

**OT7 Role of cluster size and substrate in the gas phase C-C bond coupling reaction of allyl halides mediated by  $\text{Ag}_n^+$  and  $\text{Ag}_{n-1}\text{H}^+$  cluster cations**

Farrah Qiuyun Wang<sup>1,2</sup>, George N. Khairallah<sup>1,2</sup> and Richard A.J. O'Hair<sup>1,2</sup>

1. School of Chemistry & Bio21 Institute, University of Melbourne, Victoria 3010, Australia.
2. ARC Centre of Excellence in Free Radical Chemistry and Biotechnology.

Silver clusters, silver hydride clusters, C-C bond coupling, allyl halides, DFT

Gas phase C-C bond coupling reactions of allyl halides mediated by  $\text{Ag}_n^+$  and  $\text{Ag}_{n-1}\text{H}^+$  clusters

Silver ( $\text{Ag}_n^+$ ) and silver hydride ( $\text{Ag}_n\text{H}^+$ ) cluster cations can be synthesised by multi-step CID of  $[(\text{M}+\text{Ag}-\text{H})_x + \text{Ag}]^+$  precursors (M= Glycine or N,N-dimethylglycine, x=1-4) [1]. Previous studies have shown that when  $\text{Ag}_4\text{H}^+$  reacts with allyl bromide, the C-C coupling occurs in a multistep sequence to yield 1,5-hexane [2]. In this study,  $\text{Ag}_2\text{H}^+$ ,  $\text{Ag}_4\text{H}^+$ ,  $\text{Ag}_3^+$  and  $\text{Ag}_5^+$  were allowed to react with 3 different allyl halides,  $\text{C}_3\text{H}_5\text{X}$  (X=Cl, Br, I) in modified ion trap mass spectrometer to establish the role of substrate and cluster cation structure in promoting C-C bond coupling. No C-C bond coupling was observed in the reaction of the cluster cations with  $\text{C}_3\text{H}_5\text{Cl}$ . Four C-C bond coupling reaction channels that were obtained from the reactions with  $\text{C}_3\text{H}_5\text{X}$  (X=Br, I). (i)  $\text{Ag}_n^+ \rightarrow \text{Ag}_n(\text{C}_3\text{H}_5\text{X})^+ \rightarrow \text{Ag}_n\text{X}_2^+$  (ii)  $\text{Ag}_n^+ \rightarrow \text{Ag}_{n-1}(\text{C}_3\text{H}_5)^+ \rightarrow \text{Ag}_{n-1}\text{X}^+$  (iii)  $\text{Ag}_{n-1}\text{H}^+ \rightarrow \text{Ag}_{n-1}\text{X}^+ \rightarrow \text{Ag}_{n-1}\text{X}(\text{C}_3\text{H}_5\text{X})^+ \rightarrow \text{Ag}(\text{C}_3\text{H}_5)_2^+$ ; (iv)  $\text{Ag}_{n-1}\text{H}^+ \rightarrow \text{Ag}_{n-1}\text{X}^+ \rightarrow \text{Ag}_{n-3}(\text{C}_3\text{H}_5)^+ \rightarrow \text{Ag}(\text{C}_3\text{H}_5)_2^+ + \text{Ag}_{n-3}\text{X}^+$ . DFT calculations were carried out to shed light on the structures of the reactants and products as well as the thermochemistry for the experimentally observed reactions.