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Formation of organochlorine by-products during chlorination of wastewaters containing cyclohexene and butanol

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Abstract

One of the widely accepted approaches for wastewater treatment in Russia involves its chlorination with the aim of disinfection. The present work deals with formation of organochlorine by-products during treatment of wastewaters containing butanol and cyclohexene. These two chemicals often appear in wastes of various chemical plants. Butanol and cyclohexene were subjected to chlorination in laboratory in conditions close to these used in reality. Aqueous chlorine and sodium hypochlorite were used as chlorination agents.

A significant array of organochlorine compounds, including ecotoxicants with pronounced mutagenicity was detected in both cases by means of GC-MS. Volatile and semivolatile products were identified and quantified. A possible environmental hazard of the chlorination of wastewaters containing cyclohexene and butanol was unambiguously demonstrated.

1 Introduction

In modern cities industrial wastewaters are often mixed with municipal wastewaters. The treatment of these combined wastes involves mechanical and biological methods. On the final stage chlorination is used with the aim of disinfection. As a result reaction of chlorination of organic compounds present in wastewaters takes place. The negative aspects of this procedure have never been studied in details. The most obvious among these undesirable effects is the formation of toxic and mutagenic organochlorine compounds which further appear in natural water basins.

Cyclohexene and butanol are known to be major chemical products used in various industrial processes. These compounds are quite hazardous themselves. Their maximal allowable concentration values for water in Russia are 0.02mg/l, and 0.03mg/l correspondingly. To study possible products of their transformation cyclohexene and butanol were subjected to chlorination in water with molecular chlorine and sodium hypochlorite. Both reagents are used in the industrial disinfection.

2 Methods

The chlorination was conducted in 250 ml flasks in the dark at room temperature and constant stirring in 0.02M phosphate buffer solutions (pH=7.0). Reaction time was 24 hrs. In all the experiments substrate content was 10^{-4} mol while that of active chlorine varied from 0.01 g/l to 1.40 g/l. Concentration of active chlorine was determined by iodometric titration just before every chlorination procedure. High levels of active chlorine were used in order to get higher concentrations of the products and to facilitate the elucidation of the chemical transformation mechanisms for cyclohexene and butanol. Unreacted chlorine was eliminated with sodium sulphite. Semivolatile products of chlorination were extracted with dichlormethane (15 ml x 3) at pH = 2. Acidification of the reaction mixture allowed us to isolate not only neutral compounds but also possible acidic compounds. Combined extracts were evaporated up to 1 ml.

Volatile products of chlorination in the reaction mixture were analyzed with «Purge and Trap» system (5ml) connected to HP 5973 MSD instrument using VOC (60m) column. 1,2-Dichloroethane-d4 and bromofluorobenzene were used as internal standards.

Semivolatile products were analyzed in the dichloromethane extracts with HP 5989 «Engine» mass spectrometer using HP-5 (30m) fused silica capillary column. Naphtalene-d8 and phenanthrene-d10 were used as internal standards.

Interpretation of the results (chromatograms and mass spectra) was performed using NBS and Wiley libraries and manually taking into account fragmentation pathways of organic compounds.

3 Results and discussion

Cyclohexene appeared to be quite sensitive towards chlorination. The detected products may be divided into two groups: cyclohexane derivatives and halosubstituted compounds formed after the breaking of the cycle.

The results demonstrate that at high ratio chlorine/substrate traces of the authentic compound are detected only in the case of hypochlorite while aquatic chlorine brings to complete transformation of cyclohexene (Table 1). Two other products containing double bonds (cyclohexenon and clorocyclohexene) were detected only in the case of the minimal chlorine dose.

A priori two major products were expected: 2-chlorocyclohexanol and 1,2-dichlorocyclohexane (see Table 1). 2-Chlorocyclohexanol, forming via the mechanism of conjugated addition, is in fact the principal product of transformation with both chlorinating agents. The concentration of this product remains quite high independently of the ratio chlorine/substrate. The alternative 1,2-dichlorocyclohexane forms in relatively small amounts since the concentration of nucleophilic Cl^- is incomparably lower than that of H_2O. However, at higher ratios chlorine/substrate the increase in concentration of Cl^- leeds to the adequate increase of 1,2-dichlorocyclohexane content.

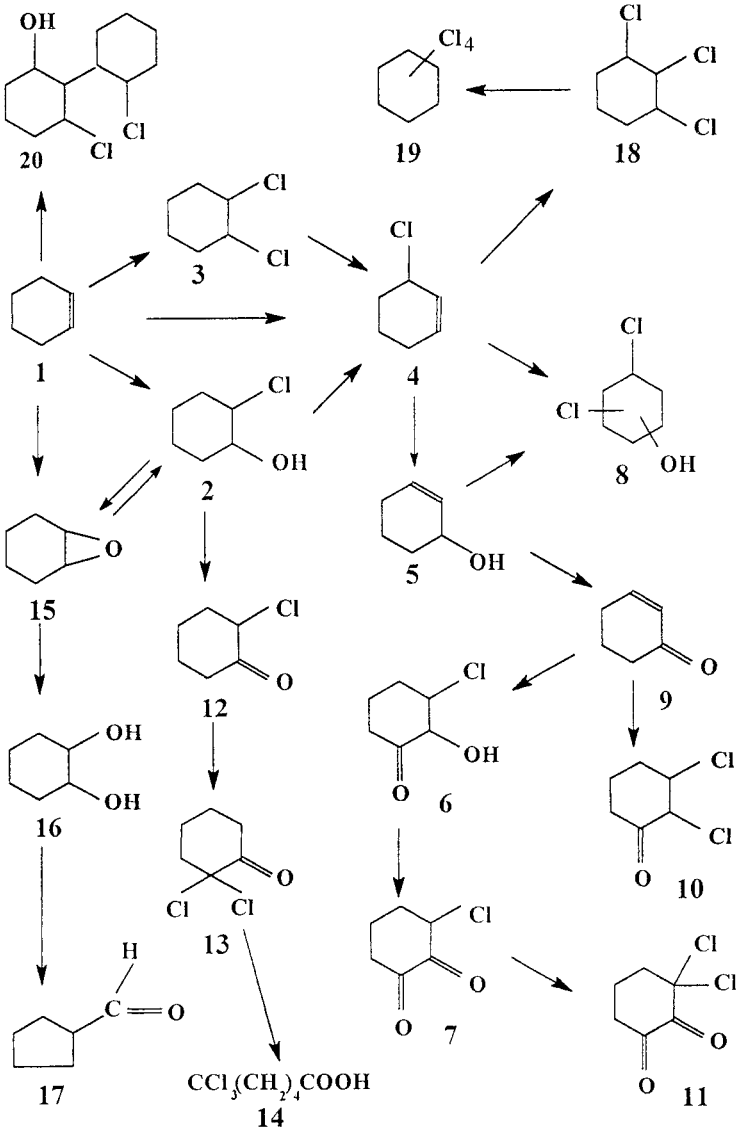
Two other products are detected in reasonable quantities . In the case of aqueous chlorine dimerization appeared to be quite a noticeable process (Table 1, Figure 1). Chlorinated dimer is never detected for ClO^-. On the other hand reaction with ClO^- brings to formation of dichlorocyclohexandione, completely absent in the experiments with aqueous chlorine. Actually the data in Table 1 demonstrate significant difference in the by-products (both qualitative and quantitative) formed using two different chlorinating agents.

The formation of compounds of the second group (first of all haloforms) during water chlorination is rather well known phenomenon for a significant array of organic substrates and natural humic matter. The most important toxicant in this group is chloroform being a major volatile by-product for cyclohexene. Besides that comparing its levels for hypochlorite and aqueous chlorine one can see that hypochlorite is much safer in terms of chloroform formation. In some cases concentration of chloroform in the experiment with chlorine was almost 100 times higher than in the similar experiment with hypochlorite. Similar situation may be marked for 1,2-dichloroethane and bromodichloromethane.

Figure 1 illustrates the formation of by-products of the first group. For example formation of clorocyclohexene may involve allylic chlorination or proceed via dehydrohalogenation of dichlorocyclohexane or dehydratation of 2-chlorocyclohexanol. This unsaturated compound is responsible for further formation of a number of isomeric dichlorocyclohexanols and trichlorocyclohexanes. Formation of cyclopentancarboxaldehyde may proceed via pinacoline rearrangement of the intermediate cyclohexanediol.

As to butanol it is difficult to propose a reliable scheme of its transformation. Transformation starts with chlorination of the hydrocarbon moiety followed by the processes of oxidation, substitution, dehydrohalogenation and C-C bonds cleavages. The most abundant products are chlorinated methanes, ethanes and

Figure 1. Scheme of cyclohexene transformation



1 - cyclohexene, 2 - 2-chlorocyclohexanol, 3 - 1,2-dichlorocyclohexane, 4 - 3-chlorocyclohexene, 5 - cyclohexene-2-ol, 6 - 3-chloro-2-hydroxycyclohexanol, 7 - chlorocyclohexandione, 8 - dichlorocyclohexanol, 9 – cyclohexenone, 10 - dichlorocyclohexanone, 11 - dichlorocyclohexandione, 12 - 2-chlorocyclohexanone, 13 –dichlorocyclohexanone, 14 - ω-trichlorohexanoic acid, 15 - cyclohexenoxide,16 - dichlorocyclohexanol, 17 – cyclopentancarboxaldehyde,18 - trichlorocyclohexane, 19 - tetrachlorocyclohexane, 20 - dichlorinated dimer

Table 1. The products (mkg) of aquatic chlorination of cyclohexene (10^{-4} mol)

Compound	Molar ratio Cl/Cyclohexene (concentration of active chlorine g/l)									
	1:1 (0.028)		1:2 (0.056)		1:10 (0.28)		1:20 (0.56)		1:50 (1.40)	
	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2
Cyclohexene	328.8	-	2.3	-	1.1	-	0.25	-	0.23	-
3-Chlorocyclohexene	**2.4**	**0.45**	-	-	-	-	-	-	-	-
Cyclopentancarboxaldehyde	0.23	-	0.34	-	0.45	1.6	0.39	1.3	0.34	2.4
Cyclohexenoxide	6.0	21.6	5.8	36.8	8.8	44.0	7.2	28.1	17.6	25.0
Cyclohexenon	35.1	-	-	-	-	-	-	-	-	-
2-Chlorocyclohexanol	7112	6129	7395	7482	9330	8767	3375	9770	1967	5210
2-Chlorocyclohexanone	2.1	8.5	2.2	4.3	7.7	10.5	5.3	18.7	4.3	44.6
1,2-dichlorocyclohexane	2.3	11.0	22.0	8.2	34.4	174.7	23.5	203.6	54.9	520.5
Dichlorocyclohexanone (Σ isomers)	0.79	-	3.4	-	12.8	8.8	8.9	34.8	2.4	19.7
Chlorocyclohexandione	16.3	-	31.1	-	-	-	-	-	-	-
ω-trichlorohexanoic acid	7.9	-	13.3	-	-	-	-	-	-	-
Dichlorocyclohexanol (Σ isomers)	16.1	-	30.5	10.3	13.3	72.6	4.2	85.7	-	387.9
Dichlorocyclohexandione	82.2	-	208.1	-	106.1	-	111.4	-	13.2	-
Trichlorocyclohexane (Σ isomers)	-	-	-	-	-	16.2	-	28.7	-	43.4
Tetrachlorocyclohexane	6.8	-	4.3	-	-	-	-	-	-	-
Dichlorinated dimer	-	-	-	-	-	148.3	-	142.8	-	434.0
Chloroform	**4.7**	**43.1**	**6.0**	**83.5**	**4.7**	**190.9**	**6.0**	**560.0**	**15.7**	**485.0**
1,2-dichloroethane	0.04	-	0.04	-	0.04	0.11	0.02	0.13	0.03	6.0
Carbon tetrachloride	**0.28**	**0.08**	**0.18**	**0.05**	**0.2**	**0.15**	**0.11**	**0.06**	**0.19**	**2.9**
Bromodichloromethane	**0.38**	**0.64**	**0.30**	**0.62**	**0.30**	**0.76**	**0.24**	**0.69**	**0.32**	**13.1**
1,1,2-Trichloroethane	-	-	-	-	-	-	-	-	-	**1.8**

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Table 2.Chlorinated methanes, ethanes and propanes (mkg), formed during chlorination of butanol (10^{-4} mol).

Compound	Molar ratio Cl/Butanol (concentration of active chlorine g/l)									
	1:1(0.028)		1:2(0.056)		1:10(0.28)		1:20(0.56)		1:50(1.40)	
	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2
Chloroform	**40.5**	**4.8**	**102.1**	**10.3**	**54.4**	**33.1**	**54.7**	**38.7**	**73.3**	**12.0**
Carbon tetrachloride	-	-	-	**0.03**	**0.02**	**0.16**	**0.06**	-	**0.09**	**0.3**
Bromodichloromethane	**0.98**	**0.22**	**0.81**	**0.43**	**0.61**	**0.96**	**0.55**	**1.24**	**0.36**	**0.21**
1,1-Dichloroethane						**0.13**		**0.03**		**0.29**
1,1,1-Trichloroethane	-	-	-	-	-	-	-	-	-	**0.10**
1,1,2-Trichloroethane	-	-	-	-	-	**0.23**	-	**0.07**	-	**0.25**
Pentachloroethane	-	-	-	-	-	**0.39**	-	**0.67**	**0.70**	**2.0**
Hexachloroethane	-	-	-	-	-	-	-	1.04	-	0.15
1-Chloropropane	1.84	0.51	8.0	1.82	3.6	2.8	0.86	1.73	1.65	0.40
1,2-Dichloropropane (Σ isomers)	-	-	**2.5**	**0.17**	**7.3**	-	**4.0**	**0.80**	**5.3**	**0.62**
1,1-Dichloropropanon-2	0.12	0.84	0.51	0.54	-	0.62	-	0.77	-	3.5
1,3-Dichloropropane	-	-	**1.0**	-	**1.0**	**0.92**	**0.41**	**0.33**	-	-
1,1,1-Trichloropropanon-2	1.0	0.98	1.57	2.4	-	2.5	-	2.7	-	7.5
1,1,2-Trichloropropane	-	-	-	-	-	-	-	-	-	0.13
1,2,3-Trichloropropane	-	-	-	-	-	-	-	**0.05**	-	**0.15**
Tetrachloropropane	-	-	-	-	-	-	-	0.17	-	0.33

Table 3. The products (mkg) of aquatic chlorination of butanol (10^{-4} mol).

Compound	Molar ratio Cl/Butanol (concentration of active chlorine g/l)									
	1:1(0.028)		1:2(0.056)		1:10(0.28)		1:20(0.56)		1:50(1.40)	
	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2	NaOCl	Cl_2
Furanon-2	-	-	-	-	-	-	-	5.1	-	2.1
4-Chlorobutanol-1	-	-	-	11.0	-	18.6	4.1	16.6	7.2	30.0
Chlorotetrahydrofuran	-	-	-	-	1.6	4.2	1.3	3.7	2.0	6.6
Butylchloroacetate	1.7	-	2.1	-	2.7	-	4.0	2.2	2.3	-
Chlorinated ester	2.1		1.8		0.56		0.87	-	-	-
Chloroketoalkohol	-	-	-	-	-	-	-	-	-	4.1
Butanoic acid	-	-	-	-	-	-	-	-	-	2.0
Chlorobutenol (Σ isomers)	-	-	-	-	-	-	-	4.7	-	16.0
Butanal	**228.8**	-	**42.0**	-	**52.3**	-	**57.6**	-	**27.9**	-
Tetrahydrofuran	1.0	0.11	6.7	0.48	4.9	1.03	1.8	1.06	0.20	2.7
Acetylchloride	-	-	-	-	-	0.66	-	0.64	-	-
Butylformiate	0.59	0.14	1.0	0.20	0.64	0.18	0.32	0.27	0.12	-
Butylacetate		0.21		0.17		0.23	0.32	0.28	0.28	0.14
Vinylbutirate	1.15	-	1.30	-	0.97	-	0.75	-	0.68	-
Propylbutirate	-	0.09	-	0.13	-	0.12	-	0.16	-	0.23
Butylisobutirate	0.65	-	1.22	-	0.78	-	0.59	-	0.61	-
Butylbutirate	0.54	-	0.65	-	0.52	0.21	0.55	0.25	0.53	0.19

propanes including chlorinated acetones. It is worth mentioning that these components are characteristic mainly for aqueous chlorine (Table 2).

On the other hand chloroform is detected in higher concentration in reaction of butanol with OCl^-. Thus, formation of chloroform is not so straightforward and seriously depends on the nature on authentic organic compound. Its formation should involve a variety of mechanisms and requires careful studies.

Chlorination of butanol brings to the formation of a number of esters (due to reaction of the forming acids and alkohols - propylbutirate, butilbutirate, butylisobutirate, butylacetate, butylchloroacetate, butylformiate). One of the major products for hypochlorite chlorination appeared to be butanal (Table 3). It is a primary by-product of oxidation. For some reason it is never detected in reaction with aqueous chlorine.

Another point worth mentioning deals with mutagenicity and cancerogenicity of the forming compounds. The chemicals which possess known mutagenicity and cancerogenicity are marked with bold in the Tables. Only occasional information may be found concerning toxicological characteristics of other detected compounds. The absence of bold font doesn't mean the absence of any hazardous biological activity. It does mean that we didn't find any available toxicological information. In fact we do not know does one or another compound which forms during chlorination represents any danger to environment or not.

To clarify at least general hazardous properties of the reaction mixtures we started biological experiments with Daphnia magna (toxicity), Ames test and micronucleus test (mutagenicity). These results will appear some time later and allow to estimate the combined effect of the by-products on the environment.

4 Conclusions

1. A significant array of by-products was detected during aquatic chlorination of butanol and cyclohexene with chlorine and hypochlorite.
2. The composition of by-products depends on the nature of authentic compound, chlorinating agent and ratio chlorine/substrate.
3. Hypochlorite is a preferential chlorinating agent in case of cyclohexene, while in case of butanol situation is not obvious.
4. Chloroform is the most important volatile by-product of chlorination forming via a number of mechanisms. These mechanisms require additional studies.
5. There is not enough information concerning toxicological properties of the arising by-products.