

GAS PHASE ION-MOLECULE CHEMISTRY OF YTTRIUM AND LANTHANUM CARBIDE CLUSTER CATIONS WITH BENZENE AND CYCLOHEXANE

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A first step in understanding the chemistry of species involved in catalysis is to study such species at a molecular level. As the techniques for nanoscale engineering improve, molecular chemistry such as size selective reactivity, is seen to be extremely valuable for providing insight into the design of new catalytic materials. Mass spectrometry represents the ideal technique for the first step of this process. In this paper we examine the gas phase ion-molecule chemistry of yttrium and lanthanum carbide cluster cations with benzene and cyclohexane.

Results for the gas phase reactions of the metal-carbon clusters, YC_n^+ ($n=2, 4$) and LaC_n^+ ($n=2, 4$ and 6) generated by laser ablation of metal-containing carbon precursors and studied by Fourier transform ion cyclotron resonance mass spectrometry will be presented. For the reactions of MC_2^+ with benzene, cluster ions such as $M(C_6H_4)(C_6H_6)_n^+$ and $MC_2(C_6H_4)(C_6H_6)_n^+$ (where $n=0-3$) are observed. For the MC_4^+ and MC_6^+ ions, non-covalent complexes such as $MC_4(C_6H_6)_n^+$ and $MC_6(C_6H_6)_n^+$ (where $n=1-2$) are observed. Sustained on and off resonance collision-induced-dissociation experiments performed on selected reaction products, e.g., $La(C_6H_4)(C_6H_6)_3^+$, reveal fragmentation patterns that illustrate the types of bonding of the various metal ligands in the ion complexes (See e.g., Figure 1). The reaction of MC_n^+ with cyclohexane indicates strong covalent interactions between the cluster ions and the reagent molecules. All the MC_n^+ cluster cations dehydrogenate the cyclohexane molecule and go on to generate ionic metal-benzene complexes of the form, $M(C_6H_6)_n^+$ (where $n=1-2$).

Density functional theory quantum chemical calculations on selected product ions are used to provide insight into the results of the various ion-molecule reactions and collision induced dissociation experiments. For example, the calculations show that for the $LaC_8H_6^+$ ion the energy difference between the two isomers, $LaC_2H_2(C_6H_4)^+$ and $LaC_2(C_6H_6)^+$, is about 36.4 kcal/mol (See Figure 2).

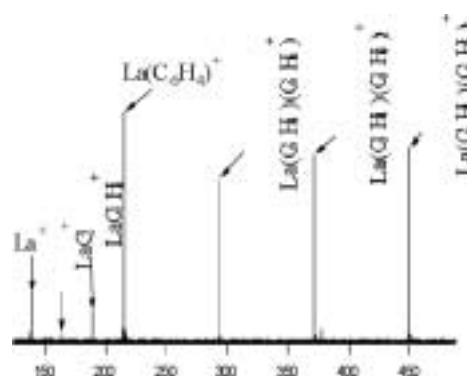


Figure 1. Collision-induced-dissociation of the $La(C_6H_4)(C_6H_6)_3^+$ ion with argon.

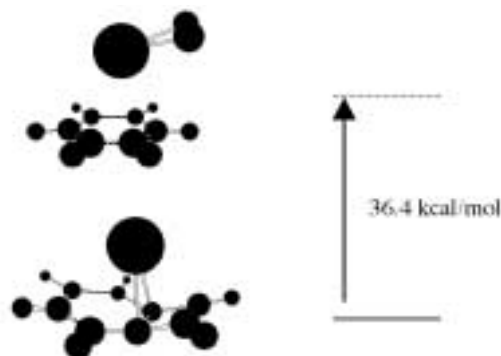


Figure 2. DFT optimized structures and energy difference between two possible isomers of the $LaC_8H_6^+$ ion.