Mass spectrometry in the study of mechanisms of aquatic chlorination of organic substrates

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Chlorination is an effective method of water disinfection. However, it has been identified as contributing to the formation of a wide variety of disinfection by-products that have been associated with adverse health effects. Natural humic matter and anthropogenic pollutants are responsible for the formation of these by-products. Mass spectrometry is the most efficient tool to analyze the rates of conversion, the nature and levels of by-products in the reactions of chlorinating agents with model organic compounds. More than 30 substrates with various functional groups were studied, while gaseous chlorine and sodium hypochlorite were used as chlorinating agents. The effects of pH, substrate/active chlorine ratio, addition of metal cations and bromides and iodides on the aqueous chlorination process of various organic substrates were investigated. Transformation schemes were proposed for the studied compounds.

Keywords: gas-chromatography-mass spectrometry, purge-and-trap, aquatic chlorination, chlorinating agents, disinfection by-products, humic matter, anthropogenic pollutants, transformation schemes, bromination

The general procedure of drinking water preparation consists of several important stages. The most controversial among them is disinfection. Being introduced to kill all the micro-organisms, it results in the formation of hazardous disinfection by-products (DBP). The most important disinfecting agents are summarized in Table 1,

Table 1. The most important disinfecting agents.

<table>
<thead>
<tr>
<th>Method</th>
<th>Agent</th>
<th>Positive results</th>
<th>Negative results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
<td>Molecular chlorine</td>
<td>Cheap, efficient, stable</td>
<td>High levels of THM* and HAA*</td>
</tr>
<tr>
<td></td>
<td>Sodium hypochlorite</td>
<td>Cheap, efficient, stable</td>
<td>High levels of THM* and HAA*</td>
</tr>
<tr>
<td></td>
<td>Chloroamine</td>
<td>Efficient, stable, less THM* and HAA*</td>
<td>Formation of DMNA*, Pb removal from the metal tubes</td>
</tr>
<tr>
<td></td>
<td>Chlorine dioxide</td>
<td>Efficient, stable, less THM* and HAA*</td>
<td>High levels of bromites, bromates, chlorites, chlorates</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Ozone</td>
<td>Efficient, no THM* and HAA*</td>
<td>More expensive, rather unstable, low water solubility, final chlorination is required</td>
</tr>
<tr>
<td>UV-irradiation</td>
<td></td>
<td>Efficient, no THM* and HAA*</td>
<td>Final chlorination is required</td>
</tr>
<tr>
<td>Organic peracids</td>
<td>RCOOOH</td>
<td>Very efficient No THM* and HAA*</td>
<td>Very high cost</td>
</tr>
</tbody>
</table>

*THM: trihalomethanes
HAA: halogenated acetic acids
DMNA: dimethylnitrosoamine
Study of Mechanisms of Aquatic Chlorination of Organic Substrates


while chlorination, being historically the first, remains the most popular.

There are two sources of carbon which form DBP. The first one is unavoidable. It involves natural humic matter. The second is due to the presence of anthropogenic organic pollutants. The latter becomes more and more relevant as not only surface water, but underground water as well, may be considerably polluted nowadays.

For a long time, fulvic and humic acids were considered to be extremely complex compounds with molecular masses up to 100,000 Da. However, when mass spectrometers started studying these compounds it became clear that they are much simpler. Matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) experiments confirmed that their molecular masses rarely exceeded 1000 Da (Figure 1). The problem deals with their variability rather than their complexity. Ultra-high mass resolution, achieved with a 7 Tesla ion cyclotron resonance (ICR) instrument, demonstrates that each peak with nominal mass splits into several peaks due to the presence of constituents with different elemental compositions. One should not forget, also, that each elemental composition is represented with an enormous number of isomers. Figure 2 represents a structure of one of the major components of a humic matter sample.

Even if we forget about thousands and thousands of structural and positional isomers, this particular structure, containing 13 asymmetric carbon atoms, has 8192 stereoisomers. Thus, a question arises: are there two identical molecules in a sample of humic matter?

Two major approaches are used in the study of aquatic chlorination. The first may be called technological. It engages in a decrease in the formation of organochlorine compounds (first, trihalomethanes and halogenic acetic acids) in drinking water by optimization of conditions of chlorination and water treatment in general. The second is more fundamental. It involves the elucidation of mechanisms of aqueous chlorination of organic substrates with various functional groups. To study these mechanisms, it is much more efficient to use model organic compounds representing structural fragments of humic acid or real individual anthropogenic pollutants. In this case, it is possible to assign the appearance of certain DBP with the presence of particular functional groups in the original molecules. When natural humic matter is introduced into the reactions of aquatic chlorination, several hundred products detected with a mass spectrometer do not allow establishing their precursors or proposing a reliable mechanism of their formation.

Selecting individual compounds for the study of the mechanisms of aquatic chlorination in the laboratory of organic analysis of the Moscow State University, the following items have been taken into account. A substance should represent a structural fragment of humic matter or should be a chemical often present in natural water samples due to anthropogenic activity. The behavior of several functional groups has been studied: double bonds, aromatic rings (activated and deactivated), hydroxyl, carbonyl and carboxyl groups, α-positions of carbonyl compounds and α-positions of aromatic rings. The research was aimed at covering the following items: comparison of reactivity of chlorinating agents, identification of by-products of aquatic chlorine.
chlorination of the selected organic compounds, elucidation of mechanisms of aquatic chlorination, the study of the influence of chlorination conditions on the formation of DBP, the establishing of transformation schemes of the selected organic compounds in conditions of aquatic chlorination and the study of the effect of additions of inorganic anions.

More than 30 individual compounds have been investigated. The reaction conditions were varied in a broad range: reaction time 1–24 h, substrate concentration $10^{-3}$–$10^{-1}$ mol L$^{-1}$, pH 2–10, ratio of substrate to active chlorine 10:1–1:50. GC-MS has been used as the main analytical tool. Standard US EPA methods were used: 8260 for volatile products (purge and trap) and 8270 for semivolatiles. Methylation was used to detect non-volatiles. Several disinfecting agents were applied while the majority of experiments involved molecular chlorine or sodium hypochlorite. Both these agents exist in water solutions as mixtures of several species:

\[
\begin{align*}
\text{NaOCl} & \rightleftharpoons \text{Na}^+ + \text{OCl}^- \\
\text{ClO}^- + \text{H}_2\text{O} & \rightleftharpoons \text{HClO} + \text{H}^+ + \text{Cl}^- \\
\text{Cl}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HCl} + \text{H}_2\text{O} + \text{Cl}^-
\end{align*}
\]

Molecular chlorine is a stronger oxidizing agent ($E^\circ = 1.59$) than hypochlorous acid ($E^\circ = 1.50$) or hypochlorite anion ($E^\circ = 0.89$).

Mass spectrometry is an ideal analytical tool to study aquatic chlorination. The only problem involves structural elucidation. Even the newest versions of the mass spectral libraries do not contain spectra of 70–80% of the products of transformation of the initial organic substrates. Usually, only the spectra of the primary products are available. Hence, manual interpretation of spectra is often required.

Nowadays, modern mass spectrometry provides not just reliable and informative, but sometimes really beautiful and convincing results even for non-specialists. Figure 3 represents a three-dimensional chromatogram (TIC) of a sample of light diesel before and after its aquatic chlorination. The analysis was done using a two-dimensional gas chromatography mass spectrometry (GC-GC-MS) instrument (Leco). In this case, before being introduced to the ion source of a time-of-flight (ToF) instrument, each component passes via two consecutively-connected columns. The first is long (30 m) and non-polar, while the second is short (1 m) and polar. More than 1500 individual ingredients were identified in each case. The aim of the study was to understand what types of hydrocarbons interact with aquatic chlorine to form DBP. The major constituents are alkanes and naphthenes. The peaks of the corresponding homologous series occupy the upper part of both chromatograms in Figure 3. Since they are non-polar, they have minimal retention time in the second column (1.2–1.3 s). Rather broad regions are marked to demonstrate the peaks due to numerous alkylbenzenes and alkynaphthalenes. The lower part of Figure 3 clearly demonstrates that if the peaks of alkanes and naphthenes remained unchanged, the peaks of alkylbenzenes became notably lower while the peaks of alkynaphthalenes disappeared. Apart from that, two marked areas represent the peaks due to numerous chloroalkylbenzenes and chloroalkynaphthalenes. The conclusion is pretty obvious. Saturated compounds are not
reactive in conditions of aquatic chlorination. The degree of conversion of alkylbenzenes is about 50%, while alkylnaphthalenes in the similar conditions transform completely to form the corresponding organochlorines.

A transformation scheme of 8-hydroxyquinoline (Figure 4) represents an example of aquatic chlorination of phenols. Only semi-volatile products are mentioned in the scheme, although it is worth mentioning that chloroform is always one of the major products, while its levels are higher at high doses of active chlorine or at basic pH values. The transformation of this substrate starts with electrophilic substitution in the activated benzene ring. The following reactions (substitution, elimination, addition, ring cleavages, oxidation, etc.) result in variety of the detected products. An important feature involves the fact that pyridine ring remains intact in all these transformations.

Cyclohexene is an extremely reactive substrate in the applied conditions. Its traces have been detected only in the case of NaOCl. Molecular chlorine is more active. It destroys cyclohexene completely even at 1:1 molar ratio substrate/active chlorine. Table 2 contains information on the levels of the selected products of cyclohexene chlorination. It allows comparing the reactivity of two chlorinating agents and demonstrates the effect of the ratio substrate/active chlorine.

The main product is always 2-chlorocyclohexanol. It forms in the reaction of conjugated addition. An increase in the chlorine dose brings to the corresponding increase

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar ratio Cl/Cyclohexene</th>
<th>1:1</th>
<th>1:10</th>
<th>1:50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NaOCl</td>
<td>Cl2</td>
<td>NaOCl</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td></td>
<td>330</td>
<td>—</td>
<td>1.1</td>
</tr>
<tr>
<td>2-Chlorocyclohexanol</td>
<td></td>
<td>9100</td>
<td>9100</td>
<td>9300</td>
</tr>
<tr>
<td>1,2-dichlorocyclohexane</td>
<td></td>
<td>2.3</td>
<td>11.0</td>
<td>34.4</td>
</tr>
<tr>
<td>Dichlorocyclohexanol (Σ isomers)</td>
<td></td>
<td>16.1</td>
<td>—</td>
<td>13.3</td>
</tr>
<tr>
<td>Dichlorinated dimer</td>
<td></td>
<td>—</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>Chloroform</td>
<td></td>
<td>4.7</td>
<td>43.1</td>
<td>4.7</td>
</tr>
</tbody>
</table>
of another primary product of electrophilic addition—1,2-dichlorocyclohexane. Both reactions are quite predictable on the basis of the rules of classic organic chemistry. The yields of other mentioned products (dichlorocyclohexanols, dichlorinated dimer and chloroform in particular) are considerably higher in case of molecular chlorine, especially at high dose of chlorine. It means that sodium hypochlorite is safer for the chlorination of organic substrates with double bonds, at least in terms of DBP formation.

The main products of anisole chlorination at various pH are summarized in Table 3. It is obvious, that hypochlorite appears to be more reactive than molecular chlorine in the reaction of electrophilic substitution in the aromatic ring. The results presented demonstrate that the reaction goes faster in acidic media and slows down in basic conditions. This effect means that aquatic chlorination of anisole is an acid catalyzed reaction. Trimolecular reaction: substrate + HOCl + H₃O⁺ should be hardly possible as it has very high variation in entropy. In 1996, Rebenne proposed that at pH < 7.54 protonated hypochlorous acid could serve as a chlorination agent. However, according to the results obtained at B3LYP/6-31(d)+G and MP2/6-31(d)+G levels, the reaction of HOCl with H₃O⁺ is endothermic and, hence, hardly possible due to energy restrictions. On the other hand, the same reaction yields a stable complex with the hydrogen bond. This particular complex, or its hydrates, could serve as the chlorinating agent in the conditions discussed.

\[
\text{HOCl} + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{OCl}^- + \text{H}_2\text{O} - 47.7 \text{kJ mol}^{-1} \text{ at B3LYP/6-31(d)+G level}
\]

The presence of bromine impurities in the chlorination agents brings to brominated compounds among the products of aquatic chlorination of organic substrates. The levels of bromine in technical products are about 5%, however, the levels of organobromines may be higher than that of the corresponding organochlorines. The presence of the most different inorganic salts is unavoidable in any water sample. Their levels may be extremely different depending on the region and source of water. The effect of bromides, iodides and copper ions was studied for the reaction of chlorination of benzyl alcohol and 1-methylnaphthalene.

Table 4 demonstrates the effect of the inorganic ion additions on the chlorination of benzyl alcohol. Although this substrate is not very active in the reaction, the effect of bromides, and especially copper ions, is really dramatic, as the conversion rate increases from 3.2% to 42% and 98%, correspondingly. Catalytic effect of these ions on the oxidation is obvious.

The conversion rate of 1-methylnaphthalene increased dramatically with the addition of any of the studied ions (Table 5). Copper is again the most efficient while Br⁻ and I⁻ lead to similar conversion rates. However, if bromide addition results in the formation of bromoderivatives as the main products, iodide addition brings about the dramatic increase in the levels of organochlorines (similar to copper). Also, the level of products with modified methyl groups are considerable higher in the case of copper ions and especially in the case of iodides. Taking into account the ability of iodine and copper to promote radical reactions, a radical mechanism of the formation of these compounds may be assumed.

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl alcohol</td>
<td>6300</td>
<td>3700</td>
<td>5900</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>—</td>
<td>780</td>
<td>190</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>—</td>
<td>2100</td>
<td>40</td>
<td>4700</td>
<td></td>
</tr>
<tr>
<td>Conversion degree</td>
<td>3.2%</td>
<td>42%</td>
<td>7.0%</td>
<td>98%</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

- Molecular chlorine and sodium hypochlorite react similarly. Sodium hypochlorite demonstrates higher activity in reactions of electrophilic substitution in the aromatic ring while Cl\(_2\) is more active in oxidation reactions and in reactions with double bonds.
- Assortment of by-products is usually higher with molecular chlorine.
- A stable complex of HOCl with H\(_3\)O\(^+\) with hydrogen bond is a reactive particle in the aquatic chlorination (electrophilic substitution in the aromatic ring).
- Addition of bromide, iodide or copper ions notably increases conversion degree in aquatic chlorination reactions.
- Bromide additions mainly form organobromines, while iodide addition results in a significant increase in the levels of organochlorines.

References


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