CHEMISTRY LETTERS, pp. 1435 - 1436, 1984.

MAJOR AQUEOUS CHLORINATION PRODUCTS OF OXIDIZED FULVIC ACID

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Dichloro- and trichloroacetic acids as well as chloroform were identified as the major chloroorganics formed by chlorination of an aqueous solution of fulvic acid extracted from leaf mold (a model raw drinking water) oxidized with ozone or by a simultaneous use of ozone and ionizing radiation.

It is an important subject at present to control carcinogenic trihalomethanes (THM) such as chloroform in drinking water disinfected with chlorine. As one of the methods controlling THM, ozone is proposed to be used for removing the THM precursors (mainly fulvic acid) in raw drinking water.[1] However, little is known as to what kinds of chloroorganics are produced in ozone-oxidized drinking water, excluding THM. Thus, it is an urgent subject to clarify the chloroorganics in ozone-oxidized drinking water. This communication is a preliminary report on the major chloroorganics formed in a fulvic acid aqueous solution (a model raw drinking water) oxidized with ozone or by a simultaneous use of ozone and ionizing radiation (ozone/radiation).

Humic materials, extracted from leaf mold in wood near our laboratory with 0.1 mol dm^{-3} NaOH and followed by cation exchange with AG MP-50 resin (Dow Chemicals Co.), were fractionated with a Sephadex G-15 gel (Pharmacia Fine Chemicals, Uppsala, Sweden). The fractions of molecular weight below 1000, estimated from the elution count of vitamin B_{12}, were collected and used as a fulvic acid aqueous solution after its total organic carbon (TOC) was adjusted to 5.2 mg/l. The ozone oxidation was performed at 25 °C by bubbling ozonized oxygen gas (ozone concentration: 1.3 wt% in O_2) into the sample solution. In some cases, the ozone oxidation was carried out under the irradiation of ^{60}Co γ-rays (dose rate: 4.9×10^4 rad/h). The oxidized solutions were chlorinated with NaOCl under the following conditions: 50 mg/l of available chlorine; pH 7; 42 h reaction time at 20 °C. After chlorination, small amounts of $NaHSO_3$ and HNO_3 were added to the solution to quench the residual chlorine and adjust pH to 2, respectively. The yield of THM was determined with a Yanagimoto model G2800 EN gas chromatograph with Silicone DC-550 20% coated Chromosorb-W, AW-DMCS columns by the head-space method. The solutions were acidified with HCl and then, extracted with diethyl ether. An aliquot of this extract was methylated with diazomethane and analyzed by gas chromatography with Silicone DC-550 10% coated Chromosorb AW-DMCS columns. The identifications were

Table 1. Yields of chlorine products from oxidized fulvic acid

Oxidation method	Oxidation time min	TOC[a] (mg/l)	Amounts of products (μg/l) $CHCl_3$	DCAA[b]	TCAA[c]	Total chlorine[d] (μg/l)	TOCl[e] (μg/l)	Chlorine recovery[f] %
Untreated	0	5.2	320	262	723	898	1490	60.5
Ozone	10	3.5	124	510	319	598	631	94.8
	20	3.5	105	499	325	579	575	100
	30	3.5	94	442	280	510	538	94.8
Ozone + radiation	10	2.0	17	62	190	173	253	68.3
	20	1.2	4.5	16	45	42	64	64.8
	30	0.8	3.2	16	25	27	42	64.8

a) Total organic carbon. b) Dichloroacetic acid. c) Trichloroacetic acid.
d) The summation of chlorine contained in $CHCl_3$, dichloroacetic acid and trichloroacetic acid. e) Total organic chlorine, determined with a TOX analyzer.
f) The ratio of the total chlorine to TOCl.

made by comparison of retention times with those of authentic samples. The total organic carbon (TOC) and total organic chlorine (TOCl) in the sample were also determined with a Model 10B TOC analyzer (Shimadzu Corp.) and a Model TOX-10 TOX analyzer (Mitsubishi Chemicals Industries Ltd.),respectively.

For both the original and oxidized fulvic acids, only chloroform was detected by the head-space method, and dichloro- and trichloroacetic acids were confirmed on the ether-extract. Table 1 summarizes the yields of these products. The results for the original fulvic acid are in fair agreement with those for aquatic fulvic acid reported by Miller and Uden[2] and Christman et al.[3] As seen in this table, the major chlorine products are chloroform, dichloro- and trichloroacetic acids for all the samples, especially for the ozone-oxidized samples, for which the above three products comprise the great majority of the chlorine products, as indicated by high chlorine recoveries in the last column in Table 1.

In addition, the yield of dichloroacetic acid is larger in ozone-oxidized sample than in the original sample, while the yield of this product is remarkably decreased by ozone/radiation. This difference may reflect differences in the oxidation processes. This problem needs a further detailed study. At present, we are also studying on the behaviors of formation and decomposition of dichloro- and trichloroacetic acids in the oxidized fulvic acid aqueous solution.

The authors wish to express their thanks to Mr. Yukio Toyoura, Yanagimoto Mfg. Ltd. for his valuable advices on the analyzing method of dichloro- and trichloroacetic acids.

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(Received April 10, 1984)