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ARTICLES

Comparison of Chlorine and Sodium Hypochlorite Activity in the Chlorination of Structural Fragments of Humic Substances in Water Using GC–MS

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Abstract—The possibility of the formation of toxic products at the stage of drinking water disinfection as a result of interaction of disinfectants, such as chlorine and sodium hypochlorite, with model organic compounds, structural fragments of natural humic substances is investigated using gas chromatography–mass spectrometry (GC–MS). Both qualitative and quantitative analysis of the products of water chlorination of dibenzoylmethane and cinnamic acid by chlorine and sodium hypochlorite was performed under the conditions of an equimolar amount and five- and fiftyfold excess of the chlorinating agent. Detailed diagrams of the transformation of organic compounds under the conditions simulating the process of natural water disinfection are drawn. The studies indicate that the use of chlorine leads to a greater variety and higher concentrations of chlorinated products compared to sodium hypochlorite.

Keywords: gas chromatography–mass spectrometry, water chlorination, chlorinating agents, dibenzoylmethane, cinnamic acid, disinfection by-products, humic substances

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INTRODUCTION

Treatment of drinking water is the most important industry. This is a multistep process related to the need of removing various impurities from water. Disinfection is the key stage of the technological circuit of potable water treatment. Chlorine and its compounds currently occupy a dominant position among the chemicals used for drinking water disinfection. Most commonly used chlorine gas and sodium hypochlorite exhibit high disinfection capacity, are relatively stable in water, and remain active for a long time, preventing the recontamination of water in the distribution network [1].

Using modern methods of analysis, not only bactericidal and virucidal properties of disinfectants can be studied, but also their chemical activity with respect to the trace contaminants in natural water. Gas chromatography–mass spectrometry is an efficient method for analyzing organic substances dissolved in water [2–4]. The highest sensitivity of the method (to 10^{-15} g) offers the required detection limits for trace impurities, and unique informativity and specificity ensure the reliable determination of the structures of substances.

It was found by mass spectrometry that, in the chlorination of drinking water, a great number of various chlorinated organic compounds forms [5, 6], including such carcinogenic disinfection products as trihalomethanes. The main sources of their formation are humic and fulvic acids dissolved in natural water [7]. Various anthropogenic compounds can also interact with disinfectants, for example, petroleum products, pesticides, dyes, surfactants, pharmaceuticals, and other contaminants [8]. The mechanisms of the transformation of humic and fulvic acids under the conditions of water chlorination were studied using various model organic substrates. Such studies are usually accompanied by drafting detailed diagrams of their transformations [9–14]. Similar studies were also conducted directly with anthropogenic ecotoxicants [15].

The term “water chlorination” is often used to refer to the degradation of organic substances by the action of chlorine, sodium hypochlorite, and various other oxidizing agents containing chlorine. However, there are some differences in the chemical activity of these disinfecting reagents. In aqueous solutions, both major chlorinating agents (chlorine and sodium hypochlorite) are present as a mixture of different particles due to equilibrium processes occurring with the participation of solvent molecules.

Being dissolved in water, chlorine gas is rapidly hydrolyzed to form hypochlorous acid, which undergoes partial dissociation by the equations

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-,$$

$$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-.$$

Sodium hypochlorite dissociates in water; as a result of equilibrium with water, both dissociated and undissociated forms of hypochlorous acid is present in solution:

$$NaOCl \rightleftharpoons Na^+ + OCl^-,$$
$$ClO^- + H_2O \rightleftharpoons HClO + OH^-.$$

All those forms of chlorine present in solution (molecular chlorine, hypochlorous acid, and hypochlorite ion) compose free active chlorine and interact with organic impurities in water. Quantum-chemical calculations showed that a complex of hydroxonium ion with hypochlorous acid H_3O^+–HOCl, stabilized by hydrogen bonds, is an electrophilic particle interacting, in particular, with the aromatic ring [16, 17]. All forms of active chlorine also exhibit oxidative properties. Among the particles present in the solution, molecular chlorine has a higher oxidation potential ($E^\circ = 1.59$ V) as compared to those of hypochlorous acid ($E^\circ = 1.50$ V) and the hypochlorite anion ($E^\circ = 0.89$ V).

To compare the reactivity of the chlorinating agents, cinnamic acid and dibenzoylmethane were selected in the present work as model structural fragments of humic substances. According to the literature data [18, 19], the most active reaction cites in the molecules of organic substrates under the conditions of water chlorination are the α-position of carbonyl and aromatic systems, a double bond, and an aromatic ring activated by electron-donating substituents. Therefore, we selected compounds bearing these structural fragments as objects of study. Changes in the degree of conversion of the initial substrates and the variety of products observed with increasing concentrations of chlorinating agents were studied using an equimolar amount of chlorinating agents and five- and fiftyfold excesses of active chlorine.

EXPERIMENTAL

Dibenzoylmethane and cinnamic acid were chlorinated in an aqueous medium under the action of chlorine and sodium hypochlorite disinfectants. Chlorinated water was prepared at the Western Water Treatment Station of Mosvodokanal by passing chlorine gas through distilled water to saturation. A commercial sodium hypochlorite reagent (Fisher) was used to prepare aqueous solutions of the desired concentration. The purity and properties of the initial organic substrates and reagents in an aqueous medium were determined by the results of control experiments using gas chromatography–mass spectrometry.

A required amount of a chlorinating agent, calculated by the results of iodometric titration, was added to 50 mL of a buffer solution, and the volume of the solution was brought to 100 mL by diluting with twice-distilled water. A 0.0001-mole portion of a test substrate, purified immediately before the experiment by double recrystallization, was placed to the resulting solution, and the contents of the flask were stirred with a magnetic stirrer for a day. After the reaction period was over, residual active chlorine was removed by adding sodium sulfite.

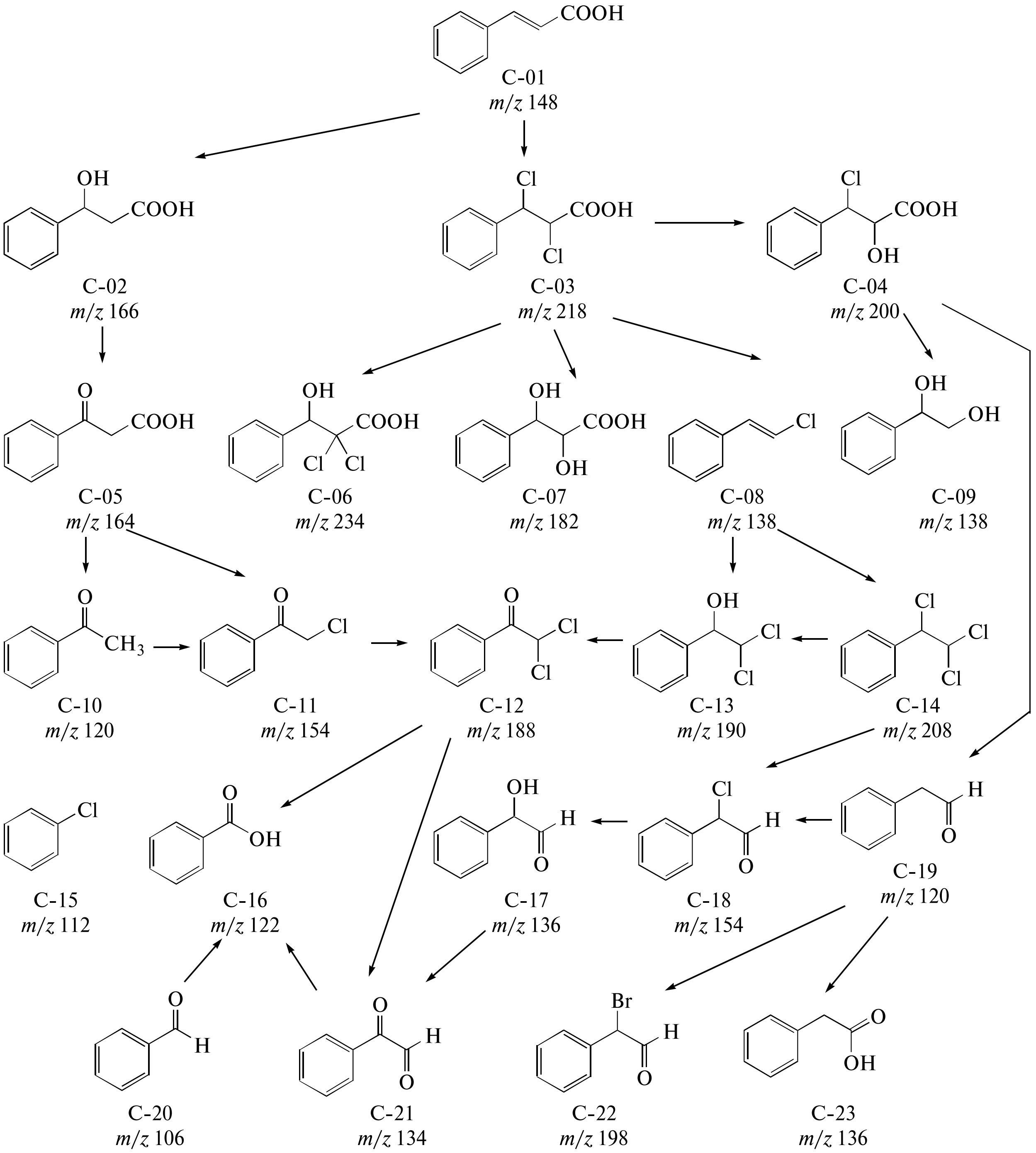
To analyze volatile organic substances formed in the chlorination of model substrates, an aliquot portion of 5 mL was taken from each reactor. Helium gas was blown through the samples for 10 min; organic substances were trapped by an adsorbent (Tenax + silica gel + activated charcoal) followed by desorption at 170°C for 4 min in a Purge&Trap autosampler. The composition of the mixtures was determined using an HP5973 gas chromatograph–mass spectrometer (chromatographic column, VOC; 60 m × 0.25 mm; carrier gas, helium; electron ionization; electron energy, 70 eV). For quantitative analysis, 4-bromofluorobenzene, fluorobenzene, and pentafluorobenzene were used as internal standards.

The composition of the products extracted from the aqueous solution by methylene chloride was found using an SSQ7000 gas chromatograph–mass spectrometer (Thermo Finnigan; chromatographic column, HP5MS; 30 m × 0.25 mm; carrier gas, helium; electron ionization; electron energy, 70 eV). Extraction was carried out with three portions (15, 10, and 10 mL, respectively) of freshly distilled methylene chloride. For a more complete extraction of organic substances, concentrated hydrochloric acid, and sodium chloride were added to the aqueous solution to pH ~ 2 before the second step of extraction. The combined fractions were dried over anhydrous sodium sulfate and evaporated on a rotary evaporator to a volume of 1 mL. The injected sample volume was 1 μL. Perdeuterated naphthalene and perdeuterated phenanthrene were introduced into the sample as internal standards for quantitative analysis.

The structures of the resulting compounds were determined on the basis of spectral and structural correlations and using standard spectra from the NIST and Wiley mass spectral libraries. The analytical signals of isomeric substances were assigned by the qualitative assessment of the retention indices of structural analogues, as well as using reference surrogate mixtures. Quantification was carried out by the areas of chromatographic peaks recorded in the total ion current mode and by individual characteristic ions in the mass chromatograms using the internal standard method.

RESULTS AND DISCUSSION

Chlorination of cinnamic acid. The reactive site in the molecule of cinnamic acid is an unsaturated bond between the α- and β-carbon atoms. Under the conditions of water chlorination, it can react with both chlorinating agents in different forms and solvent molecules.



Scheme 1. Transformation of cinnamic acid in an aqueous medium under the action of chlorine and sodium hypochlorite; *m*/*z* values are referred to the detected molecular ions.

The results of qualitative and quantitative analysis of the products of water chlorination of cinnamic acid are represented in Scheme 1 and Table 1.

With equimolar amounts of reagents, the degree of conversion of the initial substrate is greater for chlorine water; however, at the maximum concentration of chlorinating agents, the full conversion of cinnamic acid was observed in both cases; for sodium hypochlorite, the processes of conjugate addition and hydrolysis proceed more actively.

In an aqueous medium, solvent molecules actively participate in the electrophilic addition reaction. As a result, products of chlorohydroxylation (C-04) and hydration (C-02) formed along with the dichlorina-

Table 1. Products of water chlorination of cinnamic acid, detected in chlorination with chlorine and sodium hypochlorite at different molar ratios of active chlorine ($c(\mathrm{Cl}^{\mathrm{act}})$) to the test substrate ($c(\mathrm{S})$) (μg); $m = c(\mathrm{Cl}^{\mathrm{act}})/c(\mathrm{S})$

Compound code	Molecular weight, Da	Chlorine water			Sodium hypochlorite		
		$m = 1$	$m = 5$	$m = 50$	$m = 1$	$m = 5$	$m = 50$
C-01	148	10440	184	–	14100	355	–
C-02	166	–	–	0.6	–	–	–
C-03	218	–	–	4.5	–	–	–
C-04	200	–	–	3.7	–	–	–
C-05	164	–	–	0.6	–	–	–
C-06	234	–	48	227	–	–	–
C-07	182	–	435	106	–	87	15
C-08	138	1456	717	0.6	57	125	4.8
C-09	138	–	16.4	78.5	–	–	–
C-10	120	54.7	1.6	2.3	150	1.4	2.3
C-11	154	14.7	5.4	1.7	31.2	73.7	–
C-12	188	–	2.6	18.1	–	42.5	–
C-13	190	4.5	3935	2590	8.2	3986	2932
C-14	208	–	343	76.5	–	102	43
C-15	112	–	–	9.4	–	–	–
C-16	122	7.1	104	1737	12.7	340	1858
C-17	136	–	–	–	–	–	144
C-18	154	2.0	1.4	0.6	–	–	159
C-19	120	–	–	–	31.2	45.3	584
C-20	106	13	42.5	23.8	26.3	76.5	496
C-21	134	–	–	–	–	–	133
C-22	198	–	–	Traces	–	–	42.8
C-23	136	–	–	–	–	–	53.8
$\mathrm{CHCl_3}$	118	–	–	13.6	–	–	26.4

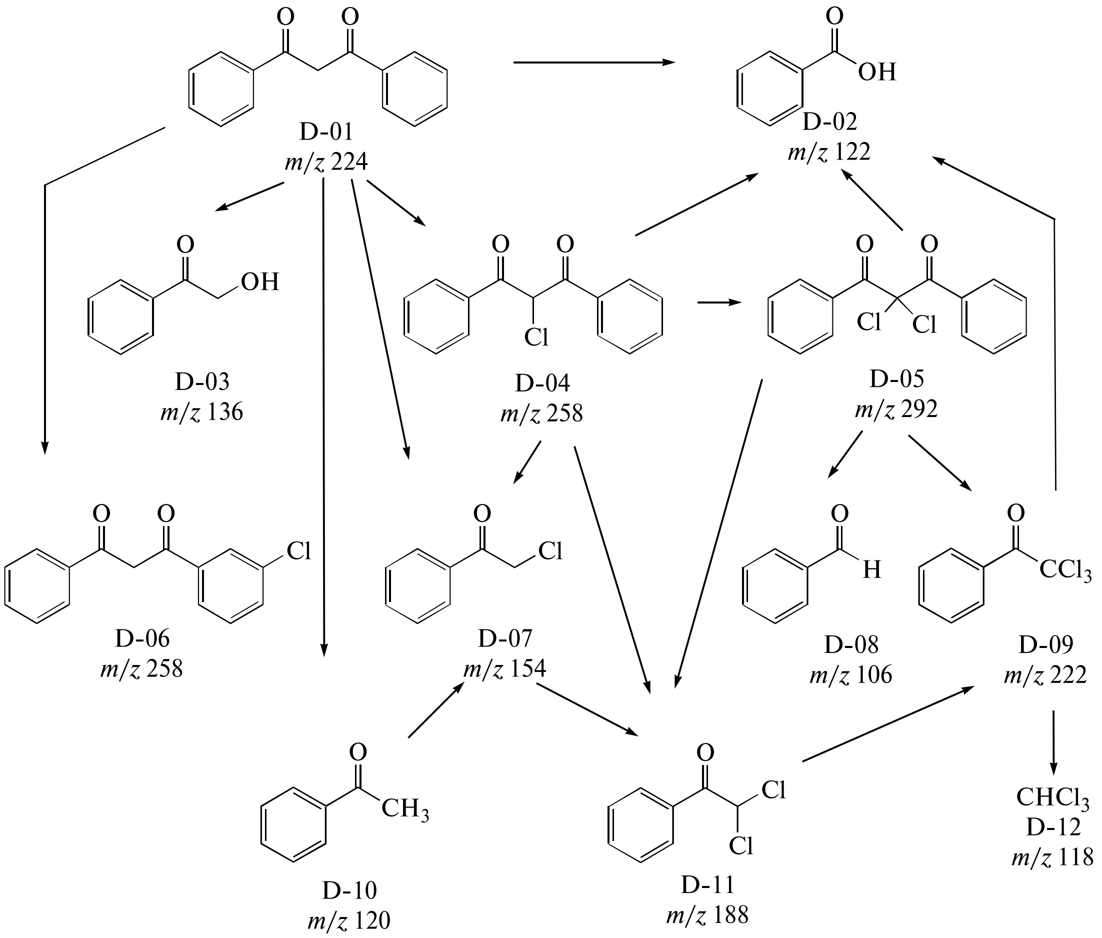
tion product (C-03). The resulting benzyl chlorides were readily converted into alcohols by nucleophilic substitution. Carboxyl group also facilitated the nucleophilic substitution of chlorine in the α-position. However, these products were not accumulated in the reaction medium, because they underwent further conversion.

β-Keto acid (C-05), which formed upon the further oxidation of β-hydroxyacid (C-02) as a result of decarboxylation, more pronounced in the case of sodium hypochlorite, was converted into acetophenone. Chloroform, detected in the analysis of volatile organochlorine compounds, formed, probably, in a haloform reaction of acetophenone. The same reaction was also responsible for the decreasing concentration of mono- and dichloroderivatives of acetophenone with increasing concentration of chlorinating agents.

The mechanism of decarboxylation, described in [20] for α,β-dibromosubstituted carboxylic acids, takes place in the case of β-chlorinated derivatives (C-03) and (C-04) as well, which causes the formation of β-chlorostyrene (C-08) and phenylacetic aldehyde (C-19) appearing in the isomerization of the enol intermediate. The former product (C-08) was dominant when chlorine water was used, while the latter (C-19) formed only in the case of sodium hypochlorite. The dihalogenation of β-chlorostyrene gave (1,2,2-trichloroethyl)benzene (C-14), the amount of which was naturally higher in the reaction of substrate with chlorine water.

At the maximum concentration of chlorinating agents, (1-hydroxy-2,2-dichloroethyl)benzene (C-13) was dominant; it could form as a result of both conjugate addition to C-08 and in the nucleophilic substitution at C-14. The formation of a keto aldehyde (C-21) was observed only in the case of sodium hypochlorite; it could appear as a halogenation product of both acetophenone (C-10) and phenylacetic aldehyde (C-19).

The electrophilic attack by the double bond was caused by a polarized chlorine molecule or hypochlorous acid in an undissociated form; their concentra-



Scheme 2. Transformation of dibenzoylmethane in an aqueous medium under the action of chlorine and sodium hypochlorite; *m/z* values are referred to the detected molecular ions.

tions were higher in chlorine water. This explains the higher degree of conversion upon the exposure of the substrate to chlorine water at an equimolar ratio of the reagents. With an excess of chlorinating agent, this difference disappeared. One should pay attention to the fact that compounds C-02 to C-16 dominate among the products of complete transformation under the action of chlorine water (Table 1). When sodium hypochlorite was used, on the contrary, the high levels of compounds C-16 to C-23 formed at late stages of transformation were recorded by gas chromatography—mass spectrometry.

Dibenzoylmethane chlorination. In the case of dibenzoylmethane, electrophilic aromatic substitution proceeded at the meta position of benzene rings due to the electrono withdrawing properties of the carbonyl group [21]. The reactive center was also the methylene moiety located between two carbonyl groups.

Based on the results of qualitative chromatographic—mass spectrometric analysis, we can assume that the transformation of dibenzoylmethane (D-01) in an aqueous medium under the action of chlorine and sodium hypochlorite proceeds in the directions shown in Scheme 2. For dibenzoylmethane, acidic decomposition, characteristic of 1,3-diketones, results in the formation of acetophenone and benzoic acid. Mono-, di-, and trichloroderivatives of acetophenone formed in the chlorination of acetophenone, and also as a result of cleavage of the molecule of dibenzoylmethane and its chlorinated derivatives. As a result of the haloform reaction, trichloroacetophenone was converted to benzoic acid; this reaction also gave chloroform (D-12), which was detected in the analysis of volatile reaction products by GC—MS.

The chlorination of dibenzoylmethane with an equimolar amount of chlorine or sodium hypochlorite in a neutral medium led to the formation monochloroderivatives of 1,3-diphenyl-2-chloropropane-1,3-dione (D-04) and 1-phenyl-3-(3-chlorophenyl)propane-1,3-dione (D-06). The degree of conversion of the initial substrate increased significantly with increasing concentration of chlorinating agents; dibenzoylmethane reacted with chlorine more actively than with sodium hypochlorite (Table 2). The formation of the D-06 compound, that is, a derivative

Table 2. Products of water chlorination of dibenzoylmethane, detected in chlorination with chlorine and sodium hypochlorite at different molar ratios of active chlorine ($c(\mathrm{Cl}^{\mathrm{act}})$) to the test substrate ($c(\mathrm{S})$) (μg); $m = c(\mathrm{Cl}^{\mathrm{act}})/c(\mathrm{S})$

Compound code	Molecular weight, Da	Chlorine water			Sodium hypochlorite		
		$m = 1$	$m = 5$	$m = 50$	$m = 1$	$m = 5$	$m = 50$
D-01	224	21570	10140	2540	20360	13100	10150
D-02	122	–	14.8	37.7	455	608	777
D-03	136	–	–	–	–	–	0.2
D-04	258	247	169	118	199	657	1286
D-05	292	–	697	1243	–	–	4.2
D-06	258	520	3030	4006	529	894	1768
D-07	154	104	54.2	8.7	2.6	5.1	7.8
D-08	106	–	–	4.5	–	–	2.8
D-09	222	–	2.5	4.6	–	–	0.6
D-10	120	–	–	–	–	–	0.3
D-11	188	452	215	68.4	1.6	2.3	4.1
D-12	118	–	8.9	25.7	–	6.4	22.1

monosubstituted by chlorine in the aromatic ring, is the dominant process in the case of chlorinated water. In the case of chlorine, the chlorination of dibenzoylmethane via its methylene moiety proceeded predominantly with the formation of a dichlorosusbstituted derivative (D-05), and for sodium hypochlorite, a monochlorosusbstituted derivative (D-04) was generated. With increasing concentration of chlorinating agents, the proportion of polychlorinated derivatives increased, especially for chlorinated water.

Thus, chlorine water is a more active chlorinating agent for ketones and 1,3-diketones. When such substrates are dissolved in water, an equilibrium between the keto and enol forms is established. The latter form preferably reacts with molecular chlorine and an undissociated form of hypochlorous acid, whose concentration is higher in chlorine water than in solutions of sodium hypochlorite. Furthermore, chlorine water appears to be a more active chlorinating agent in electrophilic aromatic substitution reactions in substrates bearing an aromatic ring deactivated by substituents. This explains the higher degree of conversion of the initial substrate, a larger variety of products, and higher levels of product chlorination attained in chlorination by chlorine water.

CONCLUSIONS

The results of the GC–MS study of water chlorination products of cinnamic acid and dibenzoylmethane with different molar excesses of chlorinating agents support the following conclusions:

(1) The chlorination of ketones and aromatic compounds bearing a deactivating substituent in the ring proceeds more actively in the case of chlorine water. Unsaturated carbon–carbon bonds are subjected to the most active chlorination.

(2) The variety of chlorinated products is larger if chlorine water is used.

(3) Increasing concentrations of chlorinating agents increase the concentration and enhance the diversity of organochlorine products.

(4) The chlorination of cinnamic acid and dibenzoylmethane leads to the formation of the following organic compounds, for which the maximum permissible concentrations (MPC) in water of water bodies for industrial, potable, domestic water use were set: acetophenone (0.1 mg/L), benzaldehyde (0.003 mg/L), benzoic acid (0.06 mg/L), chlorobenzene (0.02 mg/L), and chloroform (0.06 mg/L). However, the toxicological properties of most water chlorination products identified by mass spectrometry remain unknown so far.

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