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Adsorption of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) on a soil organic matter. A DFT M05 computational study

Liudmyla K. Sviatenko [a, b], Leonid Gorb [c], Manoj K. Shukla [d], Jennifer M. Seiter [d], Danuta Leszczynska [e], Jerzy Leszczynski [a, *]

[a] Interdisciplinary Center for Nanotoxicity, Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217, USA
[b] Department of Organic Chemistry, Oles Honchar Dnipropetrovsk National University, Dnipropetrovsk, 49000, Ukraine
[c] HX5, LLC, Vicksburg, MS 39180, USA
[d] Environmental Laboratory, Engineer Research and Development Center, Vicksburg, MS 39180, USA
[e] Interdisciplinary Center for Nanotoxicity, Department of Civil and Environmental Engineering, Jackson State University, Jackson, MS 39217, USA

HIGHLIGHTS

- Deprotonation of humic acids is required to obtain stable complexes with CL-20.
- CL-20 binds to deprotonated humic acids through the formation of hydrogen bonds.
- CL-20 adsorbed by humic acids is expected to be resistant to redox transformations.
- Solvation promotes redox transformation of CL-20, an important industrial explosive.

GRAPHICAL ABSTRACT
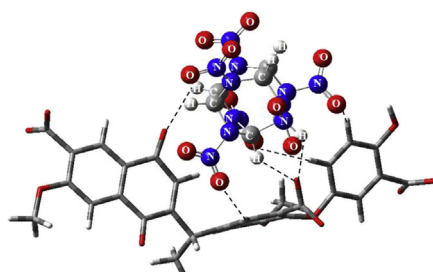
ARTICLE INFO

ABSTRACT

Adsorption of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) by soil organic matter considering the Leonardite Humic Acid (LHA) model at the M05/tzvp level of Density Functional Theory (DFT) applying cluster approximation has been investigated. Different orientations of CL-20 toward LHA surface were examined. It was found that deprotonation of LHA is required to obtain stable complexes with CL-20. Hydrogen bonds between CL-20 and deprotonated LHA were analyzed applying the atoms in molecules (AIM) theory. An attachment or removal of an electron with respect to the complex does not have significant effect on mutual orientation of the adsorbent in complexes. It was shown that adsorbed CL-20 does not undergo redox transformation and, therefore, adsorption on soil organic matter may be responsible for decrease of the degradation rate of CL-20 in soil.

* Corresponding author. Interdisciplinary Center for Nanotoxicity, Department of Chemistry and Biochemistry, Jackson State University, 1325 J.R. Lynch Street, P.O. Box 17910, Jackson, MS 39217-0510, USA.
E-mail address: jerzy@icnanotox.org (J. Leszczynski).

1. Introduction

The polycyclic nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), produced on a large scale at the

industrial level chemicals, was found to be toxic to soil invertebrates and some aquatic organisms (Kuperman et al., 2006; Robidoux et al., 2004), thereby necessitating its removal from contaminated environments. Various nitrocompounds may cause environmental contamination through manufacturing, training, storage, application, and recycling. Degradation of CL-20 by environmental agents, including microorganisms and enzymes derived from microorganisms, light, iron, and alkaline soil and water leads to similar end products. They include ammonia, carbon dioxide, formate, glyoxal, nitrate and nitrite, nitrogen, and nitrous oxide indicating that CL-20 is generally unstable and readily mineralizes in the environment (Balakrishnan et al., 2004a, 2004b; Bhushan et al., 2004; Hawari et al., 2004, 2006; Kuperman et al., 2006; Monteil-Rivera et al., 2009). One-electron transfer process was found to be the initial step for many methods of the nitrocompound decay in the environment (Balakrishnan et al., 2004b; Bhushan et al., 2004; Hawari et al., 2006; Monteil-Rivera et al., 2009). For instance, CL-20 can be efficiently decomposed within a few hours in the presence of zerovalent iron in water in the absence of oxygen (Balakrishnan et al., 2004b). Ability of neither Fe^0 in anhydrous conditions nor Fe^{2+} ions in aqueous solution to degrade CL-20 indicates that surface-bound Fe^{2+} may be responsible for its degradation. The resulting CL-20 radical-anion is expected to undergo spontaneous decomposition starting from denitration process (Bhushan et al., 2004).

The release of CL-20 to surface water largely depends on its solubility while the mobility in soil depends also on sorption to organic matter, clays, or other substances in the soil. An understanding of sorption mechanisms is therefore essential for the accurate prediction of the fate and impact of CL-20 in soils and groundwater. Experimentally it was found that CL-20 has low water solubility at room temperature (3.16 mg/L) and its sorption depends on composition and characteristics of the soil (e.g., pH, clay and organic matter content, moisture, porosity) (Balakrishnan et al., 2004a; Hawari et al., 2006). CL-20 has a low tendency to adsorb on the mineral phases such as silica, ferric oxide, montmorillonite, kaolinite, and illite with sorption constants (K_d^S) of 0–0.62 L/kg (Hawari et al., 2006). The higher values of sorption constant (K_d^S = 311 L/kg) obtained in soils with higher organic content suggest that soil organic matters may play a determining role in CL-20 sorption.[7] In addition, as compared to the degradation in water medium, presorption of CL-20 on soil leads to decrease in efficiency of abiotic as well as biotic degradation (Balakrishnan et al., 2004a; Hawari et al., 2006).

To get more detailed insight in sorption process, we studied structures of adsorbed complexes formed by CL-20 and soil organic matter, taken here as the Leonardite Humic Acid (LHA) model monomer limited to 31 carbon atoms with formula $C_{31}H_{24}O_{12}$ (Niederer and Goss, 2007). This model, contained three carboxyl groups, one phenolic group and quinone structure that are important constituents in humic substances, was shown to be very promising tool for the prediction of sorption in soil organic matter (Niederer and Goss, 2007; Nuerla et al., 2013). It should be noted that both neutral LHA as well as its deprotonated forms were used due to spectroscopic evidence for existence of both protonated/deprotonated forms of humic acids under natural pH conditions (Fang et al., 2015). Recently, we have shown that environment significantly affects the redox properties of nitrocompounds such as trinitrotoluene, 2,4-dinitrotoluene, 2,4-dinitroanisole and 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (Sviatenko et al., 2015). Therefore, we have also compared the reduction and oxidation abilities of CL-20 in the hydrated and adsorbed states.

2. Methods

Geometry optimization for all species was performed using the Gaussian 09 program package (Frisch et al., 2009). The geometries of neutral, cation- and anion-radical species were optimized using the Density Functional Theory at the M05/tzvp level (Head-Gordon et al., 1988; Weigend and Ahlrichs, 2005). The present functional and basis set were chosen because of the results of our recent study where such level of theory was able to provide accuracy close to that obtained by experimental measurements (Sviatenko et al., 2011). Harmonic vibrational frequencies were calculated for all optimized structures to establish that a minimum was obtained. Adsorption energy was calculated as a difference between the total energy of the adsorbed complex and the energy of the LHA and CL-20 monomers within the complex geometry, corrected for basis set superposition error using the counterpoise method (Boys and Bernardi, 1970). Deformation energy of the deprotonated LHA ($E_{def.}(LHA)$) was computed as a difference in energies of the deprotonated LHA within the corresponding complex geometry and that of the separately optimized deprotonated LHA. Deformation energy of CL-20 ($E_{def.}(CL-20)$) was computed as a difference in energy of CL-20 within the complex geometry (adsorbed complex) and the energy of a fully optimized CL-20. The AutoDock Vina 4.0 was used to run the rigid docking simulations (Trott and Olson, 2010).

The topological analysis of the distribution function of the electron density $\rho(r)$ was carried out for the optimized geometry of the complexes in the framework of the Bader's *atoms in molecules* (AIM) theory (Bader, 1990) using the Multiwfn program (Lu and Chen, 2012).

The solvent effects for CL-20 and adsorbed CL-20-LHA complexes were assessed by single-point energy calculations using a PCM(Pauling) and SMD solvation models for ions, ion-radical and neutral molecule calculations, respectively (Cossi et al., 2002; Marenich et al., 2009; Sviatenko et al., 2011). Adiabatic electron affinities (E_A) and ionization potentials (I_p) were calculated as the total energy difference between charged species and neutral forms, corrected for zero point energy.

The Gibbs free energy of electron transfer for CL-20 under dissolution was calculated as follows:

$$\Delta G^0_{red,solv} = \Delta G^0\left(R^{-\cdot}_{solv}\right) - \Delta G^0(O_{solv})$$
$$\Delta G^0_{ox,solv} = \Delta G^0\left(O^{+\cdot}_{solv}\right) - \Delta G^0(R_{solv}) \tag{1}$$

The values of reduction and oxidation potentials are expressed as

$$E^0_{red} = -\frac{\Delta G^0_{red}}{nF} + E_H$$

$$E^0_{ox} = \frac{\Delta G^0_{ox}}{nF} + E_H \tag{2}$$

The absolute potential of the NHE reference electrode E_H is taken as −4.36 eV (Lewis et al., 2004).

3. Results and discussion

3.1. Adsorbed complexes

There are several conformers of CL-20. Based on the reported MBPT(2)/6-311G(d,p) and B3LYP/6-31G+(d,p) calculated data the most stable one, which is β conformer, was chosen for the present