



## The aqueous chlorination of the structural fragments of humic matter

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### Abstract

Chlorination has been used in water disinfection since the beginning of the 20th century. However, in the early 70s it was found that water chlorination led to the generation of undesirable halomethanes and other organochlorines. The principal predecessor of these hazardous compounds is humic matter. Due to the complexity and variability of the composition and structures of natural humic substances simple model compounds comprising structural fragments of humic material in chlorination studies are often used in related studies. The present study deals with aquatic chlorination of phenolic species: naphthol-1, naphthol-2, 2- and 4- hydroxybiphenyls and 8-hydroxyquinoline. GC-MS was used as an analytical tool. Volatile compounds were detected using the "purge and trap" method, while extraction with dichloromethane was used for the analysis of semivolatile species. The hydroxyl group is known to activate aromatic rings towards electrophilic substitution. As a result, a significant array of organochlorines was detected in each case. The results obtained allowed us to propose a detailed transformation scheme for each compound, to estimate possible hazard of the penetration of these by-products into natural water basins. It is also necessary to note that there is no information on toxicities of the majority of the transformation products detected. The last fact complicates the elaboration of reliable conclusions in risk assessment procedures.



## Introduction

Chlorination has been used in water disinfection since the beginning of the 20th century. Being a very effective disinfectant chlorine is relatively inexpensive and stable enough (unlike ozone) to remain in water distribution systems for a long time. That is why chlorine remains the most widely used disinfectant in the world.

However, in the early 70th it was found that water chlorination led to the generation of undesirable halomethanes and other organochlorines<sup>1,2</sup>. A number of studies have confirmed that water chlorination was directly responsible for the formation of mutagenic chemicals in drinking water. The principal predecessor of these hazardous compounds is humic matter<sup>3,4</sup>.

Any attempt to reduce the concentration of chlorination products in drinking water requires the clear understanding of the reaction pathways governing their formation. Due to the complexity and variability of the composition and structures of natural humic substances it is extremely difficult to study the detailed mechanism of their reactions with formation of organochlorine products. This fact led to the wide use of simple model compounds comprising structural fragments of humic material in chlorination studies<sup>5-8</sup>. This work deals with the aquatic chlorination of  $\alpha$ - and  $\beta$ -naphthols, 2- and 4-hydroxybiphenyls and 8-hydroxyquinoline.

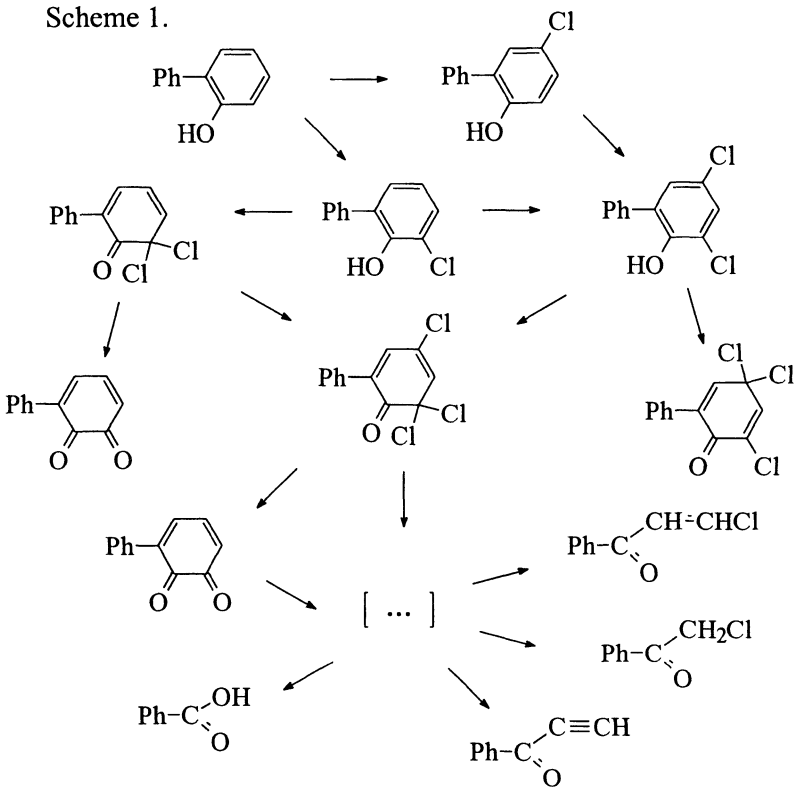
## Methods

The chlorination of the selected compounds was conducted in the dark at 20 C in 0.2M phosphate buffer solution (pH=7.2). Chlorine was used in water solution prepared by passing of gaseous chlorine through the distilled water at the Rublovo Water Treatment Station. Chlorine content was determined by iodometric titration just before every chlorination procedure. In all the reactions concentration of substrates was  $10^{-3}$  M while these of  $\text{Cl}_2$  varied from 0.14 g/l to 1.89 g/l. Reaction time was 24 hrs. Unreacted chlorine was reduced to chloride by addition of an equimolar quantity of sodium sulfite. Reaction products were extracted with three sequential aliquots of freshly distilled methylene chloride.

Dichloromethane extracts were analysed with Hewlett-Packard Engine GC-MS systems using DB-1 (30m) fused silica capillary column for semivolatile compounds. Volatile organochlorines were analyzed with HP MSD 5973 GC-MS instrument using "purge and trap" technique (DB-5) 50m fused silica capillary column. Interpretation of the results (chromatograms and mass spectra) was performed using NBS library and manually taking into account fragmentation pathways of organic compounds. Perdeuterated PAHs and 1,2-dichloroethane-d4 were used as internal standards.

## Results

A general scheme of transformation (semivolatile compounds) of 2-hydroxybiphenyl (Scheme 1) demonstrates a wide row of chlorination products derived from the compound. For some of these products concentrations grow linearly with the increase of chlorine doses (3-chlorobiphenyl-2-ol, 5-chlorobiphenyl-2-ol, 3,5-dichlorobiphenyl-2-ol). Other products reached maximal level at some intermediate concentration of chlorine (benzene, tetrachlorocyclopropene, 1,2,3,3-tetrachloropropene-1). Some products were detected only at highest concentration of chlorine (trichlorobiphenyl-2-ols). Unfortunately there is no available information concerning toxic effects of the compounds detected. Actually only very high level of chloroform in case of high chlorine concentration should be taken into account (see Table 1).





Isomeric 4-hydroxybiphenyl behaves similarly (Scheme 2). The main difference involves the formation of a number of polyhydroxy containing compounds.

Table 1. Products of aqueous chlorination of 2-hydroxybiphenyl ( $\mu\text{g}$ ).

<i>[S]/[Cl<sub>2</sub>]</i>	<i>1:2</i>	<i>1:5</i>	<i>1:20</i>	<i>1:50</i>
Chloroform	292	354	1241	1228
Methane, bromodichloro-	1.23	8.02	21.3	23.0
Benzene	0.52	7.71	25.5	4.71
Methane, tetrachloro-	-	0.42	2.33	0.32
Ethene, tetrachloro-	-	0.11	0.14	-
Cyclopropene, tetrachloro	-	3.14	21.71	-
1,2,3,3-Tetrachloropropene-1	-	1.51	15.73	5.62
1,1,2,3-Tetrachloropropene-1	-	-	-	9.91
1,1,2,3,3-Pentachloropropene-1	-	11.3	211	325
3-Chlorobiphenyl-2-ol	37.9	51.3	73.5	100
5-Chlorobiphenyl-2-ol	34.9	52.7	69.9	80.5
3,5-Dichlorobiphenyl-2-ol	32.9	58.7	55.7	133
3,3-Dichlorobiphenyl-2-ol	-	-	-	12.2
Trichlorobiphenyl-2-ol	-	-	-	5.93
Trichlorobiphenyl-2-ol	-	-	-	2.61
Trichlorobiphenyl-2-ol	-	-	-	+
Benzoic acid	-	-	86.3	110
1-Phenyl-2-propyn-1-one	-	-	4.05	7.94
3-Chloro-1-phenyl-2-propen-1-one	-	-	9.46	+
1-Chloroacetophenone	-	-	12.6	+
2-Phenylbenzoquinone	-	10.9	-	4.42
5-Chloro-3-phenyl-benzoquinone	-	18.9	-	36.2

Transformation of  $\beta$ -naphthol is represented in Scheme 3, while the concentrations of the detected compounds are listed in Table 2. This compound provides ring cleavage products as well as the products of dimerization. Chloroform is again remains the most toxic (according to the present knowledge) product. However its concentration is much lower than in the case of 2-hydroxybiphenyl. One should pay attention at very high concentration of 1-chloro-2-naphthol at the lowest concentration of chlorine. Higher chlorine content brought to sharp decrease of the concentration of this compound due to its transformation to other products, including non-volatiles, which we did not detect in this case.

Isomeric  $\alpha$ -naphthol being chlorinated brings to very extensive row of compounds. Only selected products are represented in Scheme 4 and Table 3.



Table 2. Reaction products of aqueous chlorination of  $\beta$ -naphthol ( $\mu\text{g}$ ).

<i>[S]/[Cl<sub>2</sub>]</i>	<i>1:2</i>	<i>1:10</i>	<i>1:20</i>	<i>1:50</i>
Chloroform	2.10	7.85	31.6	68.2
Methane, bromodichloro-	-	1.20	2.30	2.80
Ethane, hexachloro-	-	0.02	0.10	0.20
Benzoic acid	-	-	-	2.50
1,2-Benzenedicarbaldehyde	-	-	-	2.40
1-Chloro-2-naphthol	3456	1407	365	119
1,2-Naphthoquinone	18.2	6.10	-	-
1,3-Dichloro-2-naphthol	-	-	6.40	116
1,1-Dichloro-2-naphthol	-	-	5.20	15.3
1,4-Dichloro-2-naphthol	-	-	-	15.3
[1,1'-Binaphthalene]-2,2'-diol	7.00	65.4	23.9	-
[1,1'-Binaphthalene]-3-chloro-2,2'-diol	-	10.7	16.5	13.6
[1,1'-Binaphthalene]-4-chloro-2,2'-diol	-	57.3	9.30	-
[1,1'-Binaphthalene]-3,3'-dichloro-2,2'-diol	-	-	2.40	-

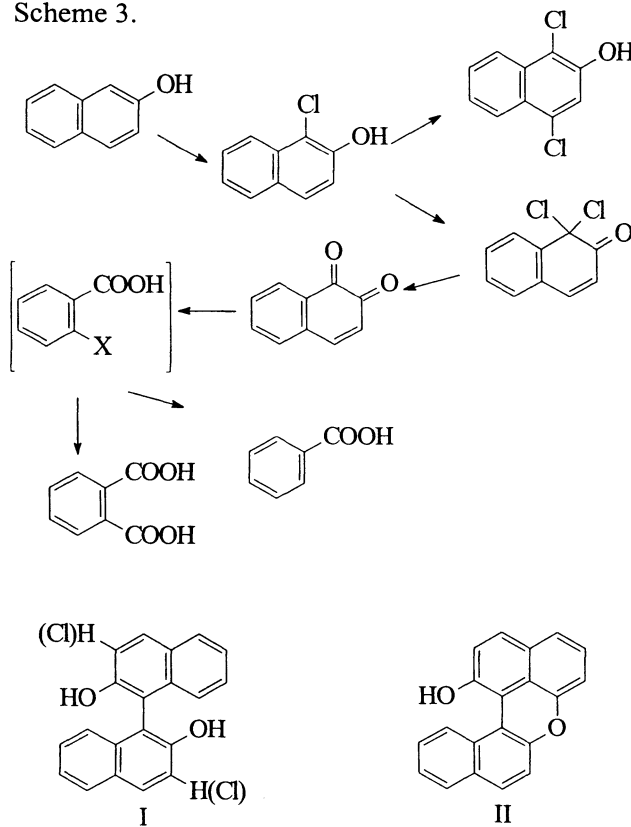
Table 3. Reaction products of aqueous chlorination of  $\alpha$ -naphthol ( $\mu\text{g}$ ).

<i>[S]/[Cl<sub>2</sub>]</i>	<i>1:2</i>	<i>1:5</i>	<i>1:10</i>	<i>1:20</i>	<i>1:50</i>
Chloroform	2.71	6.14	38.1	77.5	67.2
Bromodichloromethane,	0.33	0.51	1.02	5.91	10.2
Dibromochloromethane	-	-	-	0.13	0.35
Phthalic acid	-	5.81	9.11	9.83	217
1,4-Naphthalenedione	8.21	2.90	+	3.71	4.53
2-Chloronaphthol	248	-	3.42	12.3	48.7
4-Chloronaphthol	77.6	9.32	8.61	6.23	5.82
2,4-Dichloronaphthol	1228	28.6	-	-	-
5,6,7,8-Tetrahydro-7,8-dioxo-5,5,6-trichloroquinoline	-	-	39.1	75.1	483
2-Hydroxynaphthoquinone	16.1	15.7	7.55	7.52	-
2-Chloronaphthoquinone	-	+	8.53	40.8	476
2-Hydroxy-3-chloronaphthoquinone	16.7	418	7.6	-	-
o-Carboxyphenyl-trichloromethylketone	-	-	-	-	1564

Table 4. Reaction products of aqueous chlorination 8-hydroxyquinoline of ( $\mu\text{g}$ ).

$[S]/[Cl_2]$	1:5	1:10	1:20	1:50
Chloroform	7.70	70.4	164	232
Bromodichloromethane	0.30	1.05	4.94	22.9
Dibromochloromethane	-	-	-	0.19
Dichloroethane	0.40	0.37	1.39	1.69
Bromodichloroethane	-	-	-	0.29
Dichloroacetonitrile	-	0.35	2.03	3.2
Trichloroacetonitrile	-	-	-	0.70
7-Chloro-8-hydroxyquinoline	10.4	29.0	12.5	-
5-Chloro-8-hydroxyquinoline	43.5	120	45.6	-
5,7-Dichloro-8-hydroxyquinoline	28.5	66.6	38.5	-
5,6,7,8-tetrahydro-7,8-dioxo-5,5,6-trichloroquinoline	-	-	20.1	420

Scheme 3.

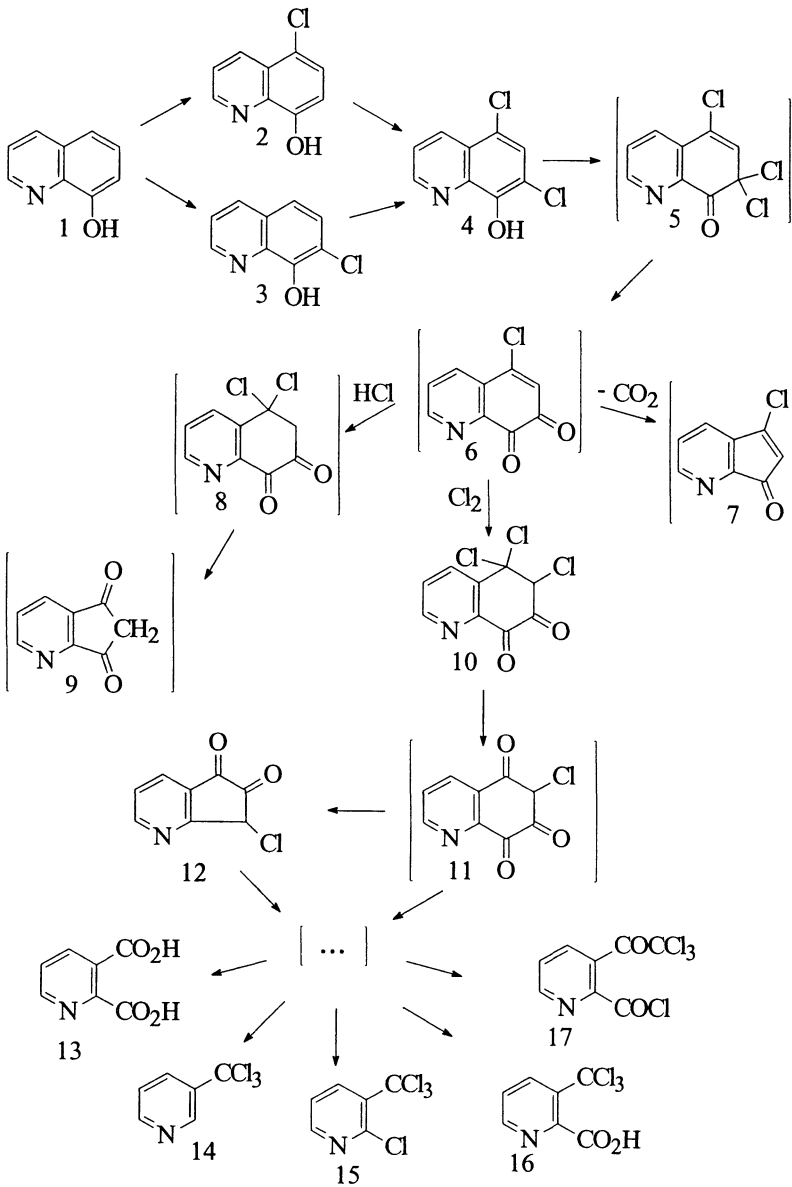








Scheme 5.





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