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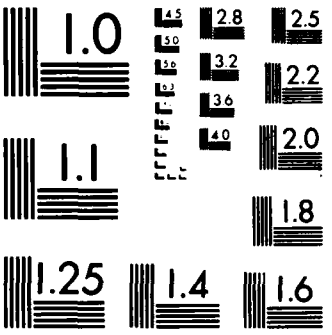

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K-CO on Transition Metals: A Local Ionic Interaction

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. 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 (≈ metal/K surface , i.e. ~ +2.0 eV) than from K in the gas phase (IP = +4.3 eV). This means that the complex is significantly stablized 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 stablization at the equilibrium geometry is ~ -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-CX bond length. The K-CO bond length was found to be 2.53 Å and the CO bondlength was 1.27 Å (cf. 1.15 Å for CO in the gas phase). The CO stretching frequency was found to be 1525 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 a C-O stretching frequency of 1600 cm^{-1} [1] and EPR studies of the same system[1] 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 isotropic scrambling results when a mixture of $^{12}C^{16}O$ and $^{13}C^{16}O$ is adsorbed with K present[2]. 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].

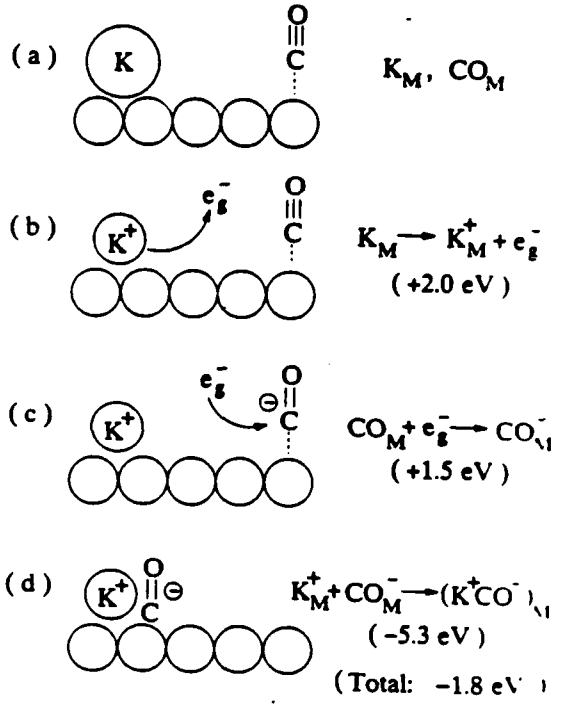

Figure 1 - Born-Haber cycle for formation of k^+CO^- complex.

(1) R.H. Hauge and J.L. Margrave, Argonne National Lab (Report) ANL 1977, ANL-77-2. Conf. High Temp. Sci. Open-cycle Coal Fired MHD Syst. pp. 283-9.

(2) R.A. dePaola, J. Hrbek and F.M. Hoffmann, J. Chem. Phys. 82, 2484 (1985).

(3) R.A. dePaola, J. Hrbek and F.M. Hoffmann, Chem. Phys. Lett. 106, 83 (1984).

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