



Mechanistic Study of the Room Temperature Acceptorless Dehydrogenation of an Isobutane σ -Complex in the Solid-State

A. L. Burnage^a, A. J. Bukvic^b, B. E. Tegner^a, S. A. Macgregor^{a*}, A. S. Weller^{b*}

^a Heriot-Watt University

^b University of York

E-mail: alb10@hw.ac.uk; s.a.macgregor@hw.ac.uk

The synthesis and characterisation of σ -alkane complexes in the solid-state via gas-solid single crystal-to-single crystal (SC-SC) transformations is now well established.^[1] For example the gas-solid hydrogenation of $[1-(C_4H_8)][BAR^F_4]$ forms the isobutane complex, $[1-(C_4H_{10})][BAR^F_4]$ (Figure 1).^[2] In the absence of H_2 $[1-(C_4H_{10})][BAR^F_4]$ dehydrogenates back to $[1-(C_4H_8)][BAR^F_4]$ at room temperature, thus providing an example of room temperature acceptorless dehydrogenation of a light hydrocarbon.

Here we report a computational study of the dehydrogenation process. Two mechanistic pathways by which the dehydrogenation occurs are computed, which feature either 1° or 3° C–H activation as the first step. These are kinetically equivalent in an isolated cation model with barriers of 17 kcal mol⁻¹. However these pathways become kinetically distinct (1° = 13 kcal mol⁻¹, 3° = 21 kcal mol⁻¹) in the solid-state when the full system is modelled with periodic DFT. Crystal Explorer is used to understand the impact of the solid-state environment on these two pathways by following each step of the reaction using Hirshfeld surfaces and cation-anion interaction energies. This shows the 3° C–H activation pathway involves a H...C short contact that occurs at the H_2 reductive coupling transition state. The resultant distortion causes a loss of dispersive stabilisation within the micro-environment accounting for the higher barrier of the 3° C–H activation pathway. Alkene rotation then relieves this short contact and retrieves the dispersive stabilisation.

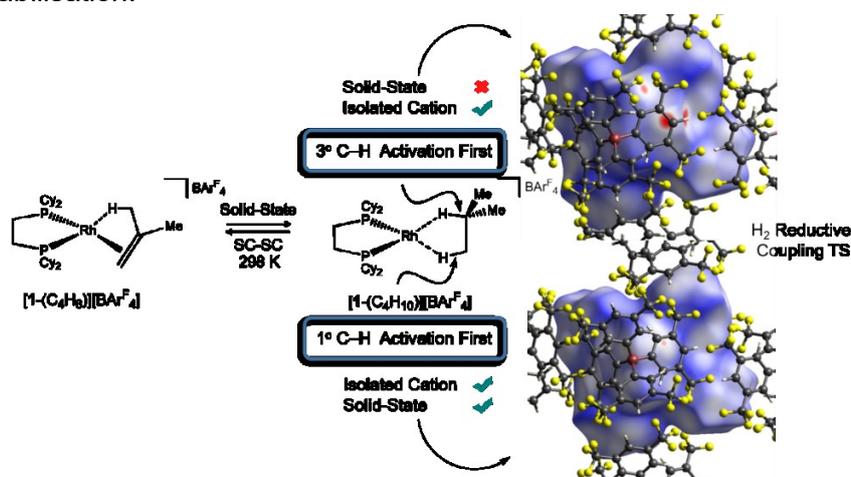


Figure 1. Hirshfeld surfaces showing short contacts at a key transition state.

References:

- [1] A. S. Weller, F. M. Chadwick and A. I. McKay, *Adv. Organomet. Chem.*, 2016, **66**, 223-276
- [2] A. I. McKay, A. J. Bukvic, B. E. Tegner, A. L. Burnage, A. J. Martínez-Martínez, N. H. Rees, S. A. Macgregor and A. S. Weller, *J. Am. Chem. Soc.*, 2019, **141**, 11700-11712