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TCDD的密度泛函理论研究

王遵尧,吴迎春,菊池修,渡边寿雄

盐城工学院化工系;日本筑波大学化学系日本筑波305－8571

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摘要 用B3LYP/6-311G~(**)方法全优经计算22个四氯二苯并对二（左口右恶）英（ 简称TCDD）分子，得到几何构型、总能量、标准熵、标准焓和标准自由能。将2， 3，7，8 －TCDD的计算构型与X射线衍射实验测定值进行了比较。计算结果表明，总 能量、标准焓和标准自由能与氯原子量换位置的相关性很高（r > 0.997）.1,3,6, 8-TCDD的总能量处自由能最低，即最稳定，以此参照，得到异构体的总能量的相对 稳定性顺序和自由能的相对稳定性顺序。1,3,7,9 －TCDD的稳定性次之，1,3,7,8- TCDD居第三，将这二个顺序与焚烧炉产生的TCDD异构体和合成的异构体对的生成面 分比进行了比较，说明焚烧炉中产生的TCDD和合成的TCDD对的分布主要受热力学控 制。

关键词 二恶英 密度泛函数理论 热力学 稳定性 构型 X射线衍射分析

分类号 41

DFT Study of Tetrachlorinated Dibenzo-p-dioxins

Wang Zunyao,Wu Yingchun,Osamu Kikuchi,Toshio Watanabe

Department of Chemical Engineering, Yancheng Institute of Technology;Department of Chemistry, University of Tsukuba

Abstract Molecular structures of 22 tetrachlorinated dibenzo-p-dioxins (TCDDs) were calculated by the B3LYP/6-311G~（**） method. The structures, total energy, standard entropy, standard enthalpy and standard free energy were obtained, in which the calculated molecular configuration of 2,3,7,8-TCDD is very close to the experimental analysis of X-ray diffraction. The results show that the total energy, the standard enthalpy and standard free energy are very well correlated with the numbers of chlorine atoms at the a positions and the parameters that represent the specific configurations of two chlorine atoms. The linear relation coefficient r is larger than 0.997. Based on the above result, a relative stability order of the total energy and standard free energy of all isomers was established. The total energy and the standard free energy of 1,3,6,8-TCDD are the lowest compared to other isomers, so it is the most stable configuration with 1,3,7,9-TCDD being the second and 1,3,7, 8-TCDD being the third in the stability of the configurations. Finally, the relative stability order was compared with the isomer pairs distribution produced in the fly ash emitted from municipal waste incinerators. Therefore, the most abundant isomer was predicted as the most stable isomer and the significance of theimodynamic control was suggested in the TCDD formation mechanism.

Key words dioxin DFT THERMODYNAMICS STABILITY CONFIGURATION XRD

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通讯作者