

# Hypochlorous Acid-Activated Carbon: An Oxidizing Agent Capable of Producing Hydroxylated Polychlorinated Biphenyls

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Granular activated carbon (GAC), in the presence of dilute aqueous hypochlorite solutions typical of those used in water treatment, was converted to a reagent capable of carrying out free-radical coupling reactions and other oxidations of dilute aqueous solutions of phenols. The products included biphenyls with chlorine and hydroxyl substitution (hydroxylated polychlorinated biphenyls). For example, 2,4-dichlorophenol, a common constituent of wastewaters and also natural waters treated with hypochlorite, was converted to 3,5,5'-trichloro-2,4'-dihydroxybiphenyl and several related compounds in significant amounts. It is possible that these products pose more of a health hazard than either the starting phenols or the unhydroxylated polychlorinated biphenyl derivatives.

## Introduction

Activated carbon, in powdered and granular forms (PAC and GAC, respectively) is widely used in drinking water and wastewater treatment for the removal of hydrophobic organic compounds. In use, activated carbon frequently contacts disinfectants, such as hypochlorous acid (HOCl,  $pK_a$  7.5) in equilibrium with its conjugate base, hypochlorite ( $OCl^-$ ), often in a prechlorination or backwashing step.

Activated carbon is known to react with many types of oxidizing agents (including HOCl, which is quantitatively reduced to chloride ion). During such reactions, carboxyl, hydroxyl, and other oxygenated functional groups accumulate on the activated carbon surface (1). The mechanisms of these redox reactions are not well understood; however, they may involve one-electron pathways, since the existence of free radicals in carbons has been established by several techniques. Using electron spin resonance (ESR) and indirect chemical methods, Donnet and Henrich (2) have estimated that about 1 to 9% of the carbon atoms on carbon black surfaces are free radicals.

Oxidation of organic compounds at activated carbon surfaces has occasionally been noted; for example, partial oxidative conversion of *n*-butyl thiol to butyl disul-

fide has been noted (3). During chlorination of drinking water or wastewater, much of the added HOCl is destroyed by oxidative reactions with dissolved organic molecules. Trihalomethanes, other chlorinated organic compounds, and oxidation products are known to be formed. McCreary et al. (4) showed that phenolic acids, which readily react with HOCl in dilute aqueous solutions, also react when adsorbed on GAC. However, in addition to the expected substitution products (chlorinated phenolic acids), compounds with introduced hydroxyl groups, quinones, and decarboxylation products were observed. We report that a different type of oxidation, dimer formation, also occurs when phenols are treated with HOCl in the presence of GAC.

## Materials and Methods

HOCl solutions were prepared by passing high-purity chlorine gas ( $Cl_2$ ) into distilled-deionized water made weakly alkaline with sodium hydroxide (NaOH) and buffered to pH 6 with 0.001 M phosphate salts. Aqueous solutions of the phenolic compound ( $1 \times 10^{-5}$  –  $5 \times 10^{-4}$  M) and HOCl ( $2 \times 10^{-5}$  –  $1 \times 10^{-4}$  M) were pumped separately through a  $1 \times 8$  cm column of virgin F-400 GAC (Calgon, Pittsburgh, PA) at 10 mL/min. In other experiments, HOCl was pumped first and then phenolic compound was applied (5). The GAC was removed, centrifuged, and extracted in a Soxhlet apparatus with 1:20 volume/volume (v/v) methanol: methylene chloride for 24 hr. The extract was dried over sodium sulfate and concentrated to approximately 1 mL in a Kuderna-Danish apparatus; then a 2- $\mu$ L aliquot was

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injected into a Hewlett-Packard 5985 gas chromatography/mass spectrometry (GC-MS) system with a DB-1 fused silica capillary column. In some cases, concentrates were methylated with diazomethane generated from Diazald (Aldrich, Milwaukee, WI). Compounds were identified by comparing their mass spectra with those reported in standard reference collections, those from reference compounds of known structure, or by comparison with or extrapolation from literature data (6-8). Biological activity of the HOCl-GAC-2,4-dichlorophenol reaction mixture was determined by using short-term microbiological assays for acute toxicity (9) and for mutagenicity (10,11).

## Results and Discussion

HOCl and 2,4-dichlorophenol reacted in aqueous solution to give 2,4,6-trichlorophenol. When they were allowed to react in the presence of GAC, however, many additional products were formed. Compounds tentatively identified from such chlorination reactions are listed in Table 1; a corresponding gas chromatogram of a Soxhlet extract of the GAC (experiment I in Table 1) is shown in Figure 1.

One type of product formed only in the presence of GAC was a group of chlorinated and/or hydroxylated derivatives of benzoquinone (compounds 1,2,3, and 8 in Table 1). Chlorinated and hydroxylated benzoic acids (compounds 12 and 17) were also identified in the extract. These compounds appear to be derived by carboxylation of the phenol ring system at the GAC surface; similar compounds have been observed in previous studies of phenolic compound-GAC-disinfectant reactions (5,12).

Another type of product was a group of chlorohydroxybiphenyls (hydroxylated polychlorinated biphenyls) (compounds 25-27,29,30). The mass spectra of compounds 25-27 were almost identical. Their fragmentation pattern was consistent with their formulation as trichlorodihydroxybiphenyls; it was similar to that of authentic trichloromonohydroxybiphenyl (7). GC-MS analysis of a methylated extract revealed three corresponding trichloromethoxybiphenyls. In one case (the major product), the mass spectroscopic fragmentation pattern allowed a clear structural assignment: 3,5,5'-trichloro-2,4'-dimethoxybiphenyl.

The mass spectra of compounds 29 and 30 (Table 1) showed characteristic fragments for tetrachlorodihydroxybiphenyls (7). Trichloro dimers were formed in approximately 21% yield; tetrachloro dimers, 1%. After methylation, compound 29 was converted to a dimethoxy derivative, whose mass spectrum was consistent with 2,2'-dimethoxy-3,3',5,5'-tetrachlorobiphenyl (6,8). Peaks 24 and 28 have apparent molecular ions (268 and 302), chlorine isotope ratios, and fragmentation characteristics suggestive of hydroxylated and chlorinated derivatives of dibenzodioxins or dibenzofurans,  $C_{12}H_6O_3Cl_2$  and  $C_{12}H_5O_3Cl_3$ , respectively. Because of a lack of suitable standards or reference spectra for such material, we cannot confirm that these molecules are

being formed. The possibility of such reactions, however, is mechanistically reasonable and indicates that further study would be desirable.

A concentrated extract (approximately 45 mg dissolved in 500  $\mu$ L of dimethyl sulfoxide) of the HOCl-2,4-dichlorophenol reaction mixture proved to be too toxic to determine mutagenicity to two *Salmonella typhimurium* strains, a frameshift mutant (TA 98), and a base-pair substitution mutant (TA 100). Destruction activity was apparent at levels of approximately 450  $\mu$ g reaction mixture/plate in a standard plate incorporation test (without addition of mammalian S9 activating enzymes). *S. typhimurium* strain SV 50 was more sensitive to the reaction mixture; mutagenic activity, expressed as forward mutations per survivor, was apparent at approximately 90  $\mu$ g mixture/plate followed immediately by destruction.

Yeast cells, however, did not show high sensitivity. When 4.5 mg of the concentrate was added to 25 mL of a *Saccharomyces cerevisiae* suspension, growth was not inhibited; in fact, it was slightly stimulated.

The HOCl dose (8-10 mg/L; 0.14-0.17 mM) used in the previous experiments is somewhat higher than that normally encountered in drinking water treatment. A separate experiment at a considerably lower and more typical (1.5 mg/L) dose, however, showed that although fewer compounds were formed, the same hydroxylated PCB dimers were produced. A similar product mixture was also obtained when the GAC column was first treated with HOCl, washed with several bed volumes of deionized water, and then treated with 2,4-dichlorophenol solution. A blank experiment without added HOCl showed that the GAC itself was incapable of promoting the reaction. The latter results indicate that the oxidizing species formed by HOCl on the GAC surface are stable for at least a short time (in some cases up to 4-5 days) and remain capable of carrying out dimerization reactions even in the absence of HOCl.

Dimeric products were also formed in experiments with 4-chlorophenol and phenol. In the former case, a mixture of chlorinated dimers (about 20%) and trimers (about 25%) were the principal products. In addition to bi- and triphenyls, hydroxylated and chlorinated diphenyl and triphenyl ethers (products of C-O coupling) were tentatively identified. In the case of phenol, the biphenyl dimers included some with and some without chlorine. In this instance, also, a C-O coupling product (4-hydroxydiphenyl ether) was present.

The formation of hydroxylated PCBs can be explained by one-electron phenol coupling mechanisms (13). Reactive free radicals on the carbon surface, produced by its oxidation with chlorine, presumably interact with 2,4-dichlorophenol to generate 2,4-dichlorophenoxy radicals by hydrogen abstraction (14). Trichlorodihydroxybiphenyls may be formed by C-C coupling of a 2,4-dichlorophenol molecule and a 2,4-dichlorophenoxy radical, with displacement of a chlorine atom (15). Tetrachloro analogs would be produced if the C-C coupling occurred at unsubstituted ring positions.

If prechlorination is used in water treatment in com-

Table 1. Reaction products from HOCl-2,4-dichlorophenol-GAC reactions.

Compound no.	Compound	MW	Experiment			
			I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	IV <sup>d</sup>
1	Chloro- <i>p</i> -benzoquinone <sup>e</sup>	142	+ <sup>f</sup>			
2	Chloro- <i>o</i> -benzoquinone <sup>e</sup>	142	+			
3	Chlorohydroxy- <i>p</i> -benzoquinone <sup>e</sup>	158	+			
4	2,4-Dichlorophenol <sup>e</sup>	162	+	+	+	+
5	Unknown <sup>h</sup>	176	+			
6	Unknown <sup>h</sup>	198	+			
7	2,4,6-Trichlorophenol <sup>e</sup>	196	+	+	+	
8	Chloromethoxy- <i>p</i> -benzoquinone <sup>e</sup>	172	+			
9	Unknown <sup>h</sup>	194	+			
10	Unknown <sup>h</sup>	220	+	+	+	+
11	S <sub>6</sub> <sup>i</sup>	192	+			
12	Methyl 2-hydroxy-3,5-dichlorobenzoate <sup>e</sup>	220	+	+	+	+
13	Unknown <sup>h</sup>	256	+			
14	Unknown <sup>h</sup>	270	+			
15	Unknown <sup>h</sup>	248	+	+		
16	S <sub>8</sub> <sup>i</sup>	224	+			
17	Methyl trichlorohydroxybenzoate <sup>e</sup>	254	+			
18	Unknown <sup>h</sup>	244	+			
19	Unknown <sup>h</sup>	280	+			
20	Unknown <sup>h</sup>	258	+	+	+	
21	Unknown <sup>h</sup>	290	+			
22	Unknown <sup>h</sup>	314	+			
23	S <sub>8</sub> <sup>i</sup>	256	+	+	+	
24	Unknown	268	+	+	+	+
25	Trichlorodihydroxybiphenyl <sup>g</sup>	288	+	+	+	+
26	Trichlorodihydroxybiphenyl <sup>g</sup>	288	+	+	+	+
27	3,5,5'-Trichloro-2,4'-dihydroxybiphenyl <sup>e</sup>	288	+	+	+	+
28	Unknown <sup>h</sup>	302	+			
29	3,3',5,5'-Tetrachloro-2,2'-dihydroxybiphenyl <sup>e</sup>	322	+	+	+	+
30	Tetrachlorodihydroxybiphenyl <sup>g</sup>	322	+	+	+	+
31	Unknown <sup>h</sup>	298	+			

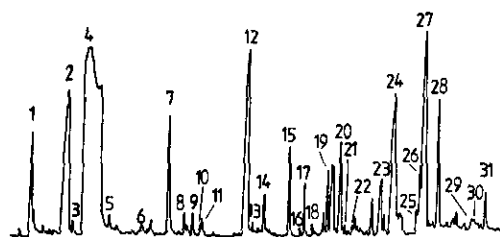
<sup>a</sup> Preadsorbed 2,4-dichlorophenol reacted with 10 mg/L HOCl as Cl<sub>2</sub>.<sup>b</sup> Preadsorbed 2,4-dichlorophenol reacted with 1.5 mg/L HOCl as Cl<sub>2</sub>.<sup>c</sup> Preadsorbed 2,4-dichlorophenol reacted with 1.5 mg/L HOCl as Cl<sub>2</sub> in the presence of peat fulvic acid.<sup>d</sup> 2,4-Dichlorophenol reacted with chlorine-preoxidized F 400 GAC.<sup>e</sup> Confirmed identification.<sup>f</sup> Compound present.<sup>g</sup> Tentative identification.<sup>h</sup> Chloro derivatives.<sup>i</sup> Impurity in water.

FIGURE 1. Gas chromatographic trace (detector: mass spectrometer total ionization current) for 2,4-dichlorophenol-GAC-HOCl reaction.

bination with GAC adsorption, chlorine may contact the GAC, and hydroxylated polychlorinated biphenyls may be formed under these drinking water treatment conditions. These compounds are *in vivo* metabolites of polychlorinated biphenyls, and their acute toxicity can be higher than that of their parent compounds (16). In addition, some of these products are not very well ad-

sorbed on GAC and can be displaced in the effluent by more strongly adsorbed materials (17). Therefore, processes that result in chlorine contacting GAC containing adsorbed organic compounds may need to be re-evaluated.

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## REFERENCES

1. Snoeyink, V. S., and Weber, Jr., W. J. Surface functional groups on carbon and silica. In: *Progress in Surface and Membrane Science*, Vol. 5 (J. F. Danielli, Ed.), Academic Press, New York, 1972, pp. 63-119.
2. Donnet, J. G., and Henrich, G. Influence de la nature du noir de carbone sur son caractere radicalaire. *Compt. Rend. Acad. Sci., Paris* 249: 97 (1959).
3. Ishizaki, C., and Cookson J. T., Jr. Influence of surface oxides on adsorption and catalysis with activated carbon. In: *Chemistry of Water Supply and Distribution* (A. J. Rubin, Ed.), Ann Arbor Science Publications, Ann Arbor, MI, 1974, pp. 201-231.
4. McCreary, J. J., Snoeyink, V. L., and Larson R. A. A comparison

- of the reaction of aqueous free chlorine with phenolic acids in solution and adsorbed on granular activated carbon. *Environ. Sci. Technol.* 16: 339-344 (1982).
5. Voudrias, E. A., Larson, R. A., and Snoeyink, V. L. Effects of activated carbon on the reactions of free chlorine with phenols. *Environ. Sci. Technol.* 19: 441-449 (1985).
  6. Jansson, B., and Sundstrom, A. Mass spectrometry of the methyl ethers of isomeric hydroxychlorobiphenyls—potential metabolites of chlorobiphenyls. *Biomed. Mass Spectrom.* 1: 386-392 (1974).
  7. Lotjonen, S., Ayra, P., and Pyysalo, H. Gas capillary gas chromatographic detection and mass spectral analysis of some hydroxyl derivatives of polychlorinated biphenyls (PCBs). *Finn. Chem. Letters*, pp. 57-60 (1979).
  8. Tulp, M. Th. M., Olie, K., and Hutzinger, O. Identification of hydroxyhalobiphenyls as their methyl ethers by gas chromatography-mass spectrometry. *Biomed. Mass Spectrom.* 4: 310-316 (1977).
  9. Larson, R. A., Hunt, L. L., and Blankenship, D. W. Formation of toxic products from a No. 2 fuel oil by photooxidation. *Environ. Sci. Technol.* 11: 492-496 (1977).
  10. Maron, D. M., and Ames, B. N. Revised methods for the *Salmonella* mutagenicity test. *Mutat. Res.* 113: 173-216 (1983).
  11. Xu, J., Whong, W. Z., and Ong, T. M. Validation of the *Salmonella* (SV50)/arabinose-resistant forward mutation assay system with 26 compounds. *Mutat. Res.*, in press.
  12. Voudrias, E. A., Dielmann, L. M. J., III, Snoeyink, V. L., Larson, R. A., McCreary, J. J., and Chen, A. S. C. Reactions of chlorite with activated carbon and with vanillic acid and indan adsorbed on activated carbon. *Water Res.* 17: 1107-1114 (1983).
  13. Taylor, W. I., and Battersby, A. R. *Oxidative Coupling of Phenols*. Marcel Dekker, New York, 1967.
  14. Voudrias, E. A., Larson, R. A., Snoeyink, V. L., and Chen, A. S. C. Activated carbon: an oxidant producing hydroxylated PCBs. Paper presented at the 5th Conference on Water Chlorination: Environmental Impact and Health Effects, Williamsburg, VA, June 3-8, 1984.
  15. Blanchard, H. S., Finkbeiner, H. L., and Russell, G. A. Polymerization by oxidative coupling. IV. Polymerization of 4-bromo and 4-chloro-2,6-dimethylphenol and preparation and decomposition of the silver and copper salts of certain other phenols. *J. Polym. Sci.* 58: 469-490 (1962).
  16. Yoshimura, H., Yamamoto, H., and Kinoshita, H. Metabolic fate of PCBs and their toxicological evaluations. In: *New Methods in Environmental Chemistry and Toxicology* (F. Coulston, F. Korte and M. Goto, Eds.), Academic Printing Co., Tokyo, 1973, pp. 291-297.
  17. Voudrias, E. A., Snoeyink, V. L., and Larson, R. A. Desorption of organic compounds produced from the reaction of chlorine with phenols adsorbed on activated carbon. *J. Am. Water Works Assoc.* 78: 82-86 (1986).