63i Dehalogenation of Dichloroethylene Isomers on □-Cr_2O_3 (1012)

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The dechlorination of 1,1-, cis-1,2-, and trans-1,2-dichloroethylene isomers has been studied over a model chromia surface by thermal desorption. Dehalogenation to acetylene occurs without significant deposition of surface carbon or production of dihydrogen. Acetylene is the sole gas-phase product molecule observed from all reactants. Thermal desorption shows a clear effect of the molecular structure of the isomers on the kinetics of acetylene formation, suggesting different stabilities of the reaction intermediates formed from the different isomers. Reaction-limited acetylene is produced at the lowest temperature from 1,1-dichloroethylene through a vinylidene intermediate. The reaction temperature to acetylene is highest from trans-1,2-dichloroethylene, where photoemission also provides evidence for intact C-Cl bonds at higher temperatures than from the other reactants. The results suggest a sequential dehalogenation of trans-1,2-dichloroethylene with a higher barrier to b-Cl elimination from a surface chlorovinyl intermediate with the C-Cl bond directed away from the surface.