Radiolytic Reduction of Hexachlorobenzene in Surfactant Solutions: A Steady-State and Pulse Radiolysis Study

GEORGE ADAM ZACHEIS, † KIMBERLY A. GRAY, *,† AND PRASHANT V. KAMAT ‡

Department of Civil Engineering, 2145 Sheridan Road, Northwestern University, Evanston, Illinois 60208-3109, and Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556-0579

Steady-state and pulse radiolysis experiments have been performed to gain insight into the mechanism of hexachlorobenzene (HCB) degradation in nonionic surfactant (Plurafac RA-40) solutions. This understanding is important for the environmental application of radiolysis to remediate soils contaminated with chlorinated aromatic compounds or to treat surfactant solution wastes from soil washing processes. Steady-state experiments showed that, after an applied dose of 50 kGy, reductive dechlorination of HCB to trichlorobenzene occurs under reducing conditions. Under oxidizing conditions at the same dose, reductive dechlorination proceeds more slowly to yield tetrachlorobenzene. Radiolytic experiments on the surfactant alone showed that the reaction rate constant between hydroxyl radicals and RA-40 (1.09 \times 10⁹ M⁻¹ s⁻¹) was nearly 2 orders of magnitude higher than that between hydrated electrons and RA-40 (2.0 \times 10⁷ M⁻¹ s⁻¹). Reaction kinetics analysis indicates efficient hydroxyl radical scavenging by surfactant molecules and the production of secondary surfactant radicals, which are reductive in nature. Thus, we observe HCB dechlorination in surfactant solutions even under strongly oxidizing conditions.

Introduction

In the United States, the contamination of soils with hydrophobic and toxic chemicals is a vast problem, and treatment is a high priority (1). An estimated 217 000 sites, contaminated with chlorinated compounds, remain to be cleaned up at an estimated cost of \$187 billion (1996 \$) (2). In addition, an estimated 500 000 ton of dioxin contaminated soils alone are in need of treatment (3). Recalcitrant chemicals including dioxins and polychlorinated biphenyls (PCBs) are resistant to remediation via less expensive technologies such as bioremediation due to low bioavailability (4-6). In many cases, incineration is the only feasible alternative for contaminant destruction (3, 7, 8). However, destruction of dioxins and PCBs requires very high combustion temperatures, and inadequate operating temperatures often leads to incomplete contaminant combustion and the formation of byproducts having similar or greater toxicity, such as chlorobenzofurans

[†] Northwestern University.

(9-11). An alternative to incineration, radiolysis, has been shown to be an economically competitive alternative for contaminant destruction (12, 13).

Recent work in our laboratory has focused on the radiolytic treatment of hexachlorobenzene (HCB) -contaminated soils and metal oxides using ⁶⁰Co and high-energy electrons produced by linear accelerators (LINACs) (*12, 14*). In soil studies, complete HCB degradation only occurred with the addition of surfactants to soil samples. Surfactant addition was found to reverse the retarding effect of soil organic matter. Furthermore, regardless of the conditions of reaction (i.e., oxidative or reductive environments created by the addition of hydroxyl radical and hydrated electron scavengers), the irradiation of contaminated soils amended with surfactants resulted in reductive dechlorination reactions (*12, 15*).

In all our work, the addition of a nonionic surfactant has determined the extent of radiolytic reaction in soil systems. Although essential, the role played by the surfactant in the complicated chemistry of radiolysis is unknown. The purpose of this work is to investigate the behavior of a nonionic surfactant, BASF Plurafac RA-40, under controlled radiolytic conditions and to probe its influence on HCB transformation.

To date, few studies concerning the radiolytic degradation of chlorinated organics solubilized within surfactants have been undertaken (16-18). To our knowledge, this is the first study of the radiolytic behavior of HCB in surfactant systems. In addition to aiding in the understanding of our soil system, this work is also directly applicable to the treatment of soil washing effluents by radiolysis (19). Furthermore, insight into the fundamental chemistry of radical reactions in surfactant solutions enhances the development of strategies to control and target selective chemical transformations as well as the ability to design efficient radiolytic processes for environmental applications.

This work involved steady-state radiolytic experiments, which allowed for the identification of byproducts and the calculation of yields in HCB surfactant solutions under reductive and oxidative conditions. In addition, pulse radiolysis studies were undertaken to calculate the reaction rates between primary radiation products and HCB as well as the surfactant, to monitor the transient intermediates produced by these interactions, and to elucidate the pathway of HCB dechlorination.

Radiation Chemistry

The radiolytic transformations of solutes may be quantified in terms of G, defined as the number of molecules formed or lost per 100 eV of energy absorbed (*20*). In aqueous solutions at pH 7, the G values of solvated electrons and hydroxyl radicals (primary products) are about 2.7 and 2.8, respectively. These radicals, or primary products, are the major species formed from the radiolysis of water.

Reductive conditions may be established through the addition of *tert*-butyl alcohol, a scavenger of hydroxyl radicals, and purged with N_2 to eliminate O_2 , an electron scavenger (21):

$$OH^{\bullet} + (CH_3)_3COH \rightarrow H_2O + (CH_3)_2\dot{C}H_2COH$$
(1)

$$O_2 + e^- \to O_2^{\bullet-} \tag{2}$$

Conversely, oxidative conditions are created using N_2O , an electron scavenger (21):

$$e_{aq}^{-} + N_2 O + H_2 O \rightarrow N_2 + 2(^{\circ}OH)$$
 (3)

^{*} Corresponding author phone: (847)467-4252; fax: (847)491-4011; e-mail: k-gray@nwu.edu.

[‡] University of Notre Dame..

Oxidation of chlorinated benzenes tends to proceed through hydroxyl substitution at the para and ortho positions (22). In many studies of halogenated benzenes, the product of hydroxyl adducts is the hydroxycyclohexadienyl radical (21, 23-26). Hydroxyl radical attachment may also occur at a chlorine atom, resulting in the formation of a phenoxyl radical (22). These products are readily identified by UV spectroscopy (27).

Chlorinated aromatics are more reactive toward solvated electrons due to electron-deficient aromatic rings resulting from chlorine atom substitution (28). Carbon–chlorine bonds may by rapidly cleaved through direct electron capture (17):

$$\mathbf{e}_{\mathrm{aq}}^{-} + \mathrm{ArX} \rightarrow (\mathrm{ArX})^{-} \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{X}^{-}$$
 (4)

Electron capture leads to the formation of intermediate electron adducts, which decay to form aryl radicals and halide ions (*21*). For example, hexafluorobenzene (HFB) has been reported to react quantitatively with electrons to yield a pentafluorobenzyl radical and fluoride (*29*).

Experimental Section

Sample Preparation. RA-40 surfactant was obtained from the BASF Corporation (Mt. Olive, NJ). Chlorinated benzenes were acquired from Aldrich (Milwaukee, WI). All chemicals were of the highest purity and were used as received without further purification. RA-40 is a nonionic, ethoxyl alcohol surfactant (CH₃(CH₂)_{12–15}[-OCH₂CH₂-]_{12–15}OH) with an average molecular weight of 820 amu. All surfactant solutions were prepared on a weight to weight basis in triple distilled water. Because of the very low aqueous solubility of HCB (1.75 × 10⁻⁸ M) (*30*), surfactant solutions were heated to 75 °C and stirred for 3 h to enhance HCB solubilization.

Pulse radiolysis experiments were performed in unbuffered surfactant solutions without pH adjustment. A 31 mM solution of RA-40 had a measured pH of 5.7.

Electron-rich solutions were created through the addition of 1% (by volume) *tert*-butyl alcohol and by purging the solution with nitrogen gas. Oxidizing conditions were created by sparging solutions with nitrous oxide.

 γ -**Radiolysis.** All steady-state radiolysis experiments were conducted using a Shepard-109, ⁶⁰Co source. ⁶⁰Co is an emitter of high-energy photons (γ -rays), having an average energy of 1.25 MeV. The Shepard-109 is a concentric welltype source with a dose rate of approximately 69 Gy/min. Dose rates were determined using Fricke dosimetry (*31*). All aqueous surfactant solutions were irradiated in 7-mL closed vials to ensure that solutions remained saturated with appropriate scavengers, such as the utilization of N₂O as a scavenger of electrons.

Pulse Radiolysis. Pulse radiolysis experiments were performed using a model TB-8/16-1S linear accelerator (LINAC). This LINAC produces electron pulses, 50 ns in duration, at 8 MeV energy. Solutions were continuously pumped through a quartz cell, and radical kinetics were monitored by UV absorption.

Extraction and Analysis. Surfactant solutions were extracted sequentially using hexane. An internal standard, 1,3,5-tribromobenzene (4 mg/L), was added prior to extraction to correct responses for extraction efficiency and changes in volume. This internal standard was used due to its structural similarity to HCB and high response in electron capture detectors (ECD). After internal standard and solvent addition, solutions were centrifuged for 3 min at 890*g* to separate surfactant/water and hexane phases. The resulting hexane phase was decanted, passed through a column of sodium sulfate, and then stored for GC analysis.

A method for the detection and quantification of HCB and reduced forms of HCB was developed in our laboratory using a Hewlett-Packard series 4890 GC with ECD detection



FIGURE 1. Steady-state, γ -radiolysis of HCB (175 μ M) in RA-40 (31 mM) under reducing (**I**) (N₂ and 1% *tert*-butyl alcohol) and oxidizing (**O**) conditions (N₂O purged) vs time.

and a Restek RTX-5 nonpolar column (*12*). Helium was used as a carrier gas, and an argon/methane (P-5) gas mixture was used for ECD makeup.

Tentative identification of reaction products by GC–ECD was verified through the use of a Hewlett-Packard 6890 GC–MS. Mass spectra were compared to NIST databases for tentative identification. Mass spectra of samples were compared to standards for final confirmation. For the GC–MS work, a J&W Scientific DB-5 column (nonpolar) was used.

Results

Steady-State, γ -**Radiolysis**. Steady-state radiolysis of 175 μ M HCB in a 31 mM RA-40 surfactant solution was carried out under different scavenger conditions over a period of 12 h (50 kGy). Figure 1 shows the decay of HCB following γ -radiolysis in oxidative and reductive environments. The overall rate of HCB disappearance was 2 times greater under reducing conditions. These data were fit with a pseudo-first-order HCB decay rate constant of 0.105 h⁻¹ under reductive conditions.

GC-ECD analysis of steady-state irradiated samples indicated that the byproducts of HCB degradation were in the form of reduced chlorinated benzenes. Products formed under reducing conditions include pentachlorobenzene (PeCB), tetrachlorobenzenes (TeCBs), and trichlorobenzenes (TCBs) as illustrated in Table 1. Two isomers of TeCB (1,3,4,5-TeCB and 1,2,3,5-TeCB) could not be individually quantified due to coelution under the conditions of the GC method employed. Some of these reduced forms of HCB were also observed under oxidizing conditions, although in different proportions.

Because of the high degree of chlorine substitution in HCB, one would expect its reaction rate with hydroxyl radicals to be slower than with hydrated electrons. Minero et al. found that HFB was less reactive than pentafluorophenol toward hydroxyl radicals (*32*). Likewise, Atkinson found that hydroxyl radical reactivity decreased with increasing chlorine substitution in PCBs (*33*). Under the conditions of these experiments, however, only reduced byproducts were observed, regardless of the level of chlorine substitution in the parent compound. As will be discussed later, this phenomenon is the direct result of hydroxyl radical scavenging by surfactant molecules, which prevents the oxidation of HCB and its byproducts.

G values for the 5-h (20.8 kGy) irradiated samples were calculated for experiments performed under both reductive and oxidative conditions. These values as well as measured concentrations of reduced products are presented in Table 1.

TABLE 1. Results of Steady-State Radiolysis: Byproduct Levels and Yields at 20.8 kGy

chemical	residual concn (µM)	σ (μM)	G (molecules/ 100 eV)ª	σ _G (molecules/ 100 eV)
Reductive Environment ^b				
HCB	76.75	5.23	3.20×10^{-2}	2.18×10^{-3}
PeCB	33.17	6.12	1.55×10^{-2}	2.85×10^{-3}
1,2,3,4-TeCB	0.53	0.09	$2.48 imes 10^{-4}$	4.31×10^{-5}
1,3,5-TCB	0.03	0.04	$1.29 imes 10^{-5}$	1.82×10^{-5}
1,2,4-TCB	0.33	0.08	1.54×10^{-4}	$3.63 imes 10^{-5}$
1,2,3-TCB	0.055	0.001	$2.57 imes10^{-5}$	$1.09 imes 10^{-6}$
Oxidative Environment ^c				
HCB	119.85	1.14	2.00×10^{-2}	1.91×10^{-4}
PeCB	16.06	0.34	7.49×10^{-3}	$1.58 imes 10^{-4}$
1,2,3,4-TeCB	0.046	0.002	$2.16 imes 10^{-5}$	1.08×10^{-6}

^{*a*} Apparent values of *G*. Initial [HCB] = 162.75 ± 4.35 μ M. ^{*b*} Reductive conditions refer to the radiolysis of HCB solution containing 31 mM RA-40 and 1% *tert*-butyl alcohol (N₂-saturated). Initial [HCB] = 145.38 ± 2.88 μ M. ^{*c*} Oxidative conditions refer to the radiolysis of HCB solution containing 31 mM RA-40 (N₂O-saturated).

As shown in Table 1, the G value for HCB transformation under reducing conditions was approximately 0.03 in comparison to 0.02 in an oxidative environment. In general, under oxidizing conditions, the concentrations of transformation products and the corresponding G values were less than G values under reducing conditions with observed differences as great as an order of magnitude. However, given the very large reaction rate constant (discussed later) between hydroxyl radicals and RA-40, hydroxyl radicals were equally scavenged by tert-butyl alcohol and RA-40. (Note that $k_{C_4H_{10}O}$ - $[C_4H_{10}O] \simeq k_{RA-40}[RA-40]$ at the concentration of *tert*-butyl alcohol used (135 mM) in the present experiments.) For this reason as well as the fact that the applied rather than absorbed dose, which is unknown for this type of heterogeneous system, was used in the calculations, the *G* values in Table 1 are apparent *G* values.

Slower reaction rates and lower G values for the dechlorination of polychlorinated benzenes can be attributed to the differences in reduction potentials with increasing chlorine substitution. A similar observation has also been made in the study of dechlorination of PCBs under γ -radiolysis in transformer oils (34). Past research by Hilarides et al. found G values in the range of $1.4-9.6 \times 10^{-6}$ for the degradation of 2,3,7,8-tetrachlorobenzo-p-dioxin (TCDD) (100 ng/g) when adsorbed to RA-40-amended soil (15). Similar *G* values for the irradiation of TCDD (100 ng/g) in ethanol, acetone, and dioxane were calculated from the data taken from Fanelli et al. (35). In general, the differences in G values observed in the dioxin and HCB research are attributed to differences in contaminant concentration. The concentration of HCB used in these experiments was 1000 times greater than the dioxin concentrations used by Hilarides et al. Table 1 does not show the measurement of all byproducts, as a mass balance of carbon was not achieved. Closure of the carbon mass balance is complicated in this system by our inability to quantify all the reaction products, especially those resulting from ring cleavage.

Figure 2 shows the formation of PeCB with time under both reductive and oxidative environments. Initially, the formation of PeCB is pseudo-first-order with the rate of PeCB formation equaling the rate of HCB decay. With increasing time, the growth of PeCB becomes asymptotic and eventually decays over larger dose periods. These data further illustrate the much slower rates of byproduct appearance under oxidizing relative to reducing conditions.

Pulse Radiolysis of HCB in RA-40 Surfactant Solutions. Pulse radiolysis experiments were performed using solutions



FIGURE 2. Pentachlorobenzene formation in RA-40 (31 mM) vs time under reducing (**■**) and oxidizing (**●**) conditions.



FIGURE 3. Difference absorption spectra recorded (a) 12.5 (**m**), (b) 25.0 (**o**), and (c) 50.0 μ s (**a**) after an electron pulse in a N₂-purged, 1% *tert*-butyl alcohol solution of HCB (175 μ M) and RA-40 (31 mM). Insert: Byproduct growth at 280 nm.

of HCB (175 µM) in aqueous RA-40 (31 mM). Under reducing conditions, the difference absorption spectra at various times showed the growth of a large peak around 270-280 nm as illustrated in Figure 3 and its insert. The transient absorption at early times (spectrum a in Figure 3) arises from the initial attack of HCB by hydrated electrons. A small amount of bleaching is observed at 320 nm representing the disappearance of parent HCB and the formation of an electron adduct. At this wavelength, the transient has a lower absorption than the parent HCB. The electron adduct so formed is unstable and undergoes dechlorination. The peak in the region of 270-280 nm is attributed to the appearance of a dechlorination product. The identification of these intermediates is explained more fully in the discussion section. The bimolecular rate constant for the formation of this transient at 280 nm was found to be 8.3 \times 10 $^7\,M^{-1}\,s^{-1}$ (Figure 3, insert).

Pulse radiolysis experiments carried out with HCB/RA-40 solutions under oxidizing conditions (Figure 4) (i.e., solutions sparged with N₂O) exhibited a difference spectrum somewhat similar to that obtained under reducing conditions (Figure 3). For example, the transient absorption spectrum in the 265–310 nm region (spectrum a in Figure 4) is similar to the transient absorption spectrum recorded at 25.0 μ s in Figure 3 (spectrum b). As shown in Table 1, similar stable products are formed in the reducing and oxidizing environments but in different proportions. Yet, there are also some spectral differences evident under oxidizing conditions. In



FIGURE 4. Difference absorption spectra recorded (a) 12.5 (**m**), (b) 25.0 (**•**), and (c) 50.0 μ s (**•**) after an electron pulse in a N₂O-purged solution of HCB (175 μ M) and RA-40 (31 mM).



FIGURE 5. Difference absorption spectra recorded (a) 5 (\blacksquare), (b) 10 (\bullet), and (c) 20.0 μ s (\blacktriangle) after an electron pulse in a N₂O-purged solution of methyl viologen (100 μ M) and RA-40 (31 mM). Insert: Growth of reduced methyl viologen at 390 nm.

contrast to the phenomena displayed under reducing conditions, the major peak in the 270-280 nm region decreases and the bleaching of the 320 nm intermediate is not observed under oxidizing conditions. These results suggest that the reaction proceeds on different time scales by a differing pathway but involves similar (270–280 nm) as well as different transients, as illustrated in Figures 3 and 4.

Surfactant Radicals as Secondary Reducing Radicals. To establish the reactivity of the surfactant radicals produced by •OH radical reaction, we added a known amount (10^{-4} M) of methyl viologen into N₂O-purged RA-40 (31.0 mM) surfactant solutions. Since MV²⁺ is a good electron acceptor and the reduced form, MV⁺⁺, has a characteristic absorption maximum at 390 and 605 nm (not shown) (*36*), we employed it as a probe to track the formation of reductive, secondary surfactant radicals. Under N₂O-saturated conditions, hydrated electrons were not detected (monitored at 600 nm) and thus did not directly reduce methyl viologen.

Figure 5 shows the transient spectrum obtained following the radiolysis of RA-40 (N₂O-purged) solution containing methyl viologen. The spectral characteristics of the transient absorption having a 390 nm maximum confirm the formation of MV⁺⁺. Two distinct steps occur in the growth of MV⁺⁺, a fast growth component in the 390 nm absorption (completed within 30 μ s) and a slow growth component over a period of 200 μ s (insert of Figure 5). The bimolecular rate constants for these two processes are 5.9 \times 10⁸ and 2.0 \times 10⁸ M⁻¹ s⁻¹, respectively. This observation is similar to the previously



FIGURE 6. Reaction rate between HCB and electrons in a N₂-purged, 1% *tert*-butyl alcohol solution of RA-40 (31 mM). Insert: Electron decay at 600 nm in the presence of (a) 44 (\blacksquare) and (b) 175 μ M (+) HCB.

reported two-step reduction processes in surfactant solutions (37). The initial component consists of a fast diffusioncontrolled electron transfer between aqueous-phase surfactant radical monomers and a given solute, while the second component arises from the slower electron transfer between micelle-attached surfactant radicals to the solute.

Although the identification of the surfactant radicals is not possible, these results establish the reducing properties of the radicals. These reactions proceed as follows:

$$^{\circ}$$
OH + R-O-CH₂CH₂OH \rightarrow
H₂O + R-O-CH₂ $^{\circ}$ CHOH (5)

$$R-O-CH_{2}^{\bullet}CHOH + MV^{2+} \rightarrow R-O-CH_{2}^{+}CHOH + MV^{*+}$$
(6)

The presence of reducing surfactant radicals has also been verified in earlier studies through the bleaching of ferricyanate, illustrating electron transfer between surfactant radicals and an oxidizing agent in solution (*38*). In addition, simple alcohol radicals such as ethanol have been shown to be capable of electron transfer (*39*).

Reaction Rates with Hydrated Electrons. Pulse radiolysis experiments enabled us to obtain the bimolecular rate constant for the reaction between HCB and hydrated electrons in RA-40 (31 mM) surfactant solutions. As shown in the insert of Figure 6, the decay rate of electrons (monitored at 600 nm) increased at higher concentrations of HCB. A bimolecular reaction rate constant of 1.1 (\pm 0.2) \times 10⁹ M⁻¹ s⁻¹ was determined for the reaction between hydrated electrons and HCB (Figure 6). Several research groups have observed similar reactivities of halogenated benzenes toward hydrated electrons. For example, Schmelling et al. found the rate constant for the reaction between electrons and decachlorobiphenyl in Triton X-100 solution to be 2.6×10^9 M^{-1} s⁻¹ (17). Shoute and Mittal reported a reaction rate constant of $8.5 \times 10^9 \, \text{M}^{-1} \, \text{s}^{-1}$ for hydrated electrons and HFB in aqueous alcohol solutions (40).

The dependence of electron decay on the concentration of RA-40 was also investigated. The insert of Figure 7A shows that increasing concentrations of RA-40 leads to an increase in the rate of electron decay. A bimolecular rate constant of 2.0 (\pm 0.5) \times 10⁷ M⁻¹ s⁻¹ was determined for the reaction between RA-40 and hydrated electrons. Again, we found that the reaction rate constant of this reaction was similar to the reaction rate constant between electrons and Triton X-100



FIGURE 7. (A) Reaction rate between RA-40 and electrons (N₂-purged and 1% *tert*-butyl alcohol). Insert: Electron decay at 600 nm in the presence of (a) 1.15 (\times), (b) 1.85 (+), and (c) 2.28 mM (**II**) RA-40. (B) Reaction rate between RA-40 and hydroxyl radicals using competition kinetics.

reported by Schmelling et al. (1.2 \times 10⁷ M⁻¹ s⁻¹) (17). Furthermore, the reaction rate constant between surfactants and electrons (2.0 \times 10⁷ M⁻¹ s⁻¹) is significantly lower than that between HCB and electrons (1.1 \times 10⁹ M⁻¹ s⁻¹).

Role of Hydroxyl Radicals. Due to the low extinction coefficient of hydroxyl radicals, competition kinetics was employed to determine the reaction rate constant between hydroxyl radicals and RA-40 in aqueous solutions (*28*). Thiocyanate (SCN⁻) was added to a RA-40 surfactant solution (N₂O-purged) at a concentration of 10^{-4} M, resulting in the two competing reactions, eqs 7 and 8, to determine the fate of 'OH radicals:

$$\mathrm{SCN}^{-} + {}^{\bullet}\mathrm{OH} \xrightarrow{\mathrm{SCN}^{-}} (\mathrm{SCN})_{2} {}^{\bullet-} + \mathrm{OH}^{-} + \mathrm{H}_{2}\mathrm{O}$$
 (7)

(8)

$$OH + R - O - CH_2CH_2OH \rightarrow$$

 $H_2O + R - O - CH_2CHOH$

Absorbance of the $(SCN)_2^{--}$ radical was monitored at 472 nm. As shown in Figure 7B, the reaction rate constant is obtained by plotting the inverse of the $(SCN)_2^{--}$ absorbance at 472 nm versus the molar ratio of RA-40 to SCN^{-} . From these data, the reaction rate between hydroxyl radicals and RA-40 was determined to be 3.3 (± 0.4) ×10⁹ M⁻¹ s⁻¹. In comparison, the reported reaction rate constant between hydroxyl radicals and Triton X-100 is $8.8 \times 10^9 M^{-1} s^{-1}$ (41). It is important to note that the reaction rate constant for the reaction between RA-40 and hydroxyl radicals (Figure 7B; $3.3 \times 10^9 M^{-1} s^{-1}$) is nearly 2 orders of magnitude greater than the rate constant of reaction between RA-40 and hydrated electrons (Figure 7A; $2.0 \times 10^7 M^{-1} s^{-1}$).

Because of the low solubility of HCB and the high reactivity of RA-40 toward 'OH radicals, we were unable to determine the reaction rate constant between hydroxyl radicals and HCB in surfactant solutions. Competition kinetic measurements showed nearly no change in the (SCN)2. absorbance when the concentration of HCB was increased from 0 to 1.75 \times 10⁻⁴ M. It is evident that, at low concentrations, HCB is unable to compete with SCN⁻ and RA-40 in the reaction with hydroxyl radicals. In an analogous study of HFB, the reaction rate constant with hydroxyl radicals was reported to be 1.4 \times 10⁹ M⁻¹ s⁻¹ (40). Even with an upper limit of the rate constant on the order of $10^9 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$ for the reaction between 'OH radical and HCB, the probability of 'OH reaction with HCB becomes significantly smaller at the concentration ratio of surfactant:HCB (170:1) used in the present experiment. The HCB transformations observed during radiolysis in N₂Opurged solutions are therefore attributed to the secondary radical reactions, i.e., reaction with reducing surfactant radicals (eqs 9 and 10):

$$^{\bullet}OH + R - O - CH_{2}CH_{2}OH \rightarrow$$

$$H_{2}O + R - O - CH_{2}^{\bullet}CHOH \quad (9)$$

$$R - O - CH_{2}^{\bullet}CHOH + C_{6}Cl_{6} \rightarrow$$

$$R - O - CH_{2}^{\bullet}CHOH + [C_{6}Cl_{6}]^{\bullet-} \quad (10)$$

Discussion

Under reductive conditions, the dechlorination of HCB in RA-40 surfactant solutions proceeded at a nearly diffusioncontrolled rate constant of $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. As illustrated by reaction rate constants, we observed that the reaction of surfactant molecules and hydroxyl radicals dominates in an oxidative environment. In these experiments the concentration of RA-40 was 170 times greater than HCB, resulting in rapid hydroxyl radical scavenging and the production of surfactant radicals. The reaction of the surfactant, an ethoxyl alcohol, with hydroxyl radicals is analogous to that with simple alcohols. For example, alcohols such as 2-propanol readily react to form α -hydroxy radicals ($k = 1.9 \times 10^9 \text{ M}^{-1}$ s⁻¹; pH 6) (42). Once produced, surfactant radicals can initiate secondary reduction of HCB in a way similar to the reduction of methyl viologen in N₂O-saturated surfactant solutions. This explains the slower rate of HCB depletion in the γ -radiolysis of N₂O-saturated surfactant solutions (Figure 1). Secondary reduction of HCB by surfactant radicals occurred at a rate half that of the reaction of HCB with hydrated electrons.

Radiolysis of HCB solubilized in RA-40 solution results in the reduction of HCB irrespective of the experimental conditions (reductive or oxidative) created in these experiments. In general, the reaction of electrons with substituted halobenzenes leads to dechlorination and the formation of radical species (*22*). This process occurs via the reactions 11 and 12 and is also illustrated in Scheme 1:

$$\mathbf{C}_{6}\mathbf{Cl}_{6} + \mathbf{e}_{aq}^{-} \rightarrow [\mathbf{C}_{6}\mathbf{Cl}_{6}]^{\bullet-} \rightarrow \mathbf{C}_{6}\mathbf{Cl}_{5} + \mathbf{Cl}^{-}$$
(11)

$$[C_6Cl_6]^{\bullet-} \xrightarrow{H_{aq}^+/H_2O} [C_6Cl_6H]^{\bullet} \rightarrow {}^{\bullet}C_6Cl_5 + H^+ + Cl^-$$
(12)

Electrons are likely to be transferred to a chlorine atom, resulting in chloride expulsion and the formation of an aryl radical (eq 11) or transferred to the aromatic ring, resulting in protonation to form a hexadienyl radical (eq 12). Protonation reactions have been found to occur in halogenated benzenes (*21, 29*) and even with benzene (*43*). Ultimately, hexadienyl radicals may further degrade to form an aryl radical and hydrogen chloride. Past research has shown aryl radicals to be efficient hydrogen abstractors (*44*).

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SCHEME 1. Reaction Mechanism for HCB Degradation in $\rm RA-40^{\it a}$



^a These results show that the surfactant plays an important role in the radiolytic chemistry of HCB. In addition to hydrogen donation, the presence of surfactant directs the reductive transformation of HCB and its lesser chlorinated byproducts. The reaction of surfactant molecules with hydroxyl radicals produces radicals that, in turn, reduce chlorinated benzenes. These results provide additional insight into why only reductive transformations have been observed in our work with contaminated soils and may suggest strategies to control radical chemistry in environmental materials.

The reaction of protons with hydrated electrons to produce hydrogen radicals occurs at near-diffusion-limited rates over a pH range of 4-5 (45). While the reaction of aryl radicals with hydrogen may occur, the yield of hydrogen radicals at neutral pH is only G = 0.6 (46). Since the pH of RA-40 solutions in our experiments is 5.6, the concentration of hydrogen radicals is not significant.

Since surfactants are a rich source of hydrogen, we propose that surfactant molecules and aryl radicals can react to form PeCB. Koster and Asmus found that HFB radical anions react quantitatively to yield pentafluorobenzyl radical and fluoride (*29*). Fluoride elimination was verified by conductivity measurements in pulse radiolysis experiments in neutral solutions. Conductivity was shown to decay with time, evidence of electron adduct protonation, to yield cyclohexadienyl radicals as in eq 10. Transients in the pulse spectra were attributed to the presence of cyclohexadienyl radicals over long irradiation pulses (~5 μ s).

Later experiments with HFB in solutions at pH 14 by Shoute and Mittel contradicted the findings of Koster and Asmus (40). They stated that HFB, following electron capture, does not undergo fluoride elimination and instead forms dimers and trimers of HFB. However, Shoute and Mittel failed to explain the conductivity findings of Koster and Asmus. In addition, the presence of an electron adduct was not detected in experiments at lower values of pH (<13). These spectra were attributed to the presence of a hexafluorocyclodienyl radical, a result of rapid protonation of the hexafluorobenzyl radical. In addition, research with pentahalophenols has shown that the reaction of electrons with pentachlorophenoxide ions results in chlorine expulsion and the formation of hydroxyphenyl radicals (21). In this case, researchers were unable to detect the presence of an electron adduct due to rapid protonation of hydroxyphenyl radicals to yield phenoxyl radicals.

Primarily on the basis of the results of Koster and Asmus, we conclude that the transient spectra of the intermediate at 320 nm to be that of the HCB electron adduct which undergoes subsequent protonation to form cyclohexadienyl radicals and, ultimately, pentachlorobenzene.

In summary, as shown in Scheme 1, reactions in our surfactant system may occur either through direct electron reaction with HCB (Route 1) involving the generation of electron adducts and reduced forms of HCB or through hydroxyl radical reactions with surfactant molecules (Route 2) to produce reducing radicals that undergo electron transfer with HCB.

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