Dioxin and Furan Abatment in Municipal Waste Incineration : an Experimental and Molecular Modeling Study

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Introduction

In the present study we use the Molecular Electrostatic Potential (MEP) as a tool to characterize the relative stabilities and reactive properties of a number of halogen substituted dibenzo-p-dioxins and dibenzo-furans. These compounds range in toxicity from virtually none to very high as that of 2,3,7,8 tetrachlorodibenzo-p-dioxin (tcdd), for example. The analysis of the patterns of the MEP around the toxic dioxins indicates that their destruction using an electrophilic reactant like $O2$, O_3 or H_2O_2 would not be an efficient solution, the large negative regions in the electrostatic potential atributed to the chlorine atoms being very diffuse. Our results are consistent with experimentally observed dioxins and furan emissions from municipal waste incineration [1]. Ab initio molecular dynamics calculations have also been carried out to investigate the mechanism of dioxin formation starting from unsaturated hydrocarbons and the effect of Oxygen on its abatement. In the present work we focus on establishing reliable experimental data concerning the chemical reactions occurring in municipal waste incineration and undertake parallel theoretical calculations to explain the reactivity of chlorinated members of the dibenzo-p-dioxin and dibenzofuran families towards oxygen.

Experimental and computational details

Experimental : The incinerator used for tests consists of the following components (as in sequence of the MSW processing): arrival and manipulation of the MSW, furnace, bottom ash handling system, boiler and heat dissipation system, flue-gas clean-up, electrostatic precipitator and the stack. The incineration furnace is of a reciprocated Stoker type. There are three grates in the furnace: the first one where the MSW arrives and where it is preheated and dried, the second one where it is almost completely combusted and the third one where the final burnout of the residual bottom ash carbon takes place. At the end of the furnace (after the third grate) the flue gases enter the boiler and the bottom ash falls into the handling system. After the boiler, flue gases pass to the semi-wet clean-up. This process neutralizes HCl and

SO_2. Before rejecting the flue gas at the stack they are cleaned from dust in the electrostatic precipitator.

Oxygen enrichment tests were done in two different configurations:

(a) second grate primary air enrichment

(b) second and third grate primary air enrichment. Details are available elsewhere [1]. Dioxins and furans samplings were done in the stack. The analyses of the collected samples were done subsequently by GC-MS technique.

Computational details : The molecular mechanics (MM) and molecular dynamics (MD) calculations were carried out with the Discover program of the MSI molecular modeling package [8] on a Silicone Graphics Workstation. The PCFF force field was used to perform the geometric optimizations and molecular dynamic simulations on all species. The Van der Waals potential was set to zero at 10 Å and the automatic parameter assignment was used for the PCFF force field. The conjugate gradient algorithm has been used for the minimization of both species combined with Newton Raphson one. The quantum mechanical semiempirical calculations were performed with the PM3 (parametric method 3) as implemented in MSI [8] program. The medium integration mesh with a relaxed core treatment the electrons using a standard basis set has been adopted in all Faststructure calculations [8]. The simulations of the mechanisms of formation of benzene (precursor for dioxin or dibenzofuran formation) have been performed using the Faststructure code for realizing a simulated annealing with " scattering boundary conditions ". DFT calculations on faststrucure-optimized geometries have been performed using the Dmol program [8] to determine the MEPs of the most stable structures.

Results and discussions

The average dioxins and furans emissions were decreased by a factor of three when oxygen enrichment was used. It is widely noted in the literature [e.g. 10] that dioxins and furans are formed from macromolecular carbon structures (by *de novo* synthesis) and from small organic molecules (precursors). Also, there exist a correlation between the quantity of fly ash and dioxins and furans emissions [11]. In the tests discussed in this communication, it is believed that both of those phenomena were altered. Carbon structures (macromolecular as well as precursors) were better combusted thanks to faster kinetics which resulted from higher oxygen concentration. On the other hand, the quantity of fly ash was reduced since the total amount of gas flowing through the system was reduced. The total organic carbon decreased in both, bottom and fly ashes. When it is known that the probability of dioxins and furans formation increases with the presence of carbon compounds in fly ash, it should be of no surprise that the emission of those pollutants decreased. These experimental observations and postulated explanation had to be verified. For this purpose the molecular modeling study has been performed.

During the last years a dominant theme of theoretical chemistry has been the search for methods able to predict the chemical behavior of chemical entities. Many indices of reactivity like atomic charges, bond orders, free valences, frontier electron densities, fukui functions and the Molecular Electrostatic Potentials (MEP) have been introduced. The shape of MEP is considered now as a standard tool in quantum chemistry for the analysis of the reactivity of

molecules [2-7]. Unlike many of the other quantities used as reactivity indices, the MEP is a real physical property which can be either determined experimentally by X-ray and electron diffraction methods [9] or calculated from the wave function. Its interpretation is simple in terms of classical electrostatics: the molecule provides a potential around itself which is felt by another approaching chemical species. In the present study we have used the MEP to localize the more electronegative sites of the molecules. As the MEP strongly depends upon the conformation and configuration of the molecule it was important to correctly define the molecular geometry (global and local minimum conformations) before starting the calculation of electronic properties. In figures 1 we report the calculated MEPs for the dibenzo-p-dioxin, 2,3,7,8-tetrachlorodibenzo-p-dioxin (tcdd) dibenzofuran and 2,3,7,8 tetrachlorodibenzofuran. The analysis of the MEP pattern indicates that the attack of the CO bonds in chlorinated compounds which are the toxic members of the family is less favored than in the unsubstituted ones. This finding suggests that the oxygen used for the abatement of the toxic dioxins would not react selectively with these compounds.
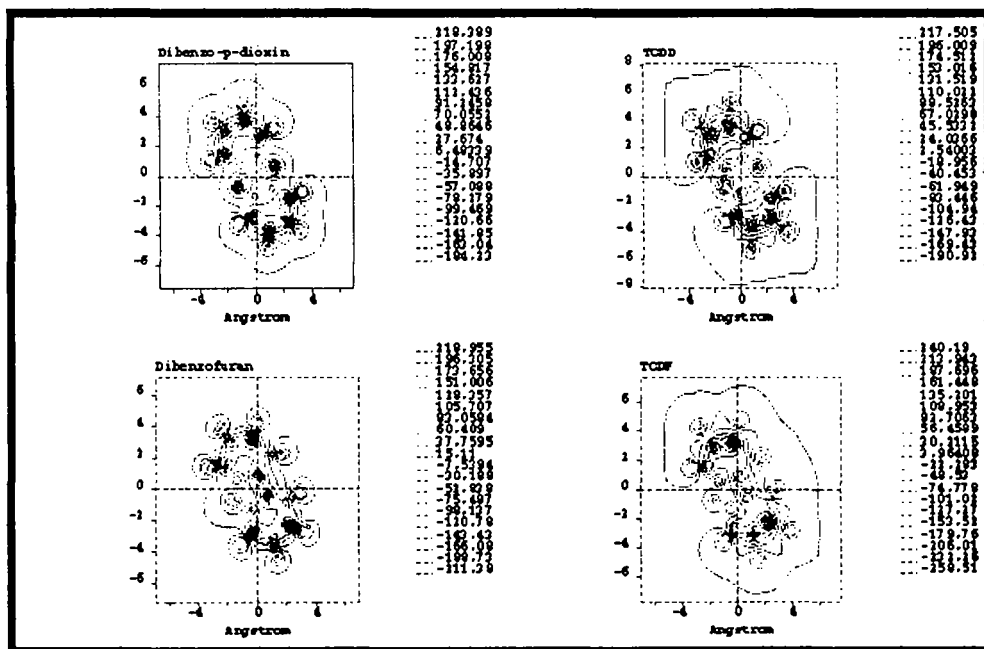
Figure 1 : Calculated MEP of dibenzo-p-dioxin, dibenzofuran , tcdd and tcdf in the molecular plane in kcal/mol.

In our study of the mechanisms of benzene (dioxin) formation we observed that the formation of propagyl radicals was an important pathway for the benzene synthesis. The runs carried out with the faststructure program showed that these radical were easily formed and

due to their structure and electron delocalisation effects they are quite stable with a reduced number of possible reaction channels. As the benzene formation resulted from efficient collisions of propagyl radicals with unsaturated molecular species the introduced oxygen in the simulated system gave rise to new products reducing the number of propagyl radicals and unsaturated hydrocarbons implying less effective collisions corresponding to benzene formation. It is to notice that this simulation result corresponds to our particular starting point and the calculation being very CPU intensive we couldn't explore other possible scenarios in order to correctly sample computationally the effect of oxygen on dioxin formation.

Conclusions

Concentrations of dioxins and furans was measured in the flue gas of a municipal waste incinerator. It was observed that oxygen enrichment of air has a positive effect on dioxins and furans destruction. It was postulated that oxygen enrichment affects the combustion in the incinerator and that the destruction efficiency is the reason of observed phenomena. It was also postulated that oxygen enrichment does not have an effect on already formed dioxins and furans. These hypotheses were confirmed by our molecular modeling study. It was shown that the already formed dioxins and furans cannot be easily decomposed by oxygen. This is mainly due to the presence of the electron-withdrawing chlorine atoms which modify the electrostatic potentials of the parent molecules reducing the reactivity of the heterocycles towards electrophilic reactants.

Acknowledgments

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