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DISPOSAL OF POISONOUS ORGANIC HALIDES BY USING THE ELECTROCHEMICAL METHOD: DFT SIMULATION

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Abstract. Geometry optimizations at the UBP86/6-311++G** level of electronic structure theory have been performed for DDT, *β*-hexachlorocyclohexane, and heptachlor organic polychlorides as well for their positive and negative ions. The HOMO composition of these neutral molecules show no participation of the carbon-chlorine atomic orbitals, while LUMO of the calculated molecules include a major contribution of the anti-bonding character atomic orbitals from the two or three carbon-chloride bonds of each calculated molecule. Consequently, the negative ions were the most sensitive structure during the geometry optimization, showing the carbon-chloride bonds cleaving during the electronic structure calculations. Further geometry optimization of the obtained neutral intermediate molecules after the first and second reducing by two electrons show that the electrochemical dehalogenation of the organic poychlorides is sequential.

Keywords: poisonous pesticides, organic chlorides, electrochemistry, DFT, carbon-chloride bonds.

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Introduction

The electrochemical method for disposal of halogenated organic compounds leads to complete mineralization of organic halides. Generally, the electro-reductive treatments using new, improved electrochemical sensors, lead to partial recovery/recycling of chemicals, are regarded as an advantageous [1]. Methods of chemical and electro-chemical oxidation applied to organic pollutants attain, in most cases, a complete mineralization, being considered to have high-energy requirements [2]. Reduction will not lead to a complete mineralization, but to a complete dehalogenation, with a possible formation of double bonds. This has been proven for organic halides with one [3,4], two [5,6], three [7], four [8] or six [9] halogen atoms in their structure.

Dehalogenation reactions of halogen-alkanes have been studied by direct and indirect electrochemical reductions and classical kinetics. The electrochemical redox processes can be divided into two categories: direct (heterogeneous) and indirect or mediated (homogeneous) ones. Direct electrochemical reduction involves electrons accepted directly by the analyte from the cathode surface, while indirect electrochemical reduction occurs between the analyte and an electrogenerated species, which serves as catalyst. Some authors use the term “mediator” as an alternative for catalyst [1]. The catalyst can exist in the electrolyte solution or can be immobilized on the electrode surface, namely CME’s or chemically modified electrodes [1,10]. By modifying the surface of the electrodes by adsorption of molecules or ions, the surface reactivity and slow kinetics can be overcome [10].

Mechanistically, the halogen atoms are removed in a successive fashion, along with a two electron transfer at more and more cathodic (negative) potentials. This has been proven for polyhalogenated aromatics [11] and remains under question for polyhalogenated aliphatics. The difficulty of attaining sufficiently cathodic potentials would explain why complete dehalogenation does not always take place. The lower the number of halogens in the molecule, the lower the oxidation potential and, therefore, the molecule becomes more prone to oxidative biodegradation and as opposed to anaerobic reduction [12]. Baron *et al*. [12] have investigated the electrochemical reduction of (1,2,5,6,9,10 hexabromo cyclododecane) and (1,2 dibromo cyclododecane) at glassy carbon electrode, under catalytic (homogeneous) and non-catalytic (heterogeneous) conditions. Their results suggest elimination of bromine ion, in presence and absence of CoTPP (cobalt tetraphenylporphyrin) as catalyst, albeit no information on the nature of products is provided.

In literature, there are several mechanisms proposed for the dehalogenation process and those depended on the structure of the compound and medium conditions [13]. According to Huang *et al*. [14] polychloroethanes suffer sequential dehydrohalogenation, favoured by the presence of protic solvent and dehalogenation, in a dry aprotic solvent. Among the cathode materials used by Huang’s group there were Ag, Cu and Pd, which exhibited good catalytic activity towards reduction of organic halides, displaying high current efficiencies and positive shifts of reduction potentials. The electrochemistry of 1,2–dibromo cyclohexane shows an irreversible reduction with the formation of an alkene [15]. Vitamin B12, a naturally occurring catalyst, has been tested in the reductive debromination of vicinal dibromides, yielding to the formation of corresponding olefins [15]. Even in presence of protic substances, vicinal dibromides failed to give monobromide or saturated hydrocarbons [16]. It is obvious that the electrochemistry is a perfect tool for dehalogenation of organic polyhalogenates.

Despite there being relevant experimental studies, theoretical studies of the dehalogenation have not been done for the organic polyhalides. Saveant [17] has developed a semi classical theory of concerted dissociative electron transfer based on the Morse curve approximation of the potential energy of the breaking bond and a Marcus-Hush solvent reorganization energy. Substantial literature on the transition between the concerted and stepwise types of dissociative ET processes has been developed [10]. Unfortunately, these studies followed by electronic structure calculations have described the excited dissociative curves [18,19] of only single carbon-halide σ bond cleavage in small organic compounds. No studies regarding the stepwise simulation of the electrochemistry of polyhalides have been done up to now to our knowledge. Generally, this paper is dedicated to the DFT simulation of the electrochemical behaviour of the organic polyhalides.

Computational details

The geometry optimizations at the UBP86/6-311++G** level of electronic structure theory of DDT, β-hexachlorocyclohexane, and heptachlor organic polychlorides and their positive (+1,+2) and negative ions (-1,-2) have been performed. The calculations were carried out with the Gaussian09 suite of programs [20]. All geometric optimizations were made to the default tolerances of Gaussian. Therefore, the structures of the initial calculated neutral pesticides were found during the geometry optimization. The obtained bond distances (and angles) are in excellent agreement with the general known values for single and double bonds (and for hybridization angles between them). CASSCF (MCSCF) calculations with various numbers of occupied and unoccupied orbitals taken into their "active space" were carried out to check for Cl interactions and for charge transfer from occupied to empty orbitals; these calculations did not show any significant charge transfer.

Results and discussion

Detection, decomposition and transformation of persistent organic pollutants in water, sediment and soil can be achieved at the laboratory level with electrochemical methods of high sensitivity and selectivity [1]. However, it is more efficient to undertake preventative measures to avoid excessive contamination of environment materials (water, soil, etc.) by polychlorinated organic compounds. Unfortunately, Republic of Moldova inherited (from the former Soviet Union) multiple stocks of extremely hazardous chemical waste. As environmental regulations become more stringent, it becomes absolutely necessary to minimize, recover and recycle industrial waste to the extent possible, lowering the amounts of generated pollutants and discovering new ecological ways of disposal. Large deposits of the pesticides DDT, heptachlor and *β*-hexachlorocyclohexane can be found in territories of the former Soviet Union. Therefore these three organic polychlorides will be the subject of our attention in this paper. The chemical structures of DDT, *β*-hexachlorocyclohexane and heptachlor are presented in Figure 1.

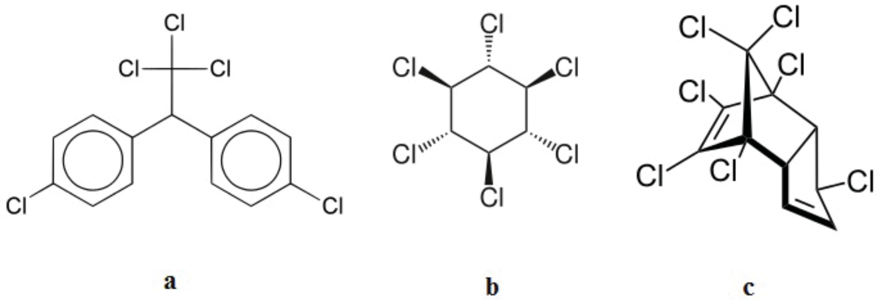


Figure 1. Molecular structures of (a) DDT, (b) *β*-hexachlorocyclohexane and (c) heptachlor.

Considering the adiabatic electron transfer between electrode (and catalyst) and organic polychlorides the DFT geometry optimization was done in order to follow their reactivity and structural modification under influence of the total charge modification. The behaviour of molecules after the receiving or leaving of one or two electrons depends decisively on the nature of frontier molecular orbitals. If the system receives one or two electrons, the nature of the lowest unoccupied orbital of the neutral molecule determines its further course, on the other hand, if the system is giving one or two electrons the nature of the highest occupied molecular orbital of the neutral molecule determines the further development of the system. The frontier molecular orbitals of the calculated systems are presented in Figure 2. One can observe from this figure that the highest occupied molecular orbital (HOMO) of every calculated organic polychloride compound does not include any significant bonding or anti-bonding contribution of the atomic orbitals to the carbon-chloride bonds. The HOMO of the DDT and *β*-hexachlorocyclohexane molecules is composed mainly from non-bonding *π*-orbital contributions of carbon and chloride atoms, while the HOMO of the heptachlor molecule is composed from a mixing of *π*- and *σ*- non-bonding orbitals. Therefore, one does not expect major modifications of the structural behaviour of the calculated positive charged ions as compared with the neutral molecules. Indeed, our DFT calculation of the +1 and even +2 ions do not show a significant structural modification of the calculated organic polychloride molecules. One can, therefore, predict little success when using the oxidation electrochemistry to dispose of these pesticides. Although, this conclusion may be affected by the nature of the electron transfer (ET) between electrode (or catalyst) and calculated organic compounds. Indeed, the electronic transfer between electrode orbitals (or catalyst orbitals) and organic polychloride orbitals might have either adiabatic or non-adiabatic nature [20]. The determination of the nature of the ET can be made by comparing the measured k(ET) of the electron transfer with a value calculated from the Marcus-Hush theory of outer-sphere adiabatic ET. If the value of k(ET) is equal or close to $\kappa \approx 1$, the ET is adiabatic, and if $\kappa <<< 1$, it is non-adiabatic [21]. For non-adiabatic ET the DFT calculation of the electronic structure of the substrate is not valid and no conclusion regarding the reactivity of the substrate ions can be made [22,23]. More sophisticated electronic structure methods, like MCSCF must be applied to these studied processes [22,24,25]. Although, the true nature of the ET can be determined using the experimental data, along with theoretical ones [21].

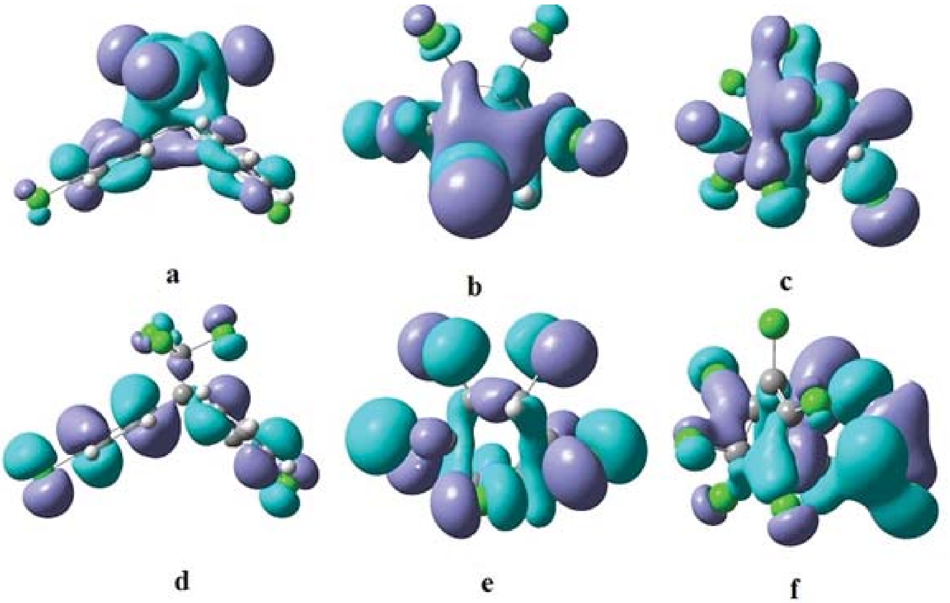
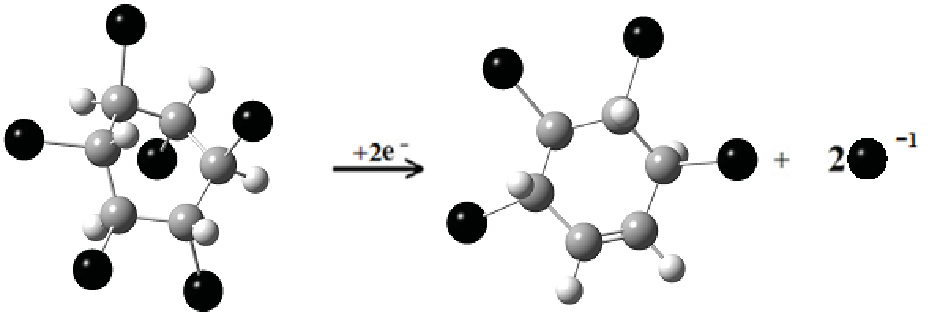


Figure 2. Frontier molecular orbital surfaces of UBP86/6-311++G DFT calculated neutral systems: a) LUMO-DDT; b) LUMO- *β*-hexachloro-cyclohexane; c) LUMO- heptachlor; d) HOMO-DDT; e) HOMO- *β*-hexachloro-cyclohexane; f) HOMO- heptachlor.**

The reactivity of the negative ions of organic polychlorides must be determined from the nature of Lowest Unoccupied Molecular Orbital (LUMO) of the neutral calculated compounds. If the LUMO of the studied compounds has an anti-bonding character along C-Cl bonds then one should expect the weakening (increasing of the C-Cl distances) or even breaking. One can observe from Figure 2 that the LUMO of the DDT molecule includes the huge antibonding contributions of the carbon and chloride atomic orbitals of the $-C-Cl_3$ group. Also, the LUMO of the heptachlor includes a consistent antibonding contribution of carbon and chloride atoms of the two side C-Cl bonds (Figure 2). The atomic orbitals of the other carbon and chloride atoms of DDT and heptachlor molecules have a negligible participation in the structure of their LUMO's. Therefore, one should expect that the transfer of an electron or two to the DDT would lead to the weakening or total cleavage of some C-Cl bonds of the CCl_3 group. Also, the transfer of an electron or two on heptachlor molecule would lead to the weakening or rupture of only two side C-Cl bonds. The rest of the C-Cl bonds in these geometry optimized systems remain at the C-Cl bond distance equal to the "normal" distance of the usual carbon-chlorine bond equal to about 1.77 Å. Indeed, our geometry optimizations of $(DDT)^{-1}$, $(DDT)^{-2}$, $(heptachlor)^{-1}$, and $(heptachlor)^{-2}$ negative ions show the one chlorine atom from $(DDT)^{-1}$ system and two chlorine atoms of the $(heptachlor)^{-1}$ depart away from carbon atoms up to the complete cleavage of the respective C-Cl bonds. This result is in full agreement with experimental [14]. The first conclusion, which must drawn is that DDT and heptachlor pesticides cannot be dehalogenated in one reducing electrochemistry step. This confirms the experimental data of the stepwise removal of the halogen atoms from polyhalogenated organic molecules [11,14]. A second conclusion regarding the geometry optimization of these four ions is that after the first dehalogenation step they form radicals at the carbon atoms of the former C-Cl bonds. These radicals would participate in various recombination and coupling reactions with the neighbouring molecules and ions. In conclusion, the next several steps of the dehalogenation of DDT and heptachlor pesticides must be studied only by using DFT method in straight connection with the results of the experimental electrochemical and analytical methods regarding the behavior of the formed ions after the first electrochemical dehalogenation.

The investigation of the direct electrochemical reduction of organic polyhalides with vicinal halogens in an aprotic medium (DMF) showed that the corresponding olefin is formed according to a two-electron stoichiometry [26]. In fact, alkyl halides do not follow a concerted mechanism in which a two electron transfer and bond rupture occur in a single step [5,14,26]. There is a clear trans- preference for the reaction in the case of dibromocyclohexane [27]. As one can observe in Figure 1, several two chloride combinations in *β*-hexachlorocyclohexane molecule can be considered as vicinal trans- atoms. Moreover, the LUMO of the *β*-hexachlorocyclohexane neutral molecule includes the anti-bonding contribution of atomic orbitals participating into two vicinal carbon-chloride bonds (Figure 2). One should expect that two vicinal C-Cl bonds with significant anti-bonding contributions present in the LUMO of *β*-hexachlorocyclohexane neutral molecule would be cleaved upon receiving one or two electrons. Geometry optimization of the (*β*-hexachlorocyclohexane)$^{-1}$ and (*β*-hexachlorocyclohexane)$^{-2}$ has shown that, indeed, both vicinal chloride atoms move from their respective carbon atoms at a distance of 2.55 Å for -1 charged ion and completely remove for the -2 ion. The role of the solvent can be critical in the further trapping of the two chlorine atoms from the *β*-hexachlorocyclohexane negative ion. For instance, in their discussion of the mechanism for the reductive cleavage reaction of Me-Cl in homogeneous solution, Martin and Finke include the effect of solvent trapping [27]. On the basis of this mechanism, they suggest that the solvent effect is more likely an effect of the solvent acting as a good or bad radical trap. Especially, the polar solvents must play an important role in the further trapping of the "cleaved" C-Cl bond since, interestingly, each chlorine atom in these two bonds have Malliken charge very close to -0.5 a.u. in the -1 ion and very close to -1 a.u. in the -2 charged ion. Their full separation leads to a neutral trans-tetrachloro-cyclohexene molecule. The illustration of the first stage of the dehalogenation of *β*-hexachlorohexane is presented in the Scheme 1.



Scheme 1. Illustration showing the first stage of the dehalogenation of *β*-hexachlorohexane. Chlorine atoms are depicted as large black spheres; hydrogen atoms are small grey spheres; carbon atoms are large grey spheres.

Fortunately, the composition of the neutral trans-tetrachloro-cyclohexene LUMO exhibits a significant antibonding contribution from the atomic orbitals of the carbon and chlorine atoms of two other cobalt chlorine bonds (Figure 3). Interestingly, the presence of the double bond in the trans-tetrachloro-cyclohexene does not influence the LUMO structure. Note, that these two carbon-chlorine bonds are not vicinal anymore. Nevertheless, the formation of the diene bonds in the case of these two carbon-chlorine bond cleavage lowers the total energy of the next electrochemical reduced products. Indeed, the geometry optimization of the -1 negative ion of the trans-tetrachloro-cyclohexene molecule leads to stretching of the carbon-chlorine bonds at the distance of about 2.8 Å with the same Mulliken charge of about -0.5 a.u.

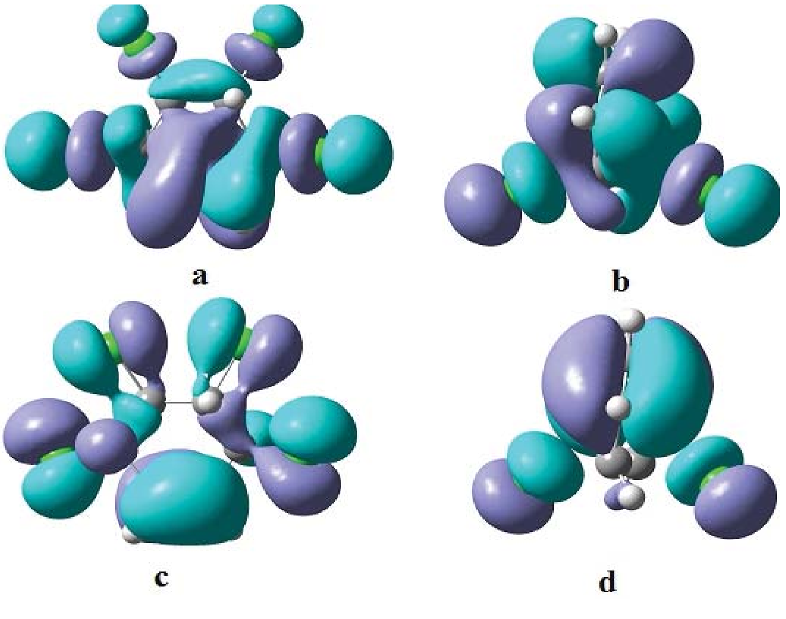
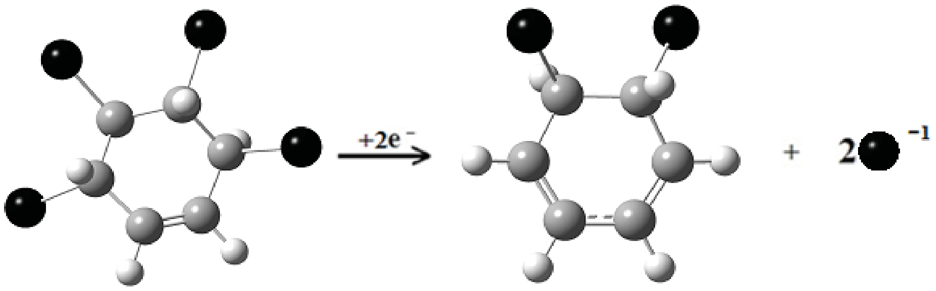


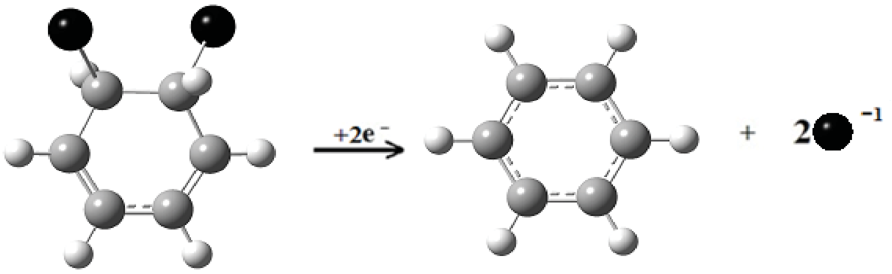
Figure 3. Frontier molecular orbital surfaces of UBP86/6-311++G DFT calculated neutral systems: a) LUMO-tetrachloro-hexene; b) LUMO- trans-dichloro-hexadiene c) HOMO-trans-tetrachloro-hexene); d) HOMO-trans-dichloro-hexadiene.**

The geometry optimization leads to complete C-Cl bond cleavage of the -2 charged ion and the Milliken charge on chlorine equal to about -1 a.u. Again, we expect that the solvent would further trap the chlorine atoms. This step is presented in Scheme 2.



Scheme 2. Illustration showing the second stage of the dehalogenation of *β*-hexachlorohexane.

The formed trans-dichloro-cyclohexadiene neutral molecule can be again reduced by one or two electrons by using electrochemistry method. One can observe that the diene bonds do not influence the presence of the huge contribution of the carbon and chloride antibonding molecular orbitals of the last carbon-chloride bonds present in the LUMO of this last neutral chlorinated compound (Figure 3). The geometry optimization of its negative ion (trans-dichloro-hexadiene)$^{-1}$ leads to the stretching of the last carbon-chlorine bonds up to 3.00 Å, while the geometry optimization of -2 ion lead to complete C-Cl bond cleavage. The last reducing step of trans-dichloro-hexadiene intermediate compound is presented in Scheme 3. One can observe that the final product of the sequential dechlorination of the *β*-hexachlorocyclohexane molecule by using reducing electrochemistry is benzene, which after its purification can be reused for next economic needs.



Scheme 3. Illustration showing the third stage of the dehalogenation of *β*-hexachlorohexane.

Conclusions

Geometry optimization of the DDT, *β*-hexachlorocyclohexane and heptachlor pesticide molecules and their positive and negative ions have been performed by using DFT method at UBV86/ 6-311++G** theory level. The positive ions of the studied molecules are quite stable during the geometry optimization. The negative ions of the studied molecules are not stable during the optimization procedure. Finally, one should conclude that the dehalogenation of the organic polychlorides is a several steps sequential procedure.

Acknowledgments

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