Application of Mechanical Activation to Decomposition of Toxic Chlorinated Organic Compounds

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Abstract

The possibilities of the application of mechanochemical method for performing dechlorination process with chlorinated aromatic compounds and polyvinylchloride are considered. On the basis of spectral investigations, we proposed possible mechanism and the composition of products of mechanochemical dechlorination of chlorinated aromatic compounds. Mechanochemical transformation of hexachlorobenzene, 1,4-dichlorobenzene and octachloronaphthalene, *o*-nitrochlorobenzene in the presence of alkaline agents proceeds with the formation of phenols and naphthols. This process can be represented as nucleophilic substitution in the aromatic ring. It is demonstrated that the intensity of mechanical action affects the relations between the main products of *o*-nitrochlorobenzene is 2-nitro-3-chlorophenol; under soft conditions, it is *o*-nitrophenol.

INTRODUCTION

Industrial production of polymers, defoliants, paper, high-temperature chlorination processes are often connected with the use and formation of chlorinated organic compounds, most of which are dangerous ecological toxicants. The application of chlorinated organics in technological processes, agriculture and as household chemical goods is also inevitable in future, but it is accompanied by the accumulation of wastes composed totally of toxic compounds or containing them among other substances [1]. At present, the amount of polyvinylchloride production in the developed countries reaches several million tons; however, not more than 10 % of its wastes are processed; other wastes are incinerated or buried. Burying into soil causes a decrease in the area of agricultural lands. Pyrolytic processing and incineration of wastes constitutes direct danger for the environment because it can be accompanied by emission of extremely toxic chlorinated derivatives, *i. e.*, dioxins, into the biosphere [2].

High cost of installations in which the combustion of chlorinated wastes occurs most completely has promoted development of new dechlorination procedures, which is still going on. However, a universal, economically profitable and ecologically safe method has not been proposed yet. Because of this, active search for methods to provide conversion of chlorinated organics is being performed.

For instance, it is proposed to conduct dechlorination of polychlorinated biphenyl in sodium borohydride solutions at a temperature of 120-162 °C for several hours [3]. It is shown that a number of toxic chlorophenols can be subjected to photosensibilized mineralization in aqueous solutions in the presence of TiO₂ and trivalent iron ions [4, 5]. Thermolysis of dichlorobenzenes and chlorophenols in the atmosphere of hydrogen at a temperature of 1000 K proceeds mainly with the formation of benzene [6]. The authors of [7] proposed to perform catalytic hydrodehalogenation of chlorinated benzenes and phenols.

A number of approaches has been proposed on the basis of the application of mechanochemical treatment of chlorinated organic wastes in mixture with inorganic reducing agents, for example calcium and magnesium, oxides of alkaline earth metals [8]. The use of calcium hydride as reducing agent turned out to be most efficient. For example, hexachlorobenzene was subjected to mechanical treatment with calcium hydride [9]:

 $3CaH_2 + C_6Cl_6 \rightarrow 3CaCl_2 + 6C + 3H_2$

This reaction, similarly to other reactions with the participation of calcium hydride, starts as a usual solid-phase mechanochemical transformation and passes into the mode of self-propagating high-temperature combustion. High temperature developed during this process (~2550 K) provides completeness of the decomposition of the chlorinated organic compound.

The possibility of complete transformation of toxic organic compounds (polychlorobiphenyl, dichlorodiphenyltrichloroethane (DDT) and chlorinated derivatives of benzene) into nontoxic products is demonstrated, when the agents binding chlorine are calcium hydride, magnesium and calcium oxide [8, 10, 11].

The authors of [12] performed mechanical activation of a mixture of calcium oxide and polyvinylchloride and demonstrated that almost complete binding of chlorine from polyvinylchloride into the basic calcium chloride can be achieved, with the simultaneous formation of polyethylene:

 $[CH_2CHCl]_n + CaO \rightarrow CaOHCl + [CH=CH]_x$

The process occurs in mechanochemical activators like planetary mill and in the apparatus of the type of multi-step attritor, specially designed and built by the authors. The process takes several hours.

Mechanochemical method of dechlorination may turn out to be promising as one of the versions to use mechanochemistry for conducting various processes in organic synthesis. For instance, solid-phase reactions are used in preparative chemistry and in chemical technology to obtain a variety of substances. As a rule, solid-phase reactions require elevated temperature, in some cases very high one. The use of mechanochemical equipment with high intensity of mechanical energy input to reagent particles allows performing solid-phase reactions of different types at low temperature [13–15].

In the present work we investigated mechanochemical transformations of chlorinated aromatic compounds (hexachlorobenzene, octachloronaphthalene, 1,4-dichlorobenzene, o-nitrochlorobenzene) and polyvinylchloride under the joint treatment with various inorganic additives to bind organic chlorine [16]. At the same time, we made an attempt to conduct this process under hydrothermal conditions. It is shown that the amount of threshold mechanical action affects the relation between the main products of o-nitrochlorobenzene transformation.

The functional nature of the products of mechanochemical transformations occurring with the participation of chlorinated aromatic compounds and polyvinylchloride is studied with the help of IR and NMR spectroscopy. On the basis of spectral investigation, we proproposed the composition of the products of mechanocemical dechlorination and the possible mechanism of their formation. The goal of the work was to develop mechanocemical approaches to the processing of chlorinates organics and to the symthesis of organic compounds with the participation of chlorinated benzenes.

EXPERIMENTAL

The following reagents were used: 1,4-diclorobenzene ("Sigma", 99 %), gexachlorobenzene ("Sigma", 99 %), o-nitrophenol ("Sigma", 99 %), o-nitrochlorobenzene ("Aldrich", 99 %), polyvinilchloride (ICN M_r 10 000), calcium hydride ("Aldrich", 99 %), acetonitrile ("Kriokhrom", first class), hexane ("Kriokhrom", first class), diethyl ether ("Ekros"), calcium oxide ("Sigma", 95 %), acetic acid (ICN, 99 %), calcium hydroxide of "ch.d.a." grade (pure for analysis) ("Alizarin", GOST 24363-80) containing halides at a level less than 0.05 %. Organic solvents were dehydrated and purified according to standard procedures [17].

Melting points were measured with Koffler stage (VEB Analytic). The IR spectra were recorded with VEKTOR 22 (Bruker) spectrometer in tablets with KBr, UV spectra were recorded with UV-240 instrument (Shimadzu). The PMR spectra were recorded with WP-200-SY instrument (Bruker) for solutions in deuterated acetonitrile, with tetramethylsilane as internal standard. The analysis by means of HPLC was performed with an analytical system for HPLC consisting of HPP 5001 high-pressure piston pump, UV-VIS detector LSD 2563 (λ = 280 nm), LCI 30 looping batcher with loop volume of 20 µl, reversed-phase column Nucleosil C-18 with dimensions 4×150 mm, filled with the particles 7 μ m in size. The systems used as elutriators were: acetonitrile - water (80:20) and acetonitrile - water - acetic acid (40:60:1).

Mechanical treatment was performed in AGO-2 planetary centrifugal mill (drum rotation frequency: 630 rpm) with water cooling, and in SPEX 8000 vibration mill with steel drums and steel milling bodies. In all the experiments, the ratio of the mass of milling bodies to the reagent mass was 20 : 1. The mass of milling bodies of spherical shape, 5 mm in diameter, loaded into a standard steel drum from the equipment of SPEX 8000 and the steel drum of AGO-2 was 60 and 200 g, respectively.

Determination of chloride ion in the products of mechanochemical treatment was performed by mercurimetric titration or by Volgard's procedure [18] after neutralization of the residual alkali or calcium oxide by diluted nitric acid.

Dechlorination by calcium oxide

A mixture of solid calcium oxide (2.0 g) and octachloronaphthalene (3.0 g) was treated in SPEX 8000 vibration mill and in AGO-2 planetary mill for 16 and 4 min, respectively. Experiments in AGO-2 were performed in inert atmosphere (argon) and in air. The amount of octachloronaphthalene after mechanical treatment was determined spectrophotometrically and by means of HPLC (elutriator - $CH_3CN : H_2O = 80 : 20$).

The products of interaction of octachloronaphthalene with calcium oxide, obtained by mechanochemical treatment in the air, were dissolved in water. The aqueous suspension was exhaustively extracted with carbon tetrachloride. The organic extract was investigated by means of IR spectroscopy after removal of the solvent under vacuum. The IR spectrum, cm^{-1} : 1100 (vAr–O), 3440 (vO–H) [19]. The concentration of chloride ion was determined by titration according to Volgard.

It was shown by means of HPLC that the octachloron aphthalene content decreases under mechanical treatment by 75 % in inert atmosphere and by a factor of 2 in the air. It was established with the help of titration according to Volgard's procedure that 65 and 37 % of chlorine, respectively, is transformed into inorganic water-soluble form Cl⁻. With a decrease in the intensity of mechanical action on the system (replacement of the planetary mill by vibration mill SPEX 8000), no noticeable transformation of octachloron aphthalene was observed. It was shown by independent methods (spectrophotometry and HPLC) that a decrease in octachloron aphthalene was about 3.5 %.

Intensive bands observed in the IR spectrum of the products of mechanical treatment of octachloronaphthalene with calcium oxide at 1100 and 3440 cm⁻¹ are assigned to stretching C–O and O–H vibrations, respectively. The IR spectrum also exhibits weakly resolved characteristic bands of the initial chlorinated organic compound due to the presence of chlorine in the aromatic ring (878, 787, 673, 572 cm⁻¹) [20].

Dechlorination by potassium hydroxide

Mixtures of octachloronaphthalene with KOH (2.0 : 3.0 g) and hexachlorobenzene – KOH (2.5 : 3.5 g) were treated in AGO-2 planetary mill for 4 min. Experiments in AGO-2 were performed in air. Amounts of octachloronaphthalene and hexachlorobenzene after mechanical treatment were determined by means of HPLC (elutriator – $CH_3CN : H_2O = 80 : 20$).

Solvent (in the order of extracting)	Mass of octachloronaphthalene transformation products, mg	Mass of hexachlorobenzene transformation products, mg
Hexane	36	70
Carbon tetrachloride	2	< 1
Diethyl ether	37	10

TABLE 1

Relative amounts of products of mechanical treatment of octachloronaphthalene and hexachlorobenzene in organic extracts

In order to estimate the transformation degree, aqueous suspensions of the products of mechanical treatment of octachloronaphthalene and hexachlorobenzene with solid potassium hydroxide were preliminarily neutralized with acid and then extracted sequentially by hexane, carbon tetrachloride and diethyl ether. The mass of transformation products, determined after the removal of solvent under vacuum, is shown in Table 1. The initial mass of octachloronaphthalene taken for mechanical treatment was 100 mg.

The products extracted with diethyl ether and hexane were dried above P_2O_5 and examined by means of IR spectroscopy (Table 2). The IR spectra of hexane and ether extracts were similar both for hexachlorobenzene and for octachloronaphthalene. The spectra of transformation products of hexachlorobenzene and octachloronaphthalene contained bands which were absent from the spectra of the initial compounds. Interpretation of absorption bands of the products extracted with diethyl ether is

TABLE 2

Bands of octachloronaph-Assignment Bands of hexachloroben-Assignment zene products, cm^{-1} thalene products, cm⁻¹ 3440 Stretching vibration 3513 Stretching vibration of O-H bond of free O-H group 1390 Bending out-of-plane 1390 Bending out-of-plane vibration of O-H vibration of O-H 1725-1660 1725-1660 Stretching vibration of C=O Stretching vibration of C=O 1080 The same C-O 1194 The same C-O 827 The same C-Cl 828 The same C-Cl 463Out-of-plane vibration 470Out-of-plane vibration of C-C ring of C-C ring

 $\label{eq:Interpretation of absorption bands in the IR spectrum of products of mechanical treatment of octachloronaphthalene and hexachlorobenzene$

presented in Table 2. Characteristic bands of the initial chlorinated organic compounds, due to the presence of chlorine in aromatic ring, are absent from the IR spectra.

An intensive wide band at 1390 cm^{-1} corresponds to the plane bending vibration of the O–H group of the aromatic ring [19]. Changes in the character of substitution in the aromatic system leads to the manifestation of out-of-plane vibrations of the ring and stretching C–Cl vibrations in the IR spectrum with a frequency of 470 and 830 cm⁻¹, respectively [21].

Dechlorination in hydrothermal mode

Octachloron aphthalene and hexachlorobenzene were treated mechanically in hydrothermal mode in AGO-2 activator mill for 4 min. The ratio of volumes of the solid and liquid phases was chosen according to [22]. A 40 % solution of potassium hydroxide was used as the liquid phase. After neutralizing the alkali with the solution of nitric acid, the products of mechanochemical synthesis were exhaustively extracted with diethyl ether. The solution was removed with the help of rotary evaporator. he resulting mixture was examined by means of IR spectroscopy. The bands observed in the IR spectra of the products of hexachlorobenzene and octachloron aphthalene were, cm⁻¹: 3460–3520 (vO–H), 1390 (δ O–H).

Mechanochemical synthesis of o-nitrophenol and 3-chloro-2-nitrophenol

A mixture of potassium hydroxide (2.0 g) and o-nitrochlorobenzene (5.0 g) was mechanically treated in AGO-2 mill for 4 min. The products of mechanical treatment were dissolved in water; a dark-orange solution was obtained. The latter was exhaustively extracted with diethyl ether. The ether extract contained 78.8 mg (19 % of the initial amount of o-nitrochlorobenzene) of the dry residue, which, according to the HPLC data (elutriator $CH_3CN : H_2O : CH_3COOH = 40 : 60 : 1$), consisted of unreacted o-nitrochlorobenzene (98 %).

The aqueous phase was acidified to pH 3; a light-yellow solution was obtained. It was exhaustively extracted with diethyl ether till complete decoloration. The major part of solvent was removed from the extract with rotary evaporator. The resulting dark-yellow oily product was used to isolate individual substances by means of column chromatography on silica gel. Air-dry silica gel of KSK grade with grain size 0.160-0.250 mm was used for column chromatography. The elutriator system was hexane with increasing fraction of diethyl ether (from 20 to 80 %) and contained acetic acid 2 %. By chromatographing the oily dark-yellow product on a column (400×9 mm) with silica gel, we obtained o-nitrophenol, in the form of straw-coloured needles from ethanol) and 3-chloro-2-nitrophenol (light-yellow needles, from a mixture of hexane and diethyl ether).

The melting point of o-nitrophenol was 45 °C (from ethanol); literature data [25]: 45 °C. The PMR spectrum: 7.09 (1H, t, C-4), 7.18 (1H, d, C-6), 7.64 (1H, t, C-5), 8.12 (1H, d, C-3), 10.27, (1H, s, OH). The IR spectrum, cm⁻¹ : 1538 (v_sNO_2), 1335 ($v_{as}NO_2$), 1184 (stretching vibration of C-O bond). The UV spectrum,

 λ_{max} (ϵ), nm: 278.5 (6620), 351.4 (3210); literature data [24]: 79 (6600), 251 (3200). The PMR, UV and IR spectra of the resulting o-nitrophenol were identical to the spectra of the reference sample.

The melting point of 3-chloro-2-nitrophenol was 46.7 °C (from a mixture of hexane and diethyl ether), literature data [25]: 45-47 °C. The PMR spectrum, δ : 7.04 (1H, d, C-6), 7.09 (1H, d, C-4), 7.35 (1H, t, C-5), 9.61 (1H, s, O-H). The IR spectrum: 1537 (v_sNO_2), 1344 ($v_{as}NO_2$), 1182 (stretching vibration of C-O bond), 854 (stretching C-N). Results of elemental analysis, %: C 41.56, H 2.08, N 8.06, Cl 20.46. Calculated values, %: C 41.52, H 2.32, N 8.07, Cl 20.43.

Dechlorination by calcium hydride

Polyvinylchloride and 1,4-dichlorobenzene were mechanically treated with solid calcium hydride in SPEX 8000 vibration mill. Treatment time was varied from 180 to 340 min. Polyvinylchloride, 1,4-dichlorobenzene, octachloronaphthalene were mechanically treated with a mixture of calcium oxide and hydride in AGO-2 activator for 4 min. Calcium oxide was added into the mixture to avoid the transition of the process to explosive mode.

After mechanical treatment, the drums were unloaded, and the products were neutralized at first by ethanol and then by the nitric acid solution to pH 3.5. The products insoluble in water were collected on a nylon filter with a pore size of 0.2 μ m, dried above P₂O₅ and examined by means of IR spectroscopy. The concentration of chloride ion in the resulting solutions was determined by mercurometric titration. The results of chlorine titration in the products of mechanical treatment of 1,4-dichlorobenzene and polyvinylchloride with calcium hydride are presented in Table 3.

RESULTS AND DISCUSSION

Mechanochemical dechlorination by alkaline reagents

The use of high-intensity activators allows achieving high transformation degree within

SubstanceMill typeTime, minPercentage of inorganic form of chlorine (CI ⁻) in the products of mechanical treatment, %PolyvinylchlorideSPEX 80002105.41,4-Dichlorobenzene>18012.4>>34017.0PolyvinylchlorideAGO-2487Octachloron aphthalene>482.51,4-Dichlorobenzene>486				
of chlorine (Cl ⁻) in the products of mechanical treatment, %PolyvinylchlorideSPEX 80002105.41,4-Dichlorobenzene»18012.4»»34017.0PolyvinylchlorideAGO-2487Octachloron aphthalene»482.51,4-Dichlorobenzene»486	Substance	Mill type	Time, min	Percentage of inorganic form
of mechanical treatment, %PolyvinylchlorideSPEX 80002105.41,4-Dichlorobenzene>18012.4>>34017.0PolyvinylchlorideAGO-2487Octachloron aphthalene>482.51,4-Dichlorobenzene>486				of chlorine (Cl $$) in the products
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1,4-Dichlorobenzene»18012.4»34017.0PolyvinylchlorideAGO-2487Octachloronaphthalene»482.51,4-Dichlorobenzene»486	Polyvinylchloride	SPEX 8000	210	5.4
»34017.0PolyvinylchlorideAGO-2487Octachloronaphthalene»482.51,4-Dichlorobenzene»486	1,4-Dichlorobenzene	»	180	12.4
PolyvinylchlorideAGO-2487Octachloronaphthalene>482.51,4-Dichlorobenzene>486	»	»	340	17.0
Octachloronaphthalene>482.51,4-Dichlorobenzene>486	Polyvinylchloride	AGO-2	4	87
1,4-Dichlorobenzene » 4 86	Octachloronaphthalene	»	4	82.5
	1,4-Dichlorobenzene	»	4	86

TABLE 3

Results of chlorine titration in the products of mechanical treatment of 1,4-dichlorobenzene, octachloronaphthalene and polyvinylchloride with calcium hydride

relatively short time (4 min) of mechanochemical dechlorination. To achieve noticeable consumption of chlorinated aromatic compounds with the equipment similar to SPEX 8000 vibration mill, treatment for several hours is necessary [9, 26].

On the basis of results of IR spectroscopic investigation of the products formed under mechanochemical treatment of the mixture of calcium oxide with octachloron aphthalene, assumption has been made that dechlorination proceeds *via* the stage of nucleophilic substitution of chlorine. The bands at 1100 (vAr–O) and 3440 cm⁻¹ (vO–H) were observed in the IR spectra of hydrolyzed products. The following potential nucleophiles can be considered:

- active centres: Chockley states, located on the surface of calcium oxide;

- hydroxide ion, provided that hydrothermal synthesis conditions exist.

In order to confirm this hypothesis, we performed experiments with solid potassium hydroxide and its solution under hydrothermal mode. After mechanical treatment with solid potassium hydroxide, it was established that the mass of the initial substances and total mass of the products of mechanochemical treatment of octachloron aphthalene and hexachlorobenzene with solid potassium hydroxide are substantially different from each other (see Table 1), which is explained by the substitution of chlorine atoms by lighter oxygen atoms. Provided that chlorine is substituted with hydroxide ion, 68 and 51 % of organic chlorine is transformed into the inorganic form (chloride ion) during mechanical treatment of octachloron aphthalene and hexachlorobenzene, respectively. The amount of extragents used at the first two stages was sufficient for complete isolation of the chlorinated aromatic compounds, so it is easy to estimate the transformation degree. It is more than 65 % for octachloron aphthalene and more than 20 % for hexachlorobenzene.

It was demonstrated by means of IR spectroscopy that mechanochemical treatment of octachloronaphthalene and hexachlorobenzene with solid potassium hydroxide and its solution results in chlorine substitution by oxy group in the aromatic ring.

It was established with the help of results of the comparative studies that the character of substitution in the aromatic system affects its reactivity under the conditions of mechanical treatment. The interaction of potassium hydroxide and calcium oxide with 1,4-dichlorobenzene proceeds only under high intensity of mechanical action (acceleration of milling bodies: 600 m/s²) for 1.5–2 h, while o-nitrochlorobenzene easily form the products of nucleophilic substitution under much milder conditions. The reactivity decreases in the row: onitrochlorobenzene, octachloron aphthalene, hexachlorobenzene, 1,4-dichlorobenzene.

Mechanical treatment of 1,2-nitrochlorobenzene with potassium hydroxide in AGO-2 activator mill proceeds with the formation of 3-chloro-2-nitrophenol as the major product; its yield is 50 %, according to the HPLC data. The side product is o-nitrophenol (19 %). As a result of mechanical treatment in SPEX 8000 vibration mill, o-nitrophenol is formed with a yield of 74 %.

Results of the investigation of products of mechanical treatment of chlorinated aromatic compounds allow us to assume that the first stage of mechanochemical dechlorination of chloroaromatic compounds is nucleophilic substitution of chlorine atom in the aromatic ring by hydroxide ion. Further phenols can get oxidizer according to the ion radical mechanism giving semiquinones. The latter compounds are able to disproportionate with the formation of quinines and phenol, or to dimerize leading to peroxides [27]. The presence of a low-intensity band in IR spectra of the products of mechanical treatment of hexachlorobenzene and octachloronaphthalene in the region 1690- 1660 cm^{-1} (see Table 2) corresponding to the carbonyl group is evidence in favour of partial oxidation of the formed phenols into quinones.

Mechanochemical dechlorination by calcium hydride

The use of mechanochemical equipment similar to the SPEX 8000 vibration mill allows achieving high transformation degree (80-90%) for organic chlorinated compounds (polyvinylchloride, hexachlorobenzene, *etc.*) under the joint treatment with calcium hydride for 6-8 h [10, 11]. For polyvinylchloride and 1,4-dichlorobenzene as examples, we showed that, depending on experimental conditions, 5 to 17 % of organic chlorine is converted into inorganic form (chloride ion) in SPEX 8000 vibration mill.

After 220-300 min of treatment of polyvinylchloride with calcium hydride, the reaction can proceed in explosive mode:

$(-\mathrm{CH}_2-\mathrm{CHCl}-)_n+\mathrm{CaH}_2\rightarrow\mathrm{CaCl}_2+\mathrm{H}_2+\mathrm{C}$

resulting in complete decomposition of polyvinylchloride with the formation of calcium chloride and carbon ash.

Mechanochemical dechlorination in high-intensity AGO-2 activator proceeds by 85-99.9 % within several minutes. The results of chlorine titration in the products of mechanochemical

treatment of 1,4-dichlorobenzene, polyvinylchloride and octachloronaphthalene with a mixture of calcium hydride and oxide are shown in Table 3. If mechanical treatment is performed with milling bodies 3 mm in diameter, dechlorination degree increases to 99.9 %. Thus, a mixture of calcium hydride and oxide can be used for complete dechlorination of chlorinated polymers and benzenes, if mechanical treatment is performed in high-intensity vibration mills or planetary activators.

Non-aromatic products containing double bonds are formed as a result of mechanical treatment of chlorinated aromatics with calcium hydride. In the spectra of products of polyvinylchloride, 1,4-dichlorobenzene and octachloronaphthalene, we observed absorption at 1650 and 1590 cm^{-1} resulting from the stretching vibration of C=C bond, 870 cm⁻¹ for out-ofplane vibration of C-H bond, 710 cm^{-1} for pendular vibration of CH₂ group. As a result of acidic hydrolysis of the products of mechanical treatment of polyvinylchloride and 1,4-dichlorobenzene, partial protonation of double bonds or destruction of intermediate organometallic compounds may occur, so intensive bands of stretching vibration of isolated O-H group is present in the IR spectra in the region of $3600-3645 \text{ cm}^{-1}$.

The authors of [9] performed chromatography-mass spectrometry investigation of the products of reaction of hexachlorobenzene with calcium hydride obtained in SPEX 8000 vibration mill. It was demonstrated that hexachlorobenzene interacts with calcium hydride with the formation of the compounds of aromatic nature: benzene, toluene, naphthalene, diphenyls, chlorinated benzenes, anthracene, *etc.* However, we established by means of IR spectroscopy that the interaction of chlorinated aromatic compounds with calcium hydride under intensive mechanical treatment proceeds without the formation of aromatic compounds. These results are confirmed also by the HPLC analysis.

CONCLUSIONS

Mechanical treatment of chlorinated arenes in the presence of solid potassium hydroxide or calcium oxide is accompanied by the formation of phenols and naphthols. The latter compounds can undergo a number of transformations as a result of ion radical oxidation by the oxygen of the air with the formation of semiquinones and quinones, the structure of which depends on the structure of initial compounds.

It is shown that the intensity of mechanical action affects the relation between the main products of *o*-nitrochlorobenzene treatment. Under high-intensity mechanical action, the main product of the interaction of *o*-nitro-chlorobenzene is 2-nitro-3-chlorophenol; under soft conditions, it is *o*-nitrophenol.

It is established that dechlorination of hexachlorobenzene and octachloronaphthalene occurs when the conditions corresponding to hydrothermal mode are created in mechanochemical reactor.

Mechanical treatment of chlorinated aromatic compounds with calcium hydride leads to the products of non-aromatic nature. As a result of mechanical treatment of polyvinylchloride with calcium hydride and potassium hydroxide, similarly to the case of calcium oxide, the corresponding chloride and polymer containing double bonds are formed.

Mechanical treatment of chlorinated organic compounds in high-intensity AGO-2 mill allows achieving high transformation degree within several minutes, while the use of SPEX 8000 vibration mill and its analogs requires 6– 18 h [26].

The obtained estimates of transformation degree of chlorinated organic compounds allow us to conclude that the alkaline and reducing agents used in the present work are promising agents for mechanochemical dechlorination and can be used for utilization of chlorinated organic wastes and in mechanosynthesis of hydroxyl-substituted arenes.

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