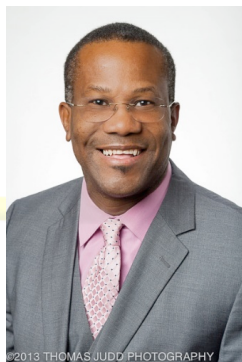


SEMINAR

DEPARTMENT OF CHEMISTRY

The Mechanisms of Methane C-H Activation and Oxy-insertion via DFT Computational Investigation

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February 27th, 2014
2:00 PM, Room 146 Science Center

ABSTRACT:

Our country continues to demand clean renewable energy to meet the growing energy needs of our time. Thus, natural gas, which is 87% by volume of methane, has become a hot topic of discussion because it is a clean burning fuel. However, the transportation of methane is not easy because it is a gas at standard temperature and pressure. The usage of transition metals for the conversion of small organic species like methane into a liquid has been a longstanding practice in stoichiometric chemistry. Nonetheless, the current two-step process takes place at a high temperature and pressure for the conversion of methane and steam to methanol via CO + H₂ (syngas). The direct oxidation of methane (CH₄) into methanol (CH₃OH) via homogeneous catalysis is of interest if the system can operate at standard pressure and a temperature less than 200 °C. Methane is an inert gas due to the high C-H bond dissociation energy (BDE) of 105 kcal/mol. This dissertation discusses a series of computational investigations of oxy-insertion pathways to understand the essential chemistry behind the functionalization of methane via the use of homogeneous transition metal catalysis.

The modeled methane C-H bond activation whereby the ground state geometry of the activating complex was already structurally pre-organized was a novel reaction concept driven by the ground state Pt-OMe complex. There are two key steps for methane to methanol (MTM) catalytic cycle: (1) C-H bond activation by a metal-methoxy complex, (2) the insertion of oxygen into the metal-methyl bond (oxy-insertion). The C-H bond activation (the first step) is well studied, however, the second step is less studied. Thus, my research focuses on oxy-insertion via a two-step mechanism, oxygen-atom transfer (OAT) and methyl migration, utilizing transition metal complexes known to activate small organic species (*e.g.*, Pt^{II} and Pd^{II} complexes). This research seeks to guide experimental investigations, probe the role that metal charge and coordination number play in C-H activation and oxy-insertion, and use computations to compare and contrast electronic potential energy surfaces (PESs) for competing pathways.