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Activation of Light Alkanes by Earth-Abundant Metal-Oxo Catalysts

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In the past year, the papers listed below were published that acknowledge our ACS-PRF grant. Two of these (papers # 2 and #4) were mentioned in an earlier report, but have now been published and have full citations, which are given. Earlier efforts funded by ACS-PRF indicated a significant degree of proton coupled electron transfer (PCET) character to the C-H activation of light alkanes by molybdenum-oxo complexes. In short, the transfer of proton and the electron to activate the light alkane, methane in our studies, was revealed to be asynchronous. As the model of PCET chemistry was not something our group had studied heretofore, we undertook studies focused on reliable modeling of PCET mechanisms involving metal complexes for which experimental data was available for calibration of suitable levels of theory (papers # 1 and # 4). In addition to the development of suitable theoretical protocols for modeling PCET, these studies revealed that even for the activation of methane significant asynchronicity in the hydrogen atom transfer is observed. To wit, our research implies that proton transfer (PT) precedes electron transfer (ET) in some cases, but this can be altered (PT then ET or even synchronous ET+PT) by altering the metal, its spin state and the redox poise of the ligand, all parameters that are relevant to the molybdenum-oxo active species of ethylbenzene dehydrogenase. As such, our ACS-PRF supported research indicates that the acid/base properties of metal-ligand active sites are critical in the facile activation of aliphatic C-H bonds. As light alkanes are very, very weak Bronsted-Lowry (B-L) acids, our research indicates that a profitable line of inquiry is the extent to which coordination (inner and outer sphere) to the transition metal center of the catalyst can reduce the B-L basicity of aliphatic C-H bonds.

1. Azadeh Nazemi, Thomas R. Cundari, "Computational Analysis of Proton-Coupled Electron Transfer in Hydrotris(triazolyl)borate Mid – Late 3d, 4d–Transition Metals Complexes" *Organometallics*, Revisions submitted (08/11/2019).
2. J. Oscar C. Jimenez-Halla, Azadeh Nazemi, Thomas R. Cundari, "DFT study of substituent effects in the hydroxylation of methane and toluene mediated by an ethylbenzene dehydrogenase active site model", *Journal of Organometallic Chemistry*, **2018**, 864, 44-49.
3. Ahmad Najafian and Thomas R. Cundari, "Effect of S-Block Metal Ion on Redox Properties of Mn(V) Salen-Crown Ether Complexes: Methane Activation" *Inorg. Chem.* Revisions submitted (08/11/2019).
4. Ahmad Najafian and Thomas R. Cundari, "Computational Study of Acetylene Hydration by Bio-inspired Group Six Catalyst Models" *Polyhedron*, **2018**, 154, 114-122. (Invited, Bill Jones 65th Birthday Special Issue)