K-CO on Transition Metals: A Local Ionic Interaction

by

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Abstract Submitted

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K-CO on Transition Metals: A Local Ionic Interaction

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We wish to address the nature of the K-CO interaction on a transition metal surface when the K:CO stoichiometry is 1:1. The interaction proposed is transfer of the K 4s electron to CO. A Born-Haber cycle (Figure 1) for this process on a surface has been calculated. The reference state is K plus CO bound separately to the surface (a). A key point in the cycle is that removal of the electron from K bound to a metal surface (b) is less costly in energy (about 0.8 eV) than from K in the gas phase (IP = +4.3 eV). This means that the complex is significantly stabilized on the surface. The removed K electron is then transported to the isolated adsorbed CO (c) at a cost of the electron affinity of CO (+1.5 eV). When the isolated ions are brought together (d) the net stabilization at the equilibrium geometry is about 1.8 eV.

Generalized valence bond calculations have been performed for the KCO complex and we find that it resembles KCN in that it is predominantly ionic (A Mulliken population analysis indicates 97% electron transfer from K to CO) and has a similar K=O bond length. The K-CO bond length was found to be 2.53 Å and the CO bond length was 1.27 Å (cf. 1.15 Å for CO in the gas phase). The CO stretching frequency was found to be 1925 cm⁻¹. Surface vibrational spectroscopies have usually found C=O stretching frequencies for K+CO coadsorption systems in the range 1300-1500 cm⁻¹. IR spectroscopy of matrix isolated KCO found K=O stretching frequency of 1800 cm⁻¹ [1] and EPR studies of the same system [2] showed that K had transferred an electron to CO in the complex. Evidence for the extreme weakening of the C=O bond by K on the surface is provided by thermal desorption: complete isotopic scrambling when a mixture of 12CO and 13CO is adsorbed with K present (1). A local interaction is indicated by the fact that K and CO desorb in coincident peaks from the coadsorbate system which are not observed for single adsorbate experiments [3].

Figure 1 - Born-Haber cycle for formation of K+CO complex.

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