

養成技術者の研究・研修成果等

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- 3 . 養成カリキュラムの達成状況

Aim/Outline:

There were number of experimental and theoretical studies in the past on structures of polychlorinated dibenzo-*p*-dioxins (PCDDs) and biphenyls (PCBs). These studies showed that structure plays an important role for the toxic nature of PCDDs and PCBs. Unfortunately there are no such structural studies on polychlorinated dibenzofurans (PCDFs) although these compounds have toxicities similar to those of PCDDs and PCBs. Earlier studies have concluded that toxins (PCDDs and PCBs) appear to act as electron acceptors in a charge-transfer complex with a receptor in living cells. Since earlier studies suggest that the toxicity and enzyme-inducing capability of halogenated aromatic hydrocarbons (HAHs) may be connected to their interactions with the arylhydrocarbon (Ah)-receptors, determining whether PCDFs act as electron acceptors or not in these important interactions is necessary for a better understanding of their toxicity. Further, it is likely that electron affinity (EA) may have an influence over the toxicity and hence, EA may act as an indicator of toxicity of PCDFs. Reductive dechlorination is a significant environmental transformation of halogenated organic contaminants under anaerobic conditions. So knowing the dechlorination sites and the reductive dechlorination process would help to make further advances in the detoxification studies on these toxins.

The foregoing facts encouraged us to study the structures and to obtain the electron affinities of the selected PCDFs, including the toxic ones. This study also helped us to know the EA's role in the toxicity of PCDFs, and to understand the reductive dechlorination process in PCDFs.

4 . 成果

Work done:

We used density functional theory to obtain the structures and adiabatic electron affinities of fifteen PCDFs. They were three trichlorodibenzofurans (1,2,3-, 1,2,4-, and 2,3,4-TrCDF), eight

tetrachlorodibenzofurans (1,2,3,4-, 1,2,4,6-, 1,2,8,9-, 1,4,6,9-, 1,4,7,8-, 2,3,6,7-, 2,3,7,8-, and 3,4,6,7-TCDF), two pentachlorodibenzofurans (1,2,3,7,8-, and 2,3,4,7,8-PeCDF), and two hexachlorodibenzofurans (1,2,3,4,7,8-, and 1,2,3,6,7,8-HCDF). Three-parameter hybrid density functional, B3LYP, with four different basis sets [up to 6-311+G(2d,2p)] were utilized for our studies.

All these structures show that all the selected 15 PCDFs have planar structures. Unsubstituted dibenzofuran also has a planar structure. So chlorine substitution doesn't change the planarity of the molecule here. Anions have some interesting differences: many of the anionic PCDFs have planar structures, but a few have nonplanar structures. The planarity or nonplanarity of the anionic PCDFs depends upon the substitution pattern. The important point is, the C–Cl bonds in anions are longer than those in their neutral counterparts. That means the additional electrons weakened the C–Cl bonds in all the PCDFs. These weak bonds in anions suggest that dechlorination will occur more easily in anions than in neutrals. However, from these results it is difficult to conclude which carbon–chlorine bond can break more easily than the other. At the same time, overall picture shows that it is very likely that the lateral C–Cl bonds are more easily breakable than the nonlateral ones. Anions of 1,2,3- and 2,3,4-trichloro and 1,2,3,4-tetrachloro dibenzofurans had a long C–Cl bond, greater than 2.2 Å, each. The peculiarity of these three PCDFs is in their substitution pattern. One of the benzene rings in these three PCDFs has three or four adjacent positions substituted with chlorine atoms while the other benzene ring is kept unsubstituted. Because of this, steric interactions are expected to be high in the substituted ring. Addition of an electron should increase the steric repulsion further and hence to get some sort of relief from the steric repulsion, one of the C–Cl bonds in these PCDFs become weakened. This point is clear from the calculated spin densities that the unpaired electrons reside entirely on the substituted benzene rings. These weak C–Cl bonds could be very susceptible to the bond cleavage reactions, and the reductive dechlorination should take place easily through these weak C–Cl bonds.

Previous studies on PCDDs and PCDFs have concluded that studies are necessary to understand the reductive dechlorination mechanism (electron acceptance and the carbon–chlorine

bond cleavage). It is clear from this study that the addition of an electron (reduction) weakens the C–Cl bonds in PCDFs. To understand the reductive dechlorination process in PCDFs, it is important to know which orbital accepts the ionizing electron. If the additional electron occupies the s^* orbital, then, through the reductive dechlorination process, a given C–Cl bond would be weakened and could break easily without any additional changes in the structure of the target molecule. But our results showed that the anions with the longer C–Cl bonds had nonplanar structures. These results may have a significant importance in explaining the reductive dechlorination process in PCDFs. The bending C–Cl bond orientations in anions prove that these molecules become nonplanar to pave the way for C–Cl bond breaking through a reductive dechlorination process. In other words, these results carry the earlier assumption that the additional electron enters into a p^* orbital, and the C–Cl bond cleavage may occur according to the bent bond model.

To support the fact that the p^* orbitals receive the ionizing electrons, we studied the lowest unoccupied molecular orbitals (LUMOs) of the PCDF neutrals and found that LUMOs of all the selected PCDFs are p orbitals. So it is clear that the ionizing electrons enter into the p antibonding orbitals of the PCDFs by considering the fact that normally ionizing electrons enter into the lowest unoccupied MO. We also studied the singly occupied molecular orbitals (SOMOs) of anions of all the considered PCDFs. Obtained SOMOs showed significant difference: SOMOs of 1,2,3-, 2,3,4-, and 1,2,3,4-PCDFs were found to be s orbitals, while SOMOs of most of the remaining PCDFs were p orbitals. That means PCDFs with longer C–Cl bond had s SOMOs. The foregoing results support the following conclusions: (1) the ionizing electron is accepted into the p^* orbitals of the neutral PCDFs at the vertical attachment region (the Franck – Condon region); (2) with the acceptance of the ionizing electron, C–Cl bond length increases; (3) while bond length increases, the C–Cl bond also bends toward the plane of the p system; and (4) when the C–Cl bond bends toward the p system, p^*-s^* orbital mixing followed by intramolecular electron transfer from p^* to s^* orbital occurs. These events pave the way for the C–Cl bond cleavage.

Anionic PCDFs other than those with a longer C–Cl bond length have p SOMOs. For these PCDFs, the C–Cl bond stretching may provide the possibility for p^*-s^* orbital mixing which is

essential for the bond cleavage mechanism. To know the changes in the structure as well as the changes in the nature of SOMO with increase of the C–Cl bond length in these PCDFs, we considered the anionic 2,3,7,8-PCDF, as an example, and optimized its structure at different C3–Cl3 bond lengths. Two important results have been noticed as the C–Cl bond length increases: (1) 3-chlorine moves from the planar orientation and bends toward the p system, and (2) the singly occupied MO is a p^* orbital at the equilibrium structure but becomes progressively s^* character at longer C–Cl distances. These results support the bent bond model and confirm the fact the bond stretching provides an opportunity for the $p^*–s^*$ orbital mixing necessary for C–Cl bond cleavage. We also studied the possible dissociative reactions involving the PCDFs. The results clearly showed that the dechlorination of the anionic PCDFs occurs via neutral PCDF radical and chloride ion.

All the PCDFs have positive electron affinities. The increase in chlorine (electron-withdrawing group) number leads to a lowering of LUMO energy and hence the EAs of the PCDFs progressively increase with the increase in chlorine number. The large positive adiabatic EA values obtained for the selected PCDFs in the present study support that PCDFs might act as electron acceptors in the charge-transfer interactions with the receptors in the living cells. These results combined with the results obtained for PCDDs and PCBs clearly indicate that HAHs act as electron acceptors and the electron affinity might be an influential parameter of toxicity. The electron affinities of the toxic PCDFs were higher than those of their non-toxic or less-toxic counterparts. The EA value of 1.029 eV calculated for the most toxic 2,3,7,8-TCDF was the largest among the EAs calculated for the eight selected TCDFs.

We started working on polychlorinated hydroxybiphenyls (PCHBs). Twenty-five PCHBs have been selected to study all possible structures, potential energy curves, atomic charges, and polarizabilities to understand their estrogenic activity. Again, density functional theory is used for this study. Two different basis sets, 6-31G(d) and 6-311G(d,p) are being utilized for this purpose. We obtained many interesting results and now we are analyzing and interpreting these results with the results derived from experimental studies.

5 . 成果の対外的発表等

Publications:

Journals:

1. ‘*Electron affinities and reductive dechlorination of toxic polychlorinated dibenzofurans: A density functional theory study*’
S. Arulmozhiraja and M. Morita
J. Phys. Chem. A **2004**, *108*, 3499–3508.
2. ‘*Structure–activity relationships for the toxicity of polychlorinated dibenzofurans: Approach through density functional theory-based descriptors*’
S. Arulmozhiraja and M. Morita
Chem. Res. Toxicol. **2004**, *17*, 348–356.

Conference:

1. ‘*Density functional theory studies on electron affinities of toxic polychlorinated dibenzofurans*’, presented at the International Conference on Theory and Applications of Computational Chemistry held at Gyeongju, Korea during February 15-20, 2004.