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Project Summary

Chlorination of Aquatic Humic Substances

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The overall objective of this research program was to increase our understanding of the chemical structures of aquatic humic material and their behavior during chemical oxidation, in particular with chlorine.

Experimental methods devised to isolate humic and fulvic acid fractions from natural surface waters involved classical precipitation of humic acids from large volumes of raw water, followed by concentration through settling and centrifugation. Fulvic acid materials were concentrated by adsorption on macroreticular XAD-2 resin followed by base elution. The controlled oxidation of these samples with solutions of potassium permanganate ($KMnO_4$) and aqueous chlorine was followed by solvent extraction, formation of methyl esters, and GC/MS analysis. The criteria for identifying degradation products with the use of low resolution EI, high resolution EI, and CI mass spectrometry are included in appended material. Results of the whole-sample degradation experiments also dictated how chlorination experiments were conducted on selected model compounds.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH 45268, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Aquatic humic material has been heavily implicated as an important reaction precursor of trihalomethanes in natural water systems exposed to chlorine. It has been assumed that humic materials are ubiquitously present in natural waters and have sufficient chemical similarity in time and space to account for the observed property of producing trichloromethane ($CHCl_3$) when exposed to chlorine. Further, it has been assumed that the mechanism of the chlorine (Cl_2)-humic interaction involves the classical haloform reaction and that trihalomethanes are the principal reaction products. Public and governmental concern over the presence of $CHCl_3$ in drinking water has focused attention to this phenomena, and the aforementioned assumptions have been made because of inadequacies in our scientific understanding of the fundamental chemical structures present in aquatic humic materials and, therefore, the reactions of these structures with chlorine.

The research described in the full report focuses on the chemical characterization of the reactions of aquatic humic materials with hypochlorous acid (HOCl), and the report begins with a comprehensive literature review. The experimental approach involved (1) the chemical degradation of natural aquatic humic material to gain insight into the dominant chemical structures in this natural product material, (2) the reaction of HOCl with model compounds

having structures similar to the degradation products, and (3) the identification of nonvolatile chlorinated and nonchlorinated degradation products of natural aquatic humics with HOCl.

Each experimental direction is described separately, although the experimental planning was heavily influenced by the results of current work. For instance, early model compound work established that total trihalomethanes were a minor portion of the total chlorine demand and, subsequently, only less volatile reaction products were emphasized in the actual humic chlorination experiments. Similarly, the dominance of aromatic products in the oxidative degradation mixtures resulted in the exclusion of aliphatic compounds in the model compound experiments.

The oxidative degradation experiments reported here have generated significantly more chemical structural information on aquatic humic material than was previously available in the literature. Controlled oxidation with $KMnO_4$ followed by solvent extraction, formation of methyl esters, and GC/MS analysis has established that the principal identified degradation products of aquatic humic acid are aromatic polybasic acids, some of which are hydroxylated. The degradation mixture also contains a complex mixture of aliphatic mono- and dibasic acids in lesser concentrations. Although most of the chromatographable degradation products were tentatively identified (low resolution EI, high resolution EI, CI mass spectrometry), only 20 to 30 wt.% of the original humic carbon is accounted for by the identified products. The chemical data generated in this study do not provide a fully adequate scientific basis for modeling humic structures. However, a hypothetical structure is presented that would account for the observed data.

Results and Conclusions

Direct chlorination of both aquatic humic materials and model compounds shown to be major component parts of the aquatic humic and fulvic materials produced chloroform. Because dihydroxy aromatic configurations were significant contributors to the humic macromolecular structure, the reaction of resorcinol with HOCl was investigated carefully as a model. A cyclic chlorinated diketone intermediate was identified along with other non-$CHCl_3$ reaction products. In addition to chloroform, a large number of chlorinated and nonchlorinated acids, phenols, and ketones were produced. Ring cleavage products such as saturated and unsaturated aliphatic mono- and dicarboxylic acids were major products of model as well as natural humic materials. Only small portions (8 to 17 wt.% of total organic carbon, TOC) of the aquatic humic material subjected to high pH and excess chlorine yielded products identifiable by GC/MC (Table 1). Thus, although hypochlorite (OCl^-) is a significant degrader of the humic macromolecule, it is not as effective as alkaline $KMnO_4$. The majority of the identified chlorine degradation products were nonchlorinated aliphatic acids. The aromatic acids are primarily polycarboxylic, suggesting carbon substituted on the aromatic rings at three or more sites in the undegraded macromolecule; this agrees with the $KMnO_4$ data. No chlorinated aromatic compounds were identified, however.

Aquatic humic materials are thus shown to be important precursors of not only chloroform but also a large number of other chlorinated and nonchlorinated organic compounds. Although aromati compounds dominate both the KMnO and HOCl degradation products, they d not appear to chlorinate directly. Th experimental procedures used in thi study have shown significant promis as a tool for increasing scientific under standing of fundamental aquatic humi chemistry. More structural informatio can be gained through additiona research on increased oxidative yiel and extraction and separation effi ciencies. A method for following th changes in macromolecular size polarity during the degradation woul be extremely useful.

The development of the technique reported here permits an even wide range of useful experimentation Questions to evaluate include (1) d fulvic acids (most of the TOC) yield quali tatively and quantitatively simila results, (2) do the chemical properties o the humic and fulvic fractions var seasonally for any source, and (3) wha chemical variability exists betwee natural water sources? In addition, th effect of oxidant/disinfectants othe than OCl^- on humic structures shoul be evaluated.

Table 1. *Non-Volatile Products of Aquatic Humic Acid Chlorination Product Identifications and Relative Yields Ether Extract (Methyl Esters)*[a]

Scan. No. from Figure 44	*Assigned Structure*	*Ether Extract*[b] *Relative Yield % Peak Weight (C)/ Total Weight C*	*Ethyl Acetate Extract*[b] *Relative Yield % Peak Weight (C)/ Total Weight C*
7	$CH_3CH_2CH(CH_3)COOCH_3$		
	RCH_2COOCH_3	*n.d.*[c]	*n.d.*
	R_1OCHXR_2		
11	$CH_3CHClCOOCH_3$	*28.4*	--[d]
16	$CHCl_2COOCH_3$	*14.7*	*0.5*
22[e]	CCl_3COOCH_3	*9.6*	--
22	$Cl_2C{=}CHCOOCH_3$	*n.d.*	--
26,37,40	*Chlorinated Aliphatic Methyl Esters*	*3.4*	--
-	$CH_3OOCCH_2COOCH_3$	--	*0.2*
-	$CH_3OOCCH{=}CHCOOCH_3$	--	*0.1*

Table 1. *Continued*

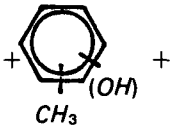
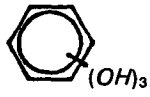
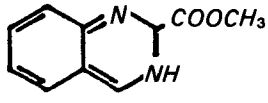
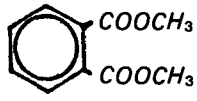
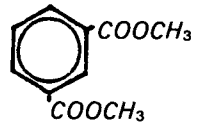
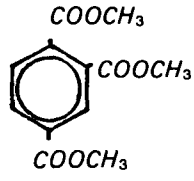
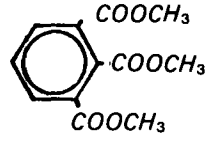
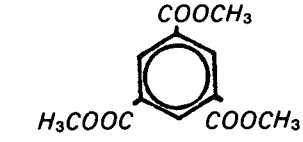
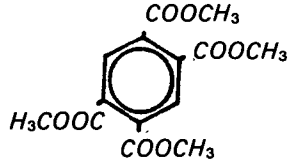
Scan. No. from Figure 44	*Assigned Structure*	*Ether Extract[b] Relative Yield % Peak Weight (C)/ Total Weight C*	*Ethyl Acetate Extract[b] Relative Yield % Peak Weight (C)/ Total Weight C*
44	$CH_3OOCCH_2CH_2\dot{C}OOCH_3$	0.2	0.7
52[e]		4.1	--
63	$CH_3OOCCH{=}CClCOOCH_3$	1.6	5.2
-	$CH_3OOCCH{=}CHCOOCH_3$	--	0.2
66	$CH_3OOCCH_2CHClCOOCH_3$	0.2	--
69	$CH_2ClCHClCOOCH_3$ or $CHCl_2CH_2COOCH_3$	0.1	--
77	*Aliphatic Methyl Ester*	0.3	--
84	$CH_3OOCCH{=}CClCOOCH_3$	0.4	2.2
84	$CH_3OOCC_3H_3ClCOOCH_3$ + $CH_3OOCC_2H_2Cl_2COOCH_3$	4.7	--
88	*Isomer of above compounds*	0.1	--
96	$CH_3OOCCCl{=}CClCOOCH_3$	0.9	--
100	$CH_3OOCC_3H_3ClCOOCH_3$ + $CH_3OOCC_3H_3RCOOCH_3$	0.5	--
115	$C_4H_9COOCH_3$	0.1	--
120,125	$C_4H_7COOCH_3$ +  + 	2.6	
151		2.3	
159[e]		0.9	--
163[e]		0.5	3.8

Table 1. Continued

Scan. No. from Figure 44	Assigned Structure	Ether Extract[b] Relative Yield % Peak Weight (C)/ Total Weight C	Ethyl Acetate Extract[b] Relative Yield % Peak Weight (C)/ Total Weight C
168		0.8	--
187	$C_6H_4(OH)(COOCH_3)$	2.9	--
198	$CH_3OOCCCl{=}C(COOCH_3)_2$	0.5	--
230	$C_{15}H_{31}COOCH_3$	1.7	
-	$C_6(OCH_3)_6$	--	1.0
255[e]		5.4	14.5
-		--	2.2
258	$C_8H_9O_5Cl_3$	n.d.	--
265[e]		1.9	--
265	$C_6H_2(CH_3)(COOCH_3)_3$	0.2	--
274	$C_6H_2(CH_2COOCH_3)(COOCH_3)_3$ + unknown chlorine compound	0.2	--
304	$C_6H_3(COOCH_3)_3$	0.3	1.6
321[e]		1.0	25.2
330	$C_6H_2(COOCH_3)_4$	0.9	15.8
355	$C_6H_2(COOCH_3)_4$	0.4	--
370	$C_6H_2(COOCH_3)_4$	0.3	2.1
408	$C_6H(COOCH_3)_5$	0.3	1.3

[a] *Reaction Conditions: Total Volume=320 ml; Carbon Concentrations=420 mg/l; OCl⁻/C Mole Ratio=X 1.0 Chlorination Time=48 hr.*
[b] *For the individual extract.*
[c] *=not determined.*
[d] *--=not detected.*
[e] *Confirmed with matching spectra.*

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***Alan A. Stevens** is the EPA Project Officer (see below).*

The complete report, entitled "Chlorination of Aquatic Humic Substances," (Order No. PB 81-161 952; Cost: $15.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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