

BOND ENERGIES OF MOLECULAR FRAGMENTS TO TRANSITION METAL CLUSTERS

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Molecular fragments (methyl groups, methylene, etc.) bound to surfaces are key intermediates important in a wide variety of catalytic processes, but thermodynamic information for such interactions is virtually non-existent. Surprisingly, we have found that the thermodynamics for atomic systems (H and O) bound to modest size metal clusters (10 – 15 atoms) reaches bulk phase values. Extension of this observation to molecular species should enable thermodynamic data relevant to surface science to be acquired. This is achieved by examining the kinetic energy dependences of the reactions of Fe_n^+ ($n = 2 - 15$) with CD_4 and ND_3 in a guided ion beam tandem mass spectrometer over the energy range of 0 - 10 eV. Iron cluster cations are formed in a laser vaporization/supersonic expansion source. Reactions are performed under single collision conditions.

In the CD_4 system, all reactions exhibit thresholds and two main products are formed, Fe_nD^+ and Fe_nCD_2^+ . In the ammonia system, Fe_nND_3^+ , Fe_nND^+ and $\text{Fe}_{n-1}\text{ND}_3^+$ are formed exothermically for $n = 3 - 5$ whereas the former is the only low-energy product formed for larger clusters. The iron tetramer is found to be particularly reactive, consistent with earlier finding of Schnabel and Irion, but we find that its reactivity is not unique. These various primary products decompose by iron atom loss and further dehydrogenation at higher energies to form secondary and higher order products.

The kinetic energy dependences are analyzed to determine thresholds for the various primary and secondary reactions, which provide thermochemistry that can be used to verify individual values. From these thresholds, bond energies for iron cluster cation bonds to C, CD, CD_2 , CD_3 , N, ND, ND_2 , and ND_3 are determined. Comparison of the primary and secondary paths for forming Fe_nCD_2^+ and Fe_nND^+ confirm that there are barriers to the primary dehydrogenation reactions for all the clusters, except $n = 3$ and 4 (and 5 in the ND_3 system).

In this work, we report thermochemistry of molecular fragments (CH_3 , CH_2 , CH, NH_2 , NH) bound to clusters of iron. As a function of cluster size, these cluster bond energies rapidly reach relatively constant values. The relative magnitudes in these bond energies are consistent with simple bond order considerations. We find that these bond energies rapidly reach a plateau with cluster size such that the values for larger clusters can be equated with surface values. We believe that this somewhat surprising result is a consequence of the local nature of chemical bonding. The key consequence of this, however, is that we have some of the very FIRST data for the thermochemistry of molecular fragments bound to surfaces.

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