ダイオキシン抑制のための計算化学的手法に関する研究

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1- Reaction Pathways of Dioxin Formation:

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are toxic compounds that are formed during some natural processes and various human activities. Some of the possible reaction pathways of PCDD/Fs inclue, e.g., high- temperature pyrosynthesis, low temperature de novo formation from macromolecular carbon and organic or inorganic chlorine present in the fly ash matrix, and formation from different organic precursors such as chlorophenols [1,2]. Although these mechanisms have been known for a number of years, few detailed reaction mechanisms can yet be offered for PCDD/F formation from macromolecular carbon or even structurally closely related precursors. Combustion of organic matter in the presence of chlorine and metals is widely recognized as a major source of PCDD/F formation. A thermal breakdown of organic materials, together with transition metals and chlorinated compounds, takes place during waste incineration. As the flue gases leave the primary combustion chamber, these compounds cool down from 1000℃ and subsequently condense. It is during this molecular rearrangement that PCDD/Fs are formed, commonly in the temperature range between 650 and 250℃, with a maximum at approximately 300℃ [1]. The basic chemical equation for the formation of PCDD/Fs is the following:

$$Cl_2 + \text{organic molecules} \rightarrow \text{chlorinated molecules (e.g., PCDD/Fs)} \quad (1)$$

PCDD/Fs will also form in the presence of hydrogen chloride (HCl), which can be converted to Cl_2. The organic member in Eq. 1 is likely to be a ring structure such as chlorobenzene or chlorophenol. The concentration of PCDD/Fs emitted can be greater than normal in the presence of a catalyst. The catalyst is usually a transition metal, such as copper, iron or one of the oxides of these. Three general pathways have been proposed so far to explain the formation of PCDD/Fs during incineration: 1- pyrosynthesis, i.e., high- temperature gas phase formation, 2- formation from macromolecular carbon (so called residual carbon) and the organic or inorganic chlorine present in the fly ash matrix at low temperature, often referred to as de novo mechanism, and 3- through various organic precursors, such as chlorophenols of polychlorinated diphenyl ethers, which may be formed in the gas phase during incomplete combustion, and combine heterogeneously and catalytically with the fly ash surface.

2- Ab Initio Studies on Dioxin:

Nowadays, ab initio studies on different molecules and reaction pathways are rather common, due to the increased power of computing facilities and more feasible computation approaches. There have been a number of studies on different properties of dioxin molecules. Structure, energy, viberational frequencies, and potential energy curves of tetrachlorinated dibenzo dioxin have been recently calculated using ab initio molecular orbital (MO) approach [3]. The structures and electrostatic potentials of some monocyclic unsaturated dioxins were studied using an ab initio self consistent field (SCF) method [4]. It was found that among different isomers, the peroxidic systems were the least stable. Computational studies [5] on some perhalodioxins, which have unusual reactivity with oxygen and their radical catalyzed homopolymerization proceeds through a fluorinated double bound, has established that introduction of the first double bound raises the energy substantially, while the second double bound results in a near planar ring with dramatically increased energy content.

On the other hand, ab initio molecular dynamics (MD) studies have attracted much attention recently,

regarding the reaction pathways of different systems. For example, ab initio MD simulations of the reaction of formaldehyde radical anion and methyl chloride have been performed recently [6]. Dynamics of ionization processes of methanol dimer has been recently studied using ab initio MD [7]. As another example, ab initio MD study of cis-trans photoisomerization in ethylene [8] has revealed that the initial motion is the stretching of the carbon-carbon bond, which is followed quickly (~50 fs after excitation by photon) by a transitional motion, i.e., cis-trans photoisomerization. To the best of our knowledge, no ab initio MD study has been done on the reaction pathways of dioxin formation yet.

3- Ab Initio MD Study of Dioxin Formation Mechanisms:

Although there have been a lot of investigations aiming at clarifying different properties of PCDD/Fs and their formation mechanisms, many unanswered questions still exist. We intend to use ab initio MD approach to study some of the possible formation mechanisms of PCDD/Fs, and to clarify the dependence of the PCDD/F structures on different pathways involved in their production.

To be more specific, we study the chlorophenol condensation process (Fig. 1), for the formation of PCDD on fly ash; no PCDF is formed. In this process, the chlorination pattern of the phenol is retained in the PCDD. Isomerization can take place through the Smiles rearrangement. we also investigate the dioxaspiro pathway for the formation of PCDDs. In this process, the condensation of a trichlorophenol and a trichlorophenol anion (Fig. 2) leads to the formation of PCDDs, through Smiles rearrangement and release of a chloride ion or a chloride radical. This can be considered as an intermediate step of the condensation of chlorophenols.

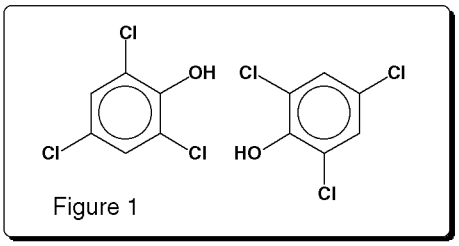

Figure 1

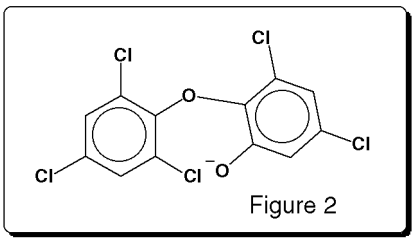

Figure 2

4- Method:

We use a fully self-consistent density-functional method [9] for performing ab initio MD of the above mentioned reaction pathways. This method can be applied to systems consisting of a large number of atoms, and uses standard norm conserving pseudopotentials and flexible linear combinations of atomic orbitals (LCAO). Exchange and correlations are treated within the local-spin-density or gradient corrected approximations. The basis functions and the electron density are projected on a real-space grid in order to calculate the Hartree and exchange-correlation potentials and matrix elements. Forces and stresses are calculated efficiently and accurately, allowing structural relaxation and MD simulations.

The calculations on different reactions pathways of dioxin and for different physical conditions (e.g., temperature and pressure) are in progress. The results would indicate how the initial configuration of atoms (Figs. 1 and 2) evolve onto the final configuration (PCDD), what the relevant temperature and pressure are, and what specific conditions should be chosen for the MD simulation to treat the reaction pathways properly. Taking into account the successful application of ab initio MD to the investigation of molecular reactions in recent years, and the fact that PCDD/Fs consist of a relatively small number of atoms (around 20), we believe that the ab initio MD study of PCDD/Fs formation mechanisms is possible and will shed some light on the details of those mechanisms.

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