325b The Transition State for Alkyl Hydrogenation on Pt

Andrew J. Gellman and Pingping Ye

Hydrogenation and dehydrogenation are among the many different elementary reaction steps that alkyl groups undergo during catalytic surface reactions. The kinetics of these elementary steps are influenced by the nature of catalyst surface and dictated by the differences in the energies of the initial state (adsorbed alkyl group) and the transition state to hydrogenation or dehydrogenation. Our study is part of an ongoing program to probe the characteristics of transition states to elementary surface reactions. The insight developed through understand the nature of the transition states to surface reactions is the key to ultimately understanding the influences of catalytic surfaces on the kinetics of catalytic processes.

Substituent effects have been used to probe the characteristics of the transition states to hydrogenation of alkyl groups on the Pt(111) surface and the transition state to β-hydride elimination in alkyl groups on the Pt(111) surface. Eight different alkyl and fluoroalkyl groups have been formed on the Pt(111) surface by dissociative adsorption of their respective alkyl and fluoroalkyl iodides. Co-adsorption of hydrogen and subsequent heating of the surface results in hydrogenation of the alkyl groups to alkanes which desorb into the gas phase. The kinetics of the hydrogenation reaction are dependent on the size of the alkyl group (polarizibility) and the degree of fluorination (field effect). The influence of the substituents on the activation barriers to hydrogenation has been correlated to the field and polarizibility substituent constants of the alkyl groups in the form of a linear free energy relationship. Increasing both the field and polarizibility constants of the alkyl groups increases the barrier to reaction. These substituent effects indicate that the α-carbon in the transition state is cationic with respect to the initial state alkyl group and that the reactant has greater charge density on the α-carbon than the transition state.

In the absence of adsorbed hydrogen, alkyl groups on Pt(111) dehydrogenate via β-hydride elimination. In the fluorinated alkyl groups this then leads to the deposition of hydrogen on the surface and the hydrogenation of the intact fluoroalkyl groups to form fluoroalkanes. The desorption kinetics of the product fluoroalkanes serves as a measure the kinetics of the β-hydride elimination. The field effects of the fluorinated substituents increase the barriers to β-hydride elimination. The interpretation of this effect is that the β-carbon atom in the transition state is cationic with respect to the reactant. This is consistent with observations made on the Cu(111) surfaces although the substituent effect is smaller on the Pt(111) surface indicating a difference in the nature of the transition states on the two surfaces.