Volume Reduction of Nonaqueous Media Contaminated with a Highly Halogenated Model Compound Using Superoxide

Olha S. Furman, Amy L. Teel, and Richard J. Watts*

Department of Civil and Environmental Engineering, Washington State University, Pullman,
Washington 99164-2910

Highly halogenated organic compounds, which include polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) formed during the synthesis of pentachlorophenol and chlorophenoxy herbicides, are often found as contaminants in less toxic nonaqueous media, such as waste oil, oily sludges, or biosolids. Superoxide is highly reactive with halogenated compounds when both are dissolved in nonaqueous media; however, superoxide is most economically generated in water, where it is unreactive with most organic compounds. Superoxide reactivity was investigated in organic solvent−water systems as a basis for treating halogenated contaminants in less toxic nonaqueous media. Such a process could potentially render a contaminated oil or sludge nonhazardous, providing a mechanism for waste volume reduction. Increasing amounts of water added to acetone and dimethyl sulfoxide systems decreased the activity of superoxide in the solvent, but enough activity remained for effective treatment. Superoxide was then generated in the aqueous phase of two-phase water−organic solvent systems, and significant superoxide activity was achieved in the organic media with the addition of phase transfer catalysts (PTCs) to transfer superoxide into the nonaqueous phase. The results of this research demonstrate that superoxide, which can be generated in water electrochemically or through the catalytic decomposition of peroxygens, has the potential to be transferred to oils, sludges, and other less toxic nonaqueous media to destroy highly refractory contaminants such as PCBs, PCDDs, and other halogenated contaminants.

KEYWORDS: Agricultural waste management; PCDDs; PCBs; flame retardants; pesticide waste treatment; phase transfer catalysts; superoxide

INTRODUCTION

Many highly halogenated hydrophobic organic contaminants, such as higher polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polybrominated diphenyl ethers (PBDEs), are a significant threat to human health and the environment. For example, a historic public health and environmental threat has been PCDDs that are formed during the synthesis of the fungicide pentachlorophenol, the chlorophenoxy herbicides 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) and Silvex (2-(2,4,5-trichlorophenoxy)propionic acid), and other xenobiotics in which chlorophenols are used as a precursor (*1, 2*). In agricultural waste management, highly halogenated contaminants are sometimes found in waste oils, mineral oils, organic sludges, and other nonaqueous environments. For example, waste oils tainted with 2,4,5-T and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) were spread on roads and at horse corrals at Times Beach, MO, making it a major Superfund site (*3*). Another pathway resulting in agricultural exposure to halogenated organic contaminants is through the accidental or inadvertent disposal of contaminated oils or sludges. For example, transformer oil containing PCBs was admixed to the fat delivered to ten animal-feed producers, resulting

in the contamination of 450000 kg of animal feed (*4*). Similar exposures to PCDDs have also occurred when contaminated rice oil (*5*), citrus pulp (*6*), or choline chloride (*7*) was accidentally added to animal feed. Biosolids collected from wastewater treatment facilities serve as another source of contaminants; biosolids are used for land application to provide nutrients and improve soil properties but are often contaminated with halogenated organic compounds. For example, Ejarrat et al. (*8*) found that PBDE concentrations in biosolids ranged from 197 to 1185 μg/kg, and Kupper et al. (*9*) documented PCBs, PCDDs, PBDEs, and perfluorinated alkyl compounds in compost collected from 39 composting plants in Switzerland.

When trace concentrations of toxic halogenated contaminants are present in much less toxic oils or sludges, the entire system is considered a hazardous waste and must be managed under the Resource Conservation and Recovery Act (RCRA). One of the most common approaches to pollution prevention is volume reduction. If traces of halogenated contaminants can be destroyed within a large pool of less toxic oil or sludge, the entire material becomes less hazardous and may no longer be considered a RCRA hazardous waste; it could then have another use, such as fuel blending or land application. However, the destruction of highly halogenated contaminants in oils and other nonaqueous media represents a unique challenge. Nearly all species capable of

*Corresponding author. Phone: 509-335-3761. Fax: 509-335-7632. E-mail: rjwatts@wsu.edu.

Article

J. Agric. Food Chem., Vol. 58, No. 3, 2010   **1839**

destroying halogenated contaminants are reactive only in water (e.g., bacteria, hydroxyl radical, zero-valent iron) (*10*). However, the transient oxygen species superoxide ($O_2\cdot^-$) is highly reactive with oxidized halogenated contaminants in nonaqueous media, though it is unreactive with such contaminants in deionized water (*11*). Furthermore, because superoxide is a reductant and a nucleophile, it reacts with halogenated contaminants but not with hydrocarbon-based oils or sludges (*12*). Superoxide can be added directly to contaminated nonaqueous media as potassium superoxide along with a phase transfer catalyst (PTC) (*13*); however, such a process is expensive due to the high cost of potassium superoxide. Less expensive methods involve generating superoxide in water; e.g., through the catalyzed decomposition of peroxygens, such as catalyzed H_2O_2 propagations (CHP−modified Fenton's reagent) (*14*):

$$H_2O_2 + Fe^{2+} \rightarrow OH\cdot + OH^- + Fe^{3+} \qquad (1)$$

$$OH\cdot + H_2O_2 \rightarrow O_2\cdot^- + H_2O + H^+ \qquad (2)$$
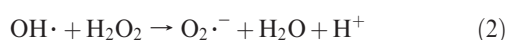
Superoxide can also be generated in water by electrochemical and photochemical processes (*12, 15−17*). However, if these more economical methods are used to generate superoxide in water, then the superoxide must be brought into contact with the contaminants in the nonaqueous phase.

The purpose of this research was to investigate the reactivity of superoxide in mixed aqueous−nonaqueous systems as a basis for the volume reduction of contaminated oils and sludges using the organic solvents acetone and dimethyl sulfoxide (DMSO) as models for nonaqueous systems. The use of aqueous superoxide solutions is necessary for economical superoxide treatment of contaminated oils and sludges, but the presence of water may decrease superoxide reactivity; therefore, the effect of adding water to superoxide−nonaqueous systems was first evaluated. If sufficient superoxide reactivity can be retained with representative addition of water [e.g., up to 10% water (v/v)], then such an approach may be viable. The second segment of this research focused on superoxide reactivity in the same two solvent systems as a basis for destroying highly halogenated contaminants by promoting the phase transfer of superoxide from the aqueous phase into the organic phase.

MATERIALS AND METHODS

Materials. Potassium superoxide (KO_2, 96.5%), polyethylene glycol-400 (PEG), and 18-crown-6 ether (99%) were purchased from Alfa Aesar (Ward Hill, MA) and used without modification. Hexachlorobenzene (HCB, 99%) and diethylenetriaminepentaacetic acid (DTPA, 97%) were purchased from Sigma-Aldrich (St. Louis, MO). Toluene (99.9%), acetone (99.7%), DMSO (99.9%), potassium hydroxide (87.9%), and sodium hydroxide (99.3%) were J. T. Baker Products (Phillipsburg, NJ). Doubly deionized water was purified to > 18 MΩ·cm using a Barnstead E-pure system.

Sodium hydroxide solutions were purified to remove transition metals by the addition of magnesium hydroxide (*18, 19*). The magnesium hydroxide−NaOH solution was stirred for 8 h, the floc that formed was allowed to settle, and the solution was passed through a 0.45 μm filter to remove the residual floc.

Model Compound. Hexachlorobenzene (HCB) was used as a model compound for the treatment of highly halogenated contaminants with superoxide ($k_{O_2\cdot^-} = 1 \times 10^3 \, M^{-1} \, s^{-1}$ in dimethylformamide) (*20−22*). HCB is a perchlorinated, highly oxidized contaminant that has chemodynamic properties similar to PCBs, PCDDs, PBDEs, and other highly halogenated contaminants. Furthermore, it has been used as a surrogate for 2,3,7,8-TCDD in environmental chemodynamic studies (*23*), because it is similarly hydrophobic and biorefractory but is significantly less toxic.

Effect of Water on Superoxide Reactivity in Model Nonaqueous Phases. The solvents acetone and DMSO were used as model nonaqueous

phases because they represent organic solvents that are miscible with water and thus have high potential for the addition of water to lower superoxide reactivity. Therefore, if superoxide reactivity can be maintained in these solvents when water is added, then even greater superoxide reactivity could be achieved in more hydrophobic oil-based systems in the presence of water. In addition, acetone and DMSO form separate nonaqueous phases when aqueous KO_2 is added, so that the phase transfer of superoxide from the aqueous to the nonaqueous phase could then be evaluated using the same model solvents.

KO_2 was dissolved in acetone and DMSO by suspending 0.6 g of KO_2 powder in 200 mL of each of the solvents followed by addition of 5.3 g of 18-crown-6 ether (*24*). The solution was mixed for 10 min; the remaining solid KO_2 was allowed to settle, and the liquid phase was decanted into reaction vessels, which were 20 mL borosilicate volatile organic analysis (VOA) vials capped with PTFE-lined septa. Hexachlorobenzene was then added to the solution followed by the addition of varying volumes of water. The total reaction volume was 20 mL and consisted of 75 mM crown ether, 30 mM KO_2, and 0.02 mM HCB, with a range of water concentrations: 0%, 2.5%, 5%, 10%, and 15% (v/v) for the acetone reactions and 0%, 5%, 10%, 15%, 20%, and 25% for the DMSO reactions. A set of reaction vials was quenched at 1 min intervals by adding 8 mL of water, and the entire vial contents were then extracted with 5 mL of toluene. The extracts were then analyzed for residual HCB by gas chromatography. All reactions were conducted in triplicate at 20 ± 2 °C, and triplicate control reactors were established in parallel without the addition of KO_2.

Superoxide Reactivity in Water−Solvent Two-Phase Systems. Two-phase reactions were conducted in triplicate 20 mL borosilicate VOA vial reactors. The two phases consisted of an aqueous phase of 5 mL of 3 M KO_2, 33 mM purified NaOH, and 1 mM DTPA (to inactivate transition metals) and a nonaqueous phase of 9 mL of organic solvent [acetone or DMSO, for a solvent proportion of 60% (v/v) spiked with 0.02 mM HCB]. Upon addition of the organic solvent, separation of the two phases was instantaneous due to the salting effect of the KO_2. Phase transfer catalysts (PTCs) (18-crown-6 ether or PEG-400) were added to a final concentration of 0.15 M and a final reaction volume of 15 mL. Control reactors contained additional solvent in place of the PTC; in addition, control reactors for the DMSO systems contained additional DMSO in place of the KO_2, because the KO_2−DMSO system resulted in HCB degradation even in the absence of PTCs. At selected time points, the entire reactor contents were extracted with 20 mL of toluene, and the extract was analyzed for HCB by gas chromatography.

The same procedure was repeated using 3 M KOH as a salting agent in place of KO_2. These reactions were run to differentiate the effect of KO_2 on HCB degradation in the organic phase from any effect that might be due to the KOH, because KO_2 in water generates KOH during disproportionation (*12, 25*).

Analysis. Toluene extracts were analyzed for HCB using a Hewlett-Packard 5890 gas chromatograph with a 0.53 mm (i.d.) × 60 m Equity 1 capillary column and electron capture detector (ECD). The injector temperature was 300 °C, the detector temperature was 325 °C, the initial oven temperature was 60 °C, the program rate was 30 °C min^{-1}, and the final temperature was 300 °C.

RESULTS AND DISCUSSION

Effect of Water on Superoxide Reactivity in Acetone and DMSO. Increasing volumes of deionized water were added to two organic solvent systems containing superoxide, and relative superoxide reactivity was measured using the probe compound HCB. These experiments provided fundamental information about potential superoxide reactivity in PCDD-containing nonaqueous phases when water is added as part of a superoxide−water solution. The effect of water addition on superoxide reactivity in crown ether−KO_2−acetone systems is shown in **Figure 1a**. The superoxide probe HCB degraded 98% in 3 min in the crown ether−KO_2−acetone system; however, HCB degradation rates decreased with increasing water concentrations. The presence of 2.5% (v/v) water in the system lowered the reactivity of superoxide, resulting in 30% HCB degradation after 5 min.
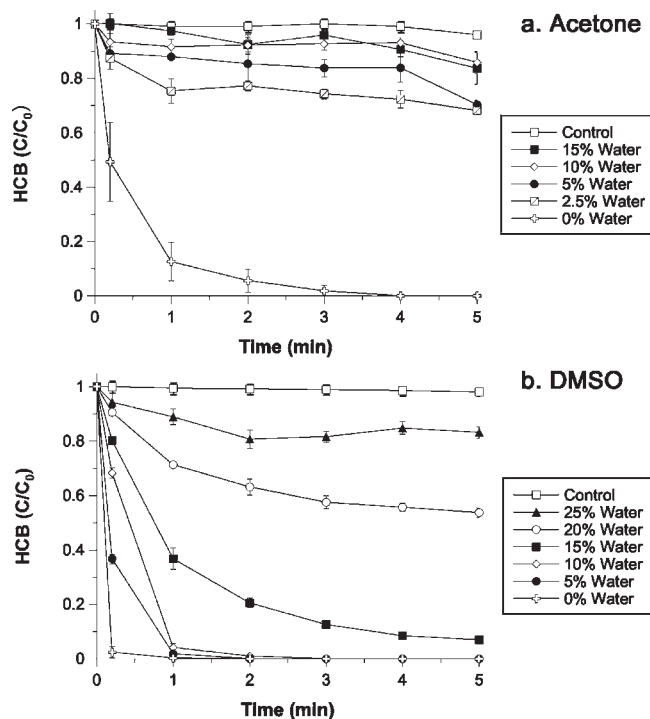
Figure 1. Effect of water addition on superoxide reactivity in (**a**) acetone/crown ether/KO_2 systems and (**b**) DMSO/crown ether/KO_2 systems (reaction conditions: 75 mM crown ether, 30 mM KO_2, and 0.02 mM HCB in acetone containing 0%−15% deionized water or DMSO containing 0%−25% deionized water). Error bars represent the standard error of the mean of three replicates.

In systems containing 10% and 15% water, HCB degradation was 12% after 5 min relative to the control system. The effect of adding water on the relative reactivity of superoxide in crown ether−KO_2−DMSO systems is shown in **Figure 1b**. The superoxide probe HCB degraded by 98% over 30 s in the crown ether−KO_2−DMSO system. As in the acetone systems, HCB degradation rates decreased with increasing water concentrations. The presence of 5% and 10% water in the DMSO systems lowered the reactivity of superoxide, resulting in 62% and 31% HCB degradation, respectively, after 30 s. In systems containing 15%, 20%, and 25% water, HCB degradation after 5 min was 90%, 40%, and 15%, respectively.

The results of **Figure 1** confirm that superoxide has different characteristics in the presence of water vs in pure organic media such as acetone or DMSO. In organic media, superoxide is long-lived (*12*) due to its solvation state, and its longevity makes it highly reactive. When superoxide is solvated by an organic molecule such as acetone, the electromotive force for a one-electron transfer (E°) ($O_2/O_2\cdot^{-}$) is −0.88 V, making superoxide highly reactive with a wide range of organic compounds including PCDDs (*26*). In contrast, four water molecules solvate superoxide in aqueous systems; because of the change in its solvation state, superoxide has an E° ($O_2/O_2\cdot^{-}$) of −0.19 V and is short-lived (half-life <1 s) because it undergoes rapid disproportionation (*12, 25−29*):

$$2O_2\cdot^{-} + H_2O \rightarrow HO_2^{-} + OH^{-} + O_2 \qquad (3)$$
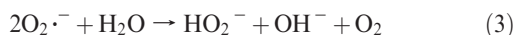
As water was added to the acetone and DMSO systems (**Figure 1**), the superoxide solvation shells that were originally filled with the organic solvent were likely partially replaced with water, resulting in a shorter lifetime and lower reactivity with HCB.

While addition of water to superoxide systems lowered the reactivity of superoxide, a measurable degree of superoxide reactivity

remained with water contents up to 15% in acetone and 25% in DMSO. Therefore, water-based superoxide generation will not likely negate superoxide reactivity in the treatment of contaminated oils and sludges. Economical approaches to generating superoxide, such as the MnO_2-catalyzed decomposition of hydrogen peroxide (*30*), would inherently add water to the nonaqueous system that is being treated (e.g., a drum of waste oil tainted with PCDDs). The results of **Figure 1** demonstrate that although adding small amounts of MnO_2−hydrogen peroxide in water to a contaminated nonaqueous phase would slow the reaction rate of superoxide with the contaminant, the process could still provide effective treatment.

Superoxide Reactivity in Heterogeneous Organic Solvent−Water Systems. The second phase of this research focused on promoting the phase transfer of superoxide generated in the aqueous phase to nonaqueous phase oils and sludges. In order to compare the results of the two parts of the study, the same two solvents, acetone and DMSO, were used. Although acetone and DMSO are miscible in water, nearly complete phase separation of water−acetone and water−DMSO systems containing >10% (v/v) water was accomplished by adding 3 M aqueous KO_2 (**Figure 2a**). KO_2 behaved as a salting agent in organic solvent−water mixtures and promoted phase separation between water and the organic solvent (*31*). To confirm that the phase separation was due to a salting effect, the procedures were repeated using KOH in place of KO_2 (**Figure 2b**). Equal volumes of the organic phases separated in both water−KO_2−acetone and water-−KOH−acetone systems. In both acetone and DMSO systems, >99% of the organic solvent was recovered as a phase separate from the water. These results demonstrate that acetone and DMSO could be used to create two-phase water−organic solvent systems that could be directly compared to the systems used in **Figure 1**.

Using these two-phase systems, the potential for superoxide added to the aqueous phase to migrate to the organic solvent phase was evaluated as a basis for the treatment of PCDDs in nonaqueous organic phases. When added to these systems, the superoxide probe HCB immediately partitioned into the organic phase. The degradation of HCB in the organic phase of water−KO_2−acetone and water−KO_2−DMSO systems when superoxide was added to the aqueous phase is shown in **Figure 3**. No measurable degradation of HCB occurred in the two-phase water−KO_2−acetone system; however, 73% HCB degradation occurred within 12.5 min in the two-phase water−KO_2−DMSO system. The results of **Figure 3** suggest that superoxide did not diffuse through the interface of the two-phase water−acetone system but did cross the water−DMSO phase boundary in the water−DMSO system. Acetone is less polar than DMSO and may have higher interfacial tension when in contact with water, which may minimize superoxide transfer from the aqueous phase into acetone (*13*).

The interface formed between two distinct liquid phases often limits reactivity in the organic phase if the reactive species is generated in the aqueous phase; therefore, phase transfer catalysts (PTCs) are often used to enhance the transfer of a nucleophile from the aqueous phase into the organic phase (*13, 32−34*).

The PTCs 18-crown-6 ether and PEG were compared for their abilities to transfer superoxide from the aqueous phase into the overlying organic phase in two-phase water−KO_2−acetone and water−KO_2−DMSO systems. PEG was chosen as a PTC because it complexes K^{+} in a manner similar to crown ethers (*35, 36*) but is less expensive and more environmentally benign (*37*); the crown ether served as a benchmark PTC because it has been used extensively in previous studies (*13, 34*). The loss of HCB in two-phase water−crown ether−KO_2−acetone systems and water−PEG−KO_2−acetone systems is shown in **Figure 4a**.

Article
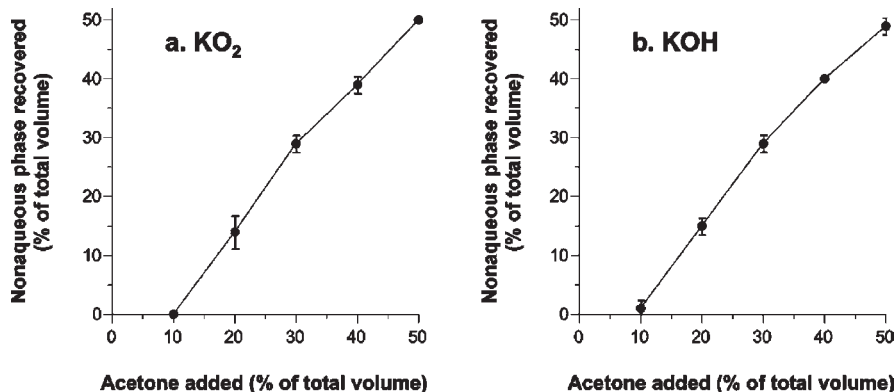
J. Agric. Food Chem., Vol. 58, No. 3, 2010 **1841**

Figure 2. Separation of the acetone phase as a function of the initial acetone volume in acetone/water systems containing (**a**) 3 M KO_2 or (**b**) 3 M KOH [reaction conditions: 25 mL of 3 M KO_2 or 3 M KOH added to 25 mL of acetone/water mixtures containing 20%−100% acetone (v/v)].
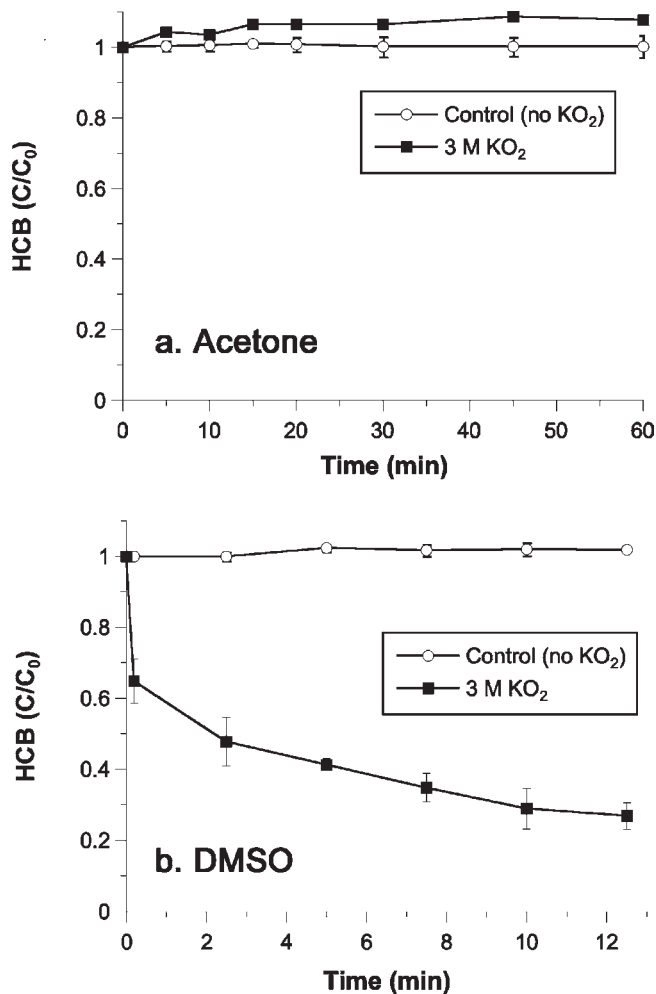

Figure 3. Superoxide reactivity in the organic phase of two-phase systems with 3 M KO_2 added to the aqueous phase of systems containing (**a**) acetone or (**b**) DMSO (reaction conditions: the 5 mL aqueous phase consisted of 3 M KO_2, 33 mM NaOH, and 1 mM DTPA; the 10 mL organic phase consisted of acetone or DMSO containing 0.02 mM HCB). Error bars represent the standard error of the mean of three replicates.

The superoxide probe HCB degraded 63% over 45 min in the acetone phase using both the PEG and the crown ether. These data demonstrate that both PTCs promoted a similar increase in superoxide activity in acetone compared to KO_2 alone by promoting the transfer of the superoxide from the aqueous phase to the organic phase.
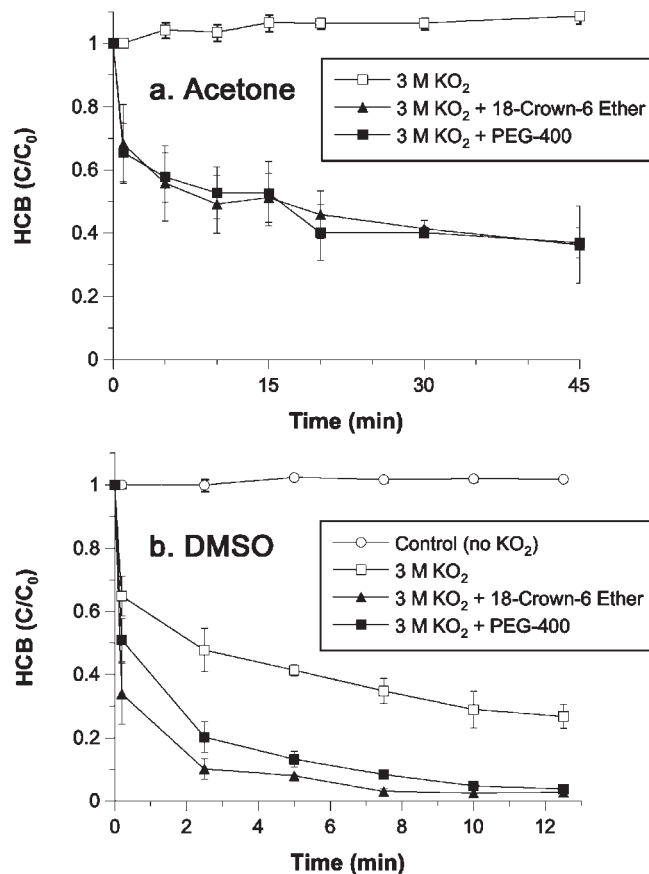

Figure 4. Superoxide reactivity in the organic phase of (**a**) aqueous KO_2−acetone systems and (**b**) aqueous KO_2−DMSO systems containing the phase transfer catalyst 18-crown-6 ether and PEG (reaction conditions: the 5 mL aqueous phase contained 3 M KO_2, 33 mM NaOH, and 1 mM DTPA; the 9 mL acetone or DMSO phase contained 0.02 mM HCB; 0.9 mL of 0.15 M crown ether or 0.15 M PEG was then added for a final volume of 15 mL in the reactors; control reactors for acetone contained additional acetone in place of the phase transfer catalyst, and control reactors for DMSO contained additional DMSO in place of the phase transfer catalyst and in place of the KO_2). Error bars represent the standard error of the mean of three replicates.

The effect of PTCs on superoxide activity in the two-phase water−KO_2−DMSO systems is shown in **Figure 4b**. The presence of both the crown ether and the PEG significantly increased degradation of the superoxide probe HCB in both of the two-phase water−PTC−KO_2−DMSO systems, compared to the control
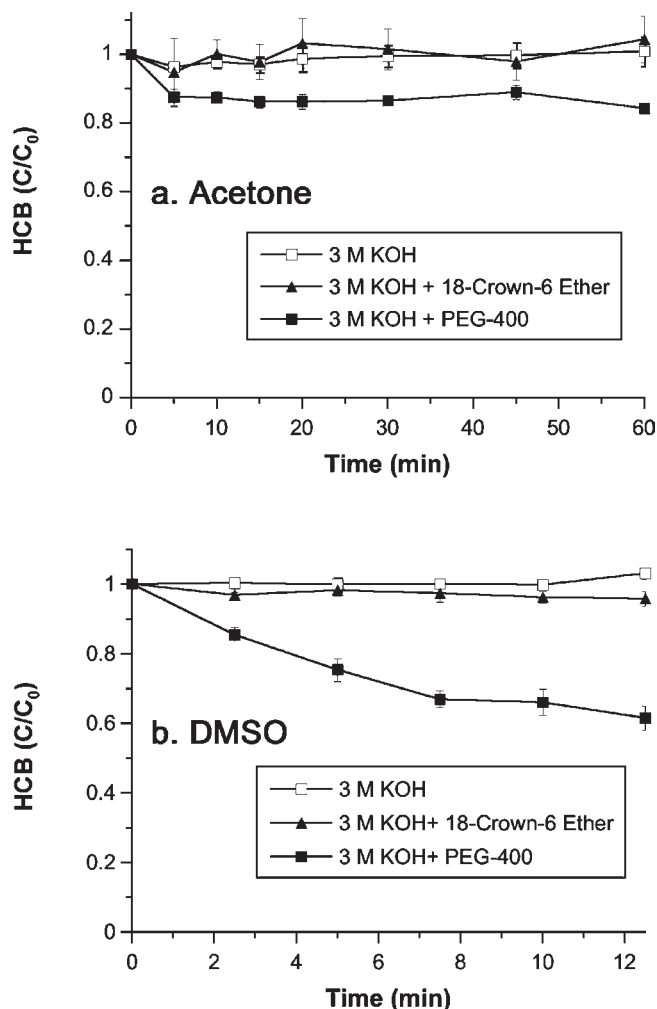
Figure 5. Superoxide reactivity in the organic phase of (**a**) aqueous KOH−acetone systems and (**b**) aqueous KOH−DMSO systems containing the phase transfer catalyst 18-crown-6 ether and PEG (reaction conditions: the 5 mL aqueous phase contained 3 M KOH, 33 mM NaOH, and 1 mM DTPA; the 9 mL acetone or DMSO phase contained 0.02 mM HCB; 0.9 mL of 0.15 M crown ether or 0.15 M PEG was then added for a final volume of 15 mL in the reactors; control reactors contained additional acetone in place of the phase transfer catalyst). Error bars represent the standard error of the mean of three replicates.

systems in which no PTC was added. Addition of the crown ether or the PEG resulted in 97% or 96% HCB degradation, respectively, over 12.5 min in the water−PTC−KO$_2$−DMSO systems.

The results shown in **Figure 4** demonstrate that the two PTCs improved the transport of superoxide across the phase boundary in both of the two-phase water−KO$_2$−organic solvent systems, allowing superoxide to react with HCB in the organic phase. Furthermore, PEG proved to be approximately as effective as the crown ether in these systems. These results also confirm that the minimal superoxide activity in the two-phase systems shown in **Figure 3** was due to a negligible mass of superoxide crossing the phase boundary.

To evaluate whether other reaction pathways in the water−PTC−KO$_2$−organic solvent systems are occurring, the experiments were repeated with the use of KOH in place of KO$_2$. A possible reaction pathway in the water−PTC−KO$_2$−solvent systems is the decomposition of KO$_2$ to KOH in the aqueous phase (eq **3**), phase transfer of KOH into the organic phase, and nucleophilic attack by hydroxide. HCB degradation in water−PTC−KOH−acetone systems is shown in **Figure 5a**. HCB

degraded 16% over 60 min in the two-phase water−PEG−KOH−acetone system; however, there was no significant HCB degradation in the two-phase water−crown−KOH−acetone system. These results suggest that hydroxide does not directly attack HCB in the organic phase. A possible pathway of HCB degradation in the two-phase water−PEG−KOH−acetone system is a nucleophilic attack by PEGO$^-$ (PEG in the presence of NaOH) (*35*, *36*, *38*). PEGO$^-$ could be partially responsible for HCB degradation in the parallel systems containing PEG and superoxide (**Figure 4a**). However, the 62% HCB degradation in the acetone phase of the water−PEG−KO$_2$−acetone systems was significantly higher than in the water−PEG−KOH−acetone systems, which indicates that superoxide is responsible for the majority of the HCB degradation in the two-phase water−PEG−KO$_2$−acetone systems. In contrast, there was no significant degradation of HCB in the two-phase water−crown ether−KOH−acetone systems (**Figure 5a**).

HCB degradation in the two-phase water−PTC−KOH−DMSO systems is shown in **Figure 5b**. Both of the two-phase systems behaved similarly to the parallel acetone systems (**Figure 5a**). HCB degradation was 39% over 12.5 min in the two-phase water−PEG−KOH−DMSO systems; these results suggest that PEGO$^-$ degraded HCB, similar to the degradation that occurred in the parallel acetone system. However, degradation of HCB was significantly more rapid in the parallel system containing superoxide (**Figure 4b**). In the two-phase water−crown ether−KOH−DMSO system, minimal HCB degradation occurred. The results of **Figures 4** and **5** demonstrate that superoxide was the predominant reactive species in the degradation of HCB in the two-phase water−organic solvent systems studied.

The results of the first part of this research demonstrate that superoxide reactivity in model nonaqueous systems was lowered by the addition of water, but sufficient reactivity was maintained to achieve destruction of the model halogenated contaminant HCB. In the second segment of the research, superoxide was generated in the aqueous phase of two-phase water−organic solvent systems, and there was minimal flux of superoxide across the phase boundary into the organic solvent. However, when a PTC was added to the system, superoxide was transferred from the aqueous phase, resulting in superoxide reactivity and associated HCB destruction in the nonaqueous phase. Superoxide can be generated in water electrochemically, photochemically, or through the metal oxide-catalyzed decomposition of hydrogen peroxide. If PTCs are used in conjunction with superoxide generation in the aqueous phase, halogenated contaminants in oils, oily sludges, biosolids, and other contaminated nonaqueous media may potentially be destroyed, providing volume reduction of the contaminated media. Furthermore, the environmentally benign PTC PEG was as effective as the crown ether in promoting superoxide phase transfer across the water−organic solvent phase boundary. The results of this research provide proof of concept that superoxide generated in the aqueous phase can be transferred to treat halogenated contaminants in a nonaqueous phase. Such a process could potentially render the nonaqueous phase nonhazardous, allowing it to be used for fuel blending, land application, or other beneficial purposes.

ABBREVIATIONS USED

CHP, catalyzed H$_2$O$_2$ propagations−modified Fenton's reagent; DMSO, dimethyl sulfoxide; DTPA, diethylenetriaminepentaacetic acid; HCB, hexachlorobenzene; PBDE, polybrominated diphenyl ethers; PCDD, polychlorinated dibenzo-*p*-dioxins; PEG, polyethylene glycol-400; PTC, phase transfer catalyst; 2,4,5-T, 2,4,5-trichlorophenoxyacetic acid.

Article

J. Agric. Food Chem., Vol. 58, No. 3, 2010 **1843**

LITERATURE CITED

(1) Rappe, C.; Choudhary, G.; Keith, L. H. *Chlorinated dioxins and dibenzofurans in perspective*; Lewis Publishers: Chelsea, MI, 1986.

(2) Keith, L. H.; Rappe, C.; Choudhary, G. *Chlorinated dioxins and dibenzofurans in the total environment II*; Butterworth-Heinemann: Stoneham, MA, 1984.

(3) Watts, R. J. *Hazardous wastes: sources pathways receptors*; John Wiley & Sons: New York, 1998.

(4) Van Larebeke, N.; Hens, L.; Schepens, P.; Covaci, A.; Baeyens, J.; Everaert, K.; Bernheim, J. L.; Vlietinck, R.; De Poorter, G. The Belgian PCB and dioxin incident of January−June 1999: exposure data and potential impact on health. *Environ. Health Perspect.* **2001**, *109*, 265–273.

(5) Yen, Y. Y.; Lan, S. L.; Ko, Y. C.; Chen, C. J. Follow-up study of reproductive hazards of multiparous women consuming PCB contaminated rice oil in Taiwan. *Bull. Environ. Contam. Toxicol.* **1989**, *43*, 647–655.

(6) Malisch, R. Increase of the PCDD/F-contamination of milk and butter in countries of the European Union by use of contaminated citrus pulp. *Chemosphere* **2000**, *40*, 1041–1053.

(7) Rivera, J.; Llerena, J. J.; Abad, E.; Caixach, J. A new episode of PCDD/PCDFs feed contamination in Europe: the choline chloride. *Organohalogen Compd.* **2001**, *51*, 283–286.

(8) Ejarrat, E.; Marsh, G.; Labandeira, A.; Barcelo, D. Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils. *Chemosphere* **2008**, *71*, 1079–1086.

(9) Kupper, T.; Braendli, R.; Pohl, M.; Bucheli, T.; Slooten, K. B. V. Organic pollutants in compost and digestate of Switzerland. *Agrarforschung* **2008**, *15*, 270–275.

(10) Larson, R. A.; Weber, E. J. *Reaction mechanisms in environmental organic chemistry*; Lewis Publishers: New York, 1994.

(11) Halliwell, B.; Gutteridge, J. M. C. *Free radicals in biology and medicine*; Clarendon Press: Oxford, 1985.

(12) Afanas'ev, I. B. *Superoxide ion: chemistry and biological implication*; CRC Press: Boca Raton, FL, 1989; Vol. 1, p 279.

(13) Weber, W. P.; Gokel, G. W. *Phase transfer catalysis in organic synthesis*; Springer-Verlag: New York, 1977.

(14) Watts, R. J.; Teel, A. L. Chemistry of modified Fenton's reagent (catalyzed H_2O_2 propagations-CHP) for in situ soil and groundwater remediation. *J. Environ. Eng.* **2005**, *131*, 612–622.

(15) Ono, Y.; Matsumura, T.; Kitajima, N.; Fukuzumi, S.-I. Formation of superoxide ion during the decomposition of hydrogen peroxide on supported metals. *J. Phys. Chem.* **1977**, *81*, 1307–1311.

(16) Anpo, M.; Che, M.; Fubini, B.; Garrone, E.; Giamello, E.; Paganini, M. C. Generation of superoxide ions at oxide surfaces. *Top. Catal.* **1999**, *8*, 189–198.

(17) Sawyer, D. T.; Martell, A. E. *Industrial environmental chemistry. Waste minimization in industrial processes and remediation of hazardous waste*; Plenum Press: New York, 1992.

(18) Monig, J.; Bahnemann, D.; Asmus, K.-D. One electron reduction of CCl_4 in oxygenated aqueous solutions: a CCl_3O_2-free radical mediated formation of Cl^- and CO_2. *Chem.-Biol. Interact.* **1983**, *47*, 15–27.

(19) Smith, B. A.; Teel, A. L.; Watts, R. J. Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems. *Environ. Sci. Technol.* **2004**, *38*, 5465–5469.

(20) Lee, J. L.; Yao, C. P.; Wang, Y. Y.; Wan, C. C. Electrochemical decomposition of chlorinated benzenes in dimethylformamide solvent. *Environ. Sci. Technol.* **1992**, *26*, 553–556.

(21) Sugimoto, H.; Matsumoto, S.; Sawyer, D. T. Oxygenation of polychloro aromatic hydrocarbons by superoxide ion in aprotic media. *J. Am. Chem. Soc.* **1987**, *109*, 8081–8082.

(22) Sugimoto, H.; Matsumoto, S.; Sawyer, D. T. Degradation and dehalogenation of polychlorobiphenyls and halogenated aromatic molecules by superoxide ion and by electrolytic reduction. *Environ. Sci. Technol.* **1988**, *22*, 1182–1186.

(23) Arthur, M. F.; Frea, J. I. Microbial activity in soils contaminated with 2,3,7,8-TCDD. *Environ. Toxicol. Chem.* **1988**, *7*, 5–13.

(24) Niehaus, W. G. A proposed role of superoxide anion as a biological nucleophile in the deesterification of phospholipids. *Bioorg. Chem.* **1978**, *7*, 77–84.

(25) Bielski, B. H. J.; Allen, O. Mechanisms of the disproportionation of superoxide radicals. *J. Phys. Chem.* **1977**, *81*, 1048–1050.

(26) Roberts, J. L.; Calderwood, T. S.; Sawyer, D. T. Oxygenation by superoxide ion of CCl_4, $FCCl_3$, $HCCl_3$, p,p′-DDT, and related trichloromethyl substrates ($RCCl_3$) in aprotic solvents. *J. Am. Chem. Soc.* **1983**, *105*, 7691–7696.

(27) Andrieux, C. P.; Hapiot, P.; Saveant, J.-M. Mechanism of superoxide ion disproportionation in aprotic solvents. *J. Am. Chem. Soc.* **1987**, *109*, 3768–3775.

(28) Che, Y.; Tsushima, M.; Matsumato, F.; Okajima, T.; Tokuda, K.; Ohsaka, T. Water-induced disproportionation of superoxide ion in aprotic solvents. *J. Phys. Chem.* **1996**, *100*, 20134–20137.

(29) Chin, D.-H.; Chiericato, G.; Nanni, E. J.; Sawyer, D. T. Proton-induced disproportionation of superoxide ion in aprotic media. *J. Am. Chem. Soc.* **1982**, *104*, 1296–1299.

(30) Furman, O.; Laine, D. F.; Blumenfeld, A.; Teel, A. L.; Shimizu, K.; Cheng, I. F.; Watts, R. J. Enhanced reactivity of superoxide in water-solid matrices. *Environ. Sci. Technol.* **2009**, *43*, 1528–1533.

(31) Matkovich, C. E.; Christian, G. D. Salting-out of acetone from water-basis of a new solvent extraction system. *Anal. Chem.* **1973**, *45*, 1915–1921.

(32) Herriott, A. W.; Picker, D. Phase transfer catalysis. An evaluation of catalysis. *J. Am. Chem. Soc.* **1975**, *97*, 2345–2349.

(33) Naik, S. D.; Doraiswamy, L. K. Phase transfer catalysis: chemistry and engineering. *AIChE J.* **1998**, *44*, 612–646.

(34) Starks, C. M. Modern perspectives on the mechanisms of phase-transfer catalysis. In *Phase-transfer catalysis mechanisms*; Halpern, M. E., Ed.; ACS: Washington, DC, 1997.

(35) Brunelle, D. J.; Mendiratta, A. K.; Singleton, D. A. Reaction/removal of polychlorinated biphenyls from transformer oil: treatment of contaminated oil with poly(ethylene glycol)/KOH. *Environ. Sci. Technol.* **1985**, *19*, 740–746.

(36) Brunelle, D. J.; Singleton, D. A. Destruction/removal of polychlorinated biphenyls from non-polar media. Reaction of PCB with poly(ethylene glycol)/KOH. *Chemosphere* **1983**, *12*, 183–186.

(37) Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. Polyethylene glycol and solutions of polyethylene glycol as green reaction media. *Green Chem.* **2005**, *7*, 64–82.

(38) Pytlewski, L. L.; Krevitz, K.; Smith, A. B. Composition for decomposing halogenated organic compounds. U.S. Patent 4471143, 1982.