569f Dft Study of Trichloroethylene Chemisorption to Iron Surfaces Using Density Functional Theory

Paul Blowers, Nianliu Zhang, and James Farrell

Zero-valent iron has been widely utilized as a reactive agent for reductive dechlorination of solvents in contaminated groundwaters. Prior research has suggested that chemical adsorption may be involved in chloroalkene reduction via an inner-sphere electron transfer mechanism. This research investigated the mechanisms for chemical adsorption of trichloroethylene (TCE) to iron surfaces using periodic density functional theory (DFT). DFT modeling of adsorbed species was performed using the generalized gradient approximation with the Perdew-Burke-Enzerhof (PBE) functional. Chemisorption structures were obtained for four adsorbed initial configurations. Di-sigma C-Fe and Cl-Fe complexes were formed by initial configurations with two carbon (C-bridge) or two chlorine atoms (Cl-bridge) adsorbed at bridge sites between adjacent iron atoms, respectively. Sigma bond formation between two C or Cl atoms and two iron atoms resulted in activation of all three C-Cl bonds. This also resulted in a shortening of the C=C bond by an amount consistent with an intermediate between a double and a triple bond. Optimizations of initial configurations with the C=C bond adsorbed at top or hollow sites on the iron surface resulted in the formation of two C-Fe sigma bonds between a single C and two Fe atoms, and only two C-Cl bonds became activated. Bond angles and bond lengths indicated that there were no changes in bond order of the C=C bond upon top and hollow adsorption. Calculated binding energies indicated that chemisorption was highly exothermic, with the complex formed at the C-bridge site being the most energetically favorable. Chemisorption at the C-bridge site had an early transition state in which all three C-Cl bonds were activated from ~1.7 to ~2.2 Å, with an activation energy of 50 kJ/mol. The early transition state and the loss of all three Cl atoms upon chemisorption are consistent with most experimental observations that TCE undergoes complete dechlorination in one interaction with the iron surface. The sigma bonded structures where only two C-Cl bonds were activated upon adsorption is consistent with experimental observations that trace amounts of chloroacetylene may be produced from reactions of TCE with iron.