Mechanism and Transformation Directions of 1,1,2-trichloroethane in the Liquid Phase by Low-voltage Electrical Discharges

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Abstract. 1,1,2-trichloroethane is transformed by the action of low-voltage (60 V DC) pulse discharge in the liquid medium in the nanostructure, cis-CICH = CHCl, trans-CICH = CHCl, CH₂ = CCl₂ and HCl. Conversion 1,1,2-trichloroethane 21 wt%, hydrogen chloride yield was 88.4 wt%, yield solid phase 11.6 wt%. The morphology and composition of solid phase products have been determined. According to energy dispersive X-ray spectroscopy, solid-phase products have an elemental composition, % atom: carbon — 90.5-94.2, chlorine — 1.3-5.4, oxygen — 3.1-4.5. The structures of 1,1-dichloroethylene and cis-, trans-1,2-dichloroethylene, as well as the isomer ratios were determined by ¹H NMR. The relative content of isomers: cis-1,2-dichlorethylene 44%, trans-1,2-dichlorethylene 34%, 1,1-dichloroethylene 22%. Quantum-chemical modeling revealed the mechanism of formation of the obtained dichlороethylene. According to the calculation results, 1,1,2-TCA is involved in the reaction in the triplet state. The difference in energy between the ground and excited states is 66.2 kcal/mol. The elimination of HCl is carried out by an activated chlorine atom generated during the transfer of 1,1,2-TCA under the action of electric discharges from the singlet state to the triplet state.

1. Introduction

The annual production of chlorine-containing hydrocarbons in the world is approaching a hundred million tons [1,2]. Only the volume of production of polyvinyl chloride (PVC) is currently about 60 million tons [3]. Along with PVC, vinylidene chloride, freons, solvents, synthetic glycerin and others are also produced. These industries accumulate large volumes of chlorine-containing technogenic waste, some of which are persistent organic pollutants [4,5].

The chlorinated solvent 1,1,2-trichloroethane (1,1,2-TCA) is widespread in the environment due to its widespread use as a degreasing agent, improper storage and disposal. 1,1,2-TCA is very stable in the environment, with an estimated half-life of 136–360 days in soil and 136–720 days in groundwater [6,7].

Destruction of 1,1,2-TCA has historically focused on direct combustion, physical adsorption, and catalytic dehydrochlorination [8-13]. Non-equilibrium atmospheric pressure plasma can be used to purify water from organochlorine pollutants. To date, devices have been developed for these purposes [14-19]. The main advantage of using discharges is the ability to destroy any chemically stable
substances without using chemical reagents, since reagents are formed under the action of the discharge itself. Methods for processing polychlorinated organic compounds based on the transformation of substrates in the liquid phase using low-voltage discharges were discussed in [20-22].

This article is devoted to identifying the directions of transformation of 1,1,2-TCA by the action of low-voltage pulsed discharges in a liquid medium. The results presented in this communication will assess the effectiveness and broad functionality of the impact of low-voltage discharges for the conversion of chlorine-containing waste into desirable products.

2. Experiment
Commercial 1,1,2-trichloroethane (>97%, SigmaAldrich) was used as a reagent. Figure 1 shows the setup of the working reactor (made of Teflon, 40 cm³ capacity) used in this study; graphite electrodes (6 mm diameter) were mounted inside it. A 60 V DC voltage source (VS) with a capacitance of 20090 μF was used to generate low-voltage discharges by varying the distance between the electrodes. The duration and power of discharge was controlled using a control unit. Under these conditions, the discharge energy is sufficient to break bonds and initiate chemical reactions [23]. A detailed description of the discharge-control unit and impact-energy calculation can be found elsewhere [24].

Figure 1. Scheme of the experimental setup. R, reactor; RC, reflux condenser; E, electrodes; M, manometer; V, valve; GT, gas trap; C, clutch; SM, stepper motor; D, stepper motor driver; PS, stepper motor power supply; CS, current sensor; MCS, microprocessor control system; VS, voltage source.

Experiment time 120 minutes. Electrical discharge parameters: average pulse duration 4.8 ms, average pulse frequency 4.3 Hz, average pulse amplitude 132.1 A, average pulse energy 0.51 J. Conversion 1,1,2-TCA 21 wt%, hydrogen chloride yield was 88.4 wt%, yield solid phase 11.6 wt%.

The morphology and elemental composition solid transformation products 1,1,2-TCA were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using Supra 50VP (Carl Zeiss AG, Germany) scanning electron microscope with the INCA (Oxford Instruments) microanalysis system.

The structure of liquid products was proved by NMR using a Bruker Avance-III spectrometer with an operating frequency of 400 and 100 MHz for 1H and 13C nuclei, respectively. CDCl₃ (δH 7.26 ppm) was added as a reference to the NMR tube.
3. Results and discussion

According to $^1$H NMR data in 1,1,2-TCA solution after discharges, the following products were found: cis-ClCH = CHCl δH 6.42 ppm, trans-ClCH = CHCl 6.24 ppm and CH$_2$ = CCl 5.38 ppm. Isomer content per 100 moles of CH$_2$Cl-CHCl$_2$: H$_2$C = CCl$_2$ - 0.46; trans-ClHC = CHCl 0.68; cis-ClHC = CHCl - 0.87. The relative content of isomers: cis-1,2-dichlorethylene 44%, trans-1,2-dichlorethylene 34%, 1,1-dichloroethylene 22%.

Solid-phase products show on Figure 2. These products consist mainly of nanostructures with an admixture of oligomeric components. The gaseous part of the 1,1,2-TCA transformation products contains mainly HCl.

According to energy dispersive X-ray spectroscopy, solid-phase products have an elemental composition, % atom: carbon — 90.5-94.2, chlorine — 1.3-5.4, oxygen — 3.1-4.5. The appearance of oxygen in the samples is not associated with the action of the plasma, since the discharge is generated in an oxygen-free atmosphere. Oxygen is found in nanostructures because carbon nanostructures adsorb oxygen from the surrounding atmosphere [25, 27].

![Figure 2. Scanning electron micrographs of the solid products.](image)

The probable mechanism for the transformation of 1,1,2-TCA into isomeric dichloroethylenes (Figure 3) under the action of electric discharges was determined by quantum-chemical modeling using Gaussian 09 software [26]. Computational methods based on density functional theory (DFT), B3LYP hybrid functional, and basis 6-311 + + G (d, p).

![Figure 3. Directions of transformation 1,1,2-TCA.](image)

In quantum-chemical calculations of the mechanism of the induced dehydrochlorination of 1,1,2-TCA, the action of low-voltage discharges is presented as the transfer of 1,1,2-TCA molecules from the ground singlet to the excited - triplet state. The structures of 1,1,2-TCA indicating the charges on the atoms in the singlet and triplet states are shown in Figure 4.
The difference in energy between the ground and excited states is 66.2 kcal/mol. The energy released during an electric discharge exceeds 900 kJ/mol [23]. An analysis of the structure of the excited states of 1,1,2-TCA shows that one of the carbon atoms retains a tetrahedral configuration, in which the C-Cl bond is stretched (1.87 Å) relative to the usual values (1.67 Å). Another carbon atom passed into a geometric state close to flat. One of the C-Cl bonds of this carbon has a length of 1.72 Å, the other C-Cl bond is stretched to 3.45 Å (an activated chlorine atom). The structure of the excited 1,1,2-TCA molecule indicates the possibility of intramolecular interaction of active chlorine atoms with hydrogens to form HCl and an unsaturated compound.

Since the excitation of 1,1,2-TCA molecules revealed the formation of a chlorine radical, quantum-chemical modeling performed calculations of several routes for the dehydrochlorination of 1,1,2-TCA into isomeric dichloroethylenes. The attack of activated chlorine on hydrogen at the neighboring carbon atom (intramolecular dehydrochlorination) or on the hydrogen of the second 1,1,2-TCA molecule in the singlet state (intermolecular dehydrochlorination) was chosen as the key stage in the analyzed routes of 1,1,2-TCA transformation. With the elimination of hydrogen, biradicals of the π- and σ-type are formed. The interaction of two biradicals of this type in the common triplet state leads to the intermolecular elimination of HCl.

The transfer of the binary system of radicals from the triplet state to the singlet state leads to the formation of 1,1-dichlorethylene (reaction 3) and trans-1,2-dichloroethylene (reaction 2). The mechanism of formation of cis-1,2 - dichlorethylene (reaction 1) was revealed by rotating the chloromethyl fragments of the cis-1,2 - dichloroethyl radical relative to each other by 360°. The resulting cis- and trans-dichloroethylenes are formed as a result of HCl elimination. A probable mechanism for the formation of isomeric dichloroethylenes was revealed by the method of quantum-chemical modeling. According to the calculation results, 1,1,2-TCA is involved in the reaction in the triplet state. The elimination of HCl is carried out by an activated chlorine atom generated during the transfer of 1,1,2-TCA under the action of electric discharges from the singlet state to the triplet state. Dehydrochlorination of 1,1,2-TCA proceeds along two routes - intramolecular and intermolecular with the participation of intermediates such as biradicals.

4. Conclusions
1,1,2-TCA under the action of low-voltage pulsed discharges in the liquid phase is transformed in several ways. Solid-phase products consist of nanostructures with an admixture of oligomeric formations with an elemental composition, atom%: carbon — 90.5-94.2, chlorine — 1.3-5.4, oxygen — 3.1-4.5. Liquid-phase products 1,1-dichlorethylene and cis-, trans-1,2-dichloroethylenes are formed as a result of HCl elimination. A probable mechanism for the formation of isomeric dichloroethylenes was revealed by the method of quantum-chemical modeling. According to the calculation results, 1,1,2-TCA is involved in the reaction in the triplet state. The elimination of HCl is carried out by an activated chlorine atom generated during the transfer of 1,1,2-TCA under the action of electric discharges from the singlet state to the triplet state. Dehydrochlorination of 1,1,2-TCA proceeds along two routes - intramolecular and intermolecular with the participation of intermediates such as biradicals.
5. References

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