obtained after a 0.5-μs pulse has maxima at 300, 410, and 430 nm (Figure 6) with the extinction coefficient at 430 nm of $\epsilon(430) = 2100\ M^{-1}\ cm^{-1}$ (assuming $G(OH) = 3.95$ at pH 2). A similar spectrum was obtained when radiolysis was carried out at pH 9.2, where pentafluorophenol ($pK_a = 5.5$) is oxidized to $C_6F_5O^{\bullet}$ by $OH^{\bullet}$.

When radiolysis of C_6F_6 was done at higher pH, where $O^{\bullet-}$ is the reactive species, slow formation of the absorbance at 300 and 430 nm was observed. At pH 14.3 the spectrum obtained at 40 μs after a 0.5-μs pulse has absorption bands at 300, 410, and 430 nm as shown in Figure 6. It is seen that the spectrum overlaps with that of the pentafluorophenoxide radical spectrum. The rate constant for growth of the absorbance at 430 nm increases with increase in pH but is not proportional to KOH concentration. This shows that the formation of pentafluorophenoxide radical is base-catalyzed elimination of fluoride ion as follows:

$$C_6F_6 + O^{\bullet-} \rightarrow C_6F_6O^{\bullet-} \qquad (5)$$

$$C_6F_6O^{\bullet-} \xrightarrow{OH^-} C_6F_5O^{\bullet} + F^-$$

The rate constant for reaction of C_6F_6 with $OH^{\bullet}$ was measured by the competition between C_6F_6 and SCN^- for $OH^{\bullet}$, i.e., eqs 4 and 6

$$OH^{\bullet} + SCN^- \rightarrow SCN^{\bullet} + OH^- \qquad (6)$$

From this competition it follows that

$$\frac{OD_0}{OD_s} = 1 + \frac{k_4[C_6F_6]}{k_6[SCN^-]} \qquad (III)$$

where OD_0 and OD_s are the optical densities at 480 nm for absorption due to $(SCN)_2^{\bullet-}$ in the absence and the presence of C_6F_6, respectively. A plot of OD_0/OD_s versus $[C_6F_6]/[SCN^-]$ at a fixed concentration of SCN^- (2.8×10^{-4} M) at pH 7 gives a straight line (Figure 7). From the slope, $k_4 = 1.4 \times 10^9\ M^{-1}\ s^{-1}$ was obtained, taking $k_6 = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$.[31] The rate constant obtained is similar to the value reported earlier.[12]

The rate constant for reaction of hexafluorobenzene with $O^{\bullet-}$ was determined by using eq III at pH 14 from the competition between C_6F_6 and SCN^- for $O^{\bullet-}$, i.e., eqs 5 and 7.

$$O^{\bullet-} + SCN^- \xrightarrow{H^+} SCN^{\bullet} + OH^- \qquad (7)$$

A plot of OD_0/OD_s versus $[C_6F_6]/[SCN^-]$ yields a straight line. From the slope, k_5 was determined to be $9.4 \times 10^7\ M^{-1}\ s^{-1}$, taking $k_7 = 1 \times 10^9\ M^{-1}\ s^{-1}$.[31]

At lower pH, hydroxyhexafluorocyclohexadienyl radical undergoes acid-catalyzed water elimination to yield the radical cation[33] as follows:

$$C_6F_6OH^{\bullet} + H^+ \rightleftarrows C_6F_6^{\bullet+} + H_2O$$

Figure 8 shows time-resolved spectra obtained on pulse radiolysis of 2 mM C_6F_6 aqueous solution bubbled with N_2O at pH 0.04. The spectrum due to the cation $C_6F_6^{\bullet+}$ recorded at 20 μs after 0.5 μs has maxima at 275 and 390 nm. The cation decays by first-order kinetics with a half-life $\tau_{1/2} = 130$ μs, and the decay does not seem to depend on C_6F_6 in the concentration range studied. This indicates that the cation does not react to give dimer and/or polymer radical cation which is normally the fate of unfluorinated aromatic hydrocarbons.[34] The absence of polymeric radical cations in perfluoroaromatic hydrocarbons has been reported by Bartlett et al. in the preparation of their salts and by us in low-temperature matrix isolation studies[35] (although the dimer cation $C_6F_6^{\bullet+}(C_6F_6)$ has been reported in the gas phase[24]). This is believed to be due to a consequence of the repulsive exchange interaction of the electron-rich F ligands.

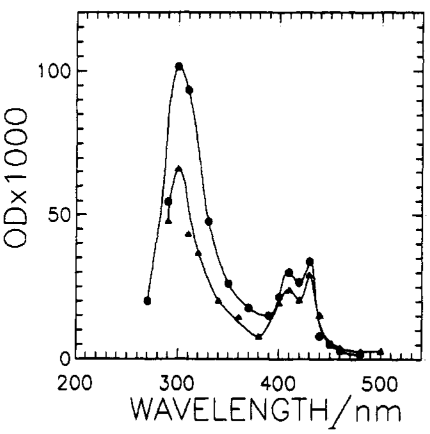

Figure 6. Absorption spectra obtained on pulse radiolysis of N_2O-bubbled aqueous solution containing different solutes: (●) 1.7 mM C_6F_5OH at pH 2, immediately after the pulse, and (▲) 2 mM C_6F_6 at pH 14, 40 μs after a 0.5-μs electron pulse.

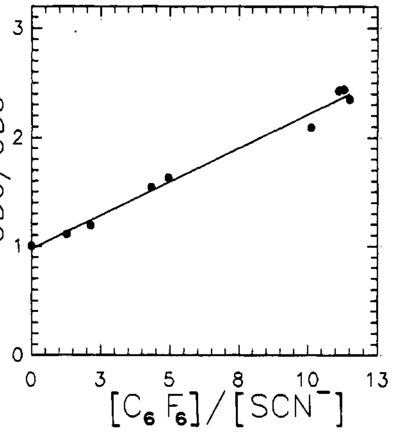

Figure 7. Competition kinetics plot, OD_0/OD_s versus $[C_6F_6]/[SCN^-]$, at a fixed concentration of SCN^-, obtained on pulse radiolysis of N_2O-bubbled aqueous solutions of 0.28 mM KSCN at pH 7 containing different C_6F_6 concentrations.

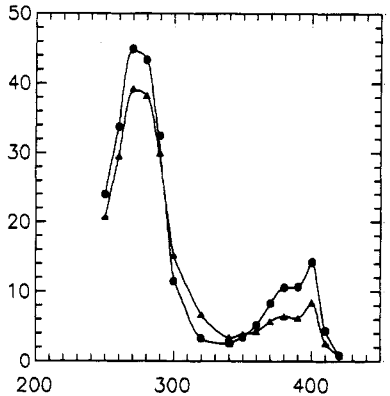

Figure 8. Time-resolved spectra obtained on pulse radiolysis of N_2O-bubbled aqueous solutions of 2 mM C_6F_6 at pH 0.04: (●) end of the pulse and (▲) 20 μs after a 0.5-μs electron pulse.

Hexafluorobenzene also undergoes one electron oxidation reaction with $SO_4^{\bullet-}$ radical to yield radical cation. A rate constant of $7.1 \times 10^8\ M^{-1}\ s^{-1}$ was measured for the reaction $SO_4^{\bullet-} + C_6F_6 \rightarrow C_6F_6^{\bullet+} + SO_4^{2-}$ by monitoring the decay kinetics of $SO_4^{\bullet-}$ at 450 nm. The spectrum obtained in the pulse radiolysis of N_2-bubbled 2 mM C_6F_6 aqueous solution containing 0.12 M $K_2S_2O_8$

and 0.095 M *t*-BuOH at pH 7, attributed to the radical cation, $C_6F_6^{\bullet +}$, is similar to that shown in Figure 8. With other oxidizing agents such as $Cl_2^{\bullet -}$, no discernible reaction was observed with C_6F_6 for concentration up to 2 mM. From the oxidation reaction of C_6F_6 with $SO_4^{\bullet -}$, $OH^{\bullet}$ (pH = 0.04) and $Cl_2^{\bullet -}$ (pH = 3) which have reduction potentials[36] of 2.6, 2.7, and 2.3, respectively, the reduction potential $E(C_6F_6^{+}/C_6F_6)$ can be estimated to be in the range 2.3–2.6.

Conclusion

Hexafluorobenzene forms a long-lived radical anion which is stable with respect to fluoride elimination. The absorption spectrum is sensitive to the environment. The radical anion/cation does not seem to react with the parent hexafluorobenzene unlike their hydrocarbon counterparts. The study shows evidence that carbanion derived from hexafluorobenzene forms a living polymer capable of propagating anionic polymerization in aqueous solution. Hexafluorobenzene shows considerable resistance to radical addition reactions. It is unreactive toward most of the well-known oxidizing and reducing radicals.

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