

CHEMICAL ACTIVATION OF MOLECULES BY METALS:
EXPERIMENTAL STUDIES OF ELECTRON DISTRIBUTIONS AND BONDING

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Objectives.

This research program is directed at obtaining detailed experimental information on the different ways metals bond and activate small organic molecules. It is understood that the chemical behavior of a molecule is different when attached to a metal because its electron distribution and bonding has been altered. This opens up new avenues for reaction and makes possible the many important chemical and catalytic processes. In a simple sense the altered reactivity is a consequence of delocalization of electron density (bonding and otherwise) from the molecule into empty metal levels, and/or a backflow of electrons from filled metal levels into empty orbitals of the molecule. Knowledge of the relative importance of individual electronic structure changes on different aspects of the reaction, such as the breaking and forming of particular bonds, the promotion of electrophilic or nucleophilic attack, the transfer of charge, or acid/base behavior, can lead to more rational modification and improvement of these systems. The goal of this research program is to uncover the fundamental principles of these electronic interactions, and to develop experimental methods of probing and analyzing the relative significance of these interactions in currently important chemical systems.

Present Methods.

A major feature of the program is the continued application and development of our special high-resolution HeI/HeII valence and high-precision X-ray core photoelectron spectroscopy instrumentation utilizing a 36cm radius hemispherical analyzer. Most of the studies involve small molecules attached to metals in the form of organometallic molecules in the gas phase. The research includes preparation and synthesis of the materials most significant to these studies.

The high-resolution gas-phase HeI studies provide precise valence ionization band energies and profiles, and we have accomplished a breakthrough in the observation of vibrational fine structure in the predominantly metal ionizations. In the case of metal-carbonyls the metal density giving rise to these ionizations is backdonating to the antibonding π orbitals of the carbonyls, and observation of metal-carbon vibrational fine structure gives a direct measure of the change in metal-carbonyl bonding force constant and the lengthening of the metal-carbonyl bond when the predominantly metal electron is removed. Thus a direct measure of the role of the metal electron in bonding the carbonyl and weakening the carbon-oxygen bond is obtained. More recently we have also been able to observe metal-metal vibrational fine structure and bond distance changes when a metal-metal bonding electron is removed, and have learned how the change in metal oxidation state changes metal-metal interactions.

The HeII and gas-phase XPS experiments are especially informative when used in combination with the HeI studies. The relative intensities of ionizations in the HeI and HeII excited spectra show the metal character associated with the ionizations. Knowledge of the precise gas-phase core ionization shifts, when compared with the valence ionization information, provides a unique experimental method of separating bonding effects from charge distribution and relaxation effects.

Current Projects.

Studies currently underway include investigations of the electronic interactions and activation of bound methylenes, vinylidenes, alkenes, alkynes, carbenes, carbynes, alkylidenes, alkylidyne and others with various monometal, dimetal, and cluster metal species. An especially interesting and illustrative example of these studies involves the important process of carbon-hydrogen bond activation by transition metals. The electronic mechanism of carbon-hydrogen bond activation can be viewed in two limiting extremes. In one the metal donates electrons into the antibonding C-H orbital to break the carbon-hydrogen bond and form a M(H)(alkyl) complex. This is basically the oxidative addition process commonly invoked by chemists, but it has also been stated that the C-H antibonding orbital is too high in energy to be significantly involved. A second view is that bonding C-H density is lost to the metal, weakening the C-H bond and forming a more acidic proton. This mechanism requires an electron-deficient metal center with a suitable unfilled low-lying orbital.

Cyclohexenylmanganese tricarbonyl has proven to be an excellent system for experimentally measuring the relative significance of these two modes in the early states of activation. The ground-state structure of the molecule corresponds to an intermediate stage of the β -hydride elimination process. The long C-H distance of 119pm and relatively close M-H contact of 184pm indicates a three-center M-CH interaction. From our previous ionization studies of cyclohexadienylmanganese tricarbonyl we know that these molecules have both high-lying filled metal orbitals of correct symmetry for donation to the C-H antibonding orbital, and low-lying empty orbitals for accepting density from the C-H bond. The experimental ionizations clearly show that donation into the C-H antibonding orbital is negligible in this system. It is also found that formal oxidation states and qualitative classification of the electron donor ability of the ligands can be misleading.

Future Directions.

We are currently progressing in two related directions with the capabilities of this program. One direction is toward additional gas-phase electron spectroscopies, including gas-phase Auger spectroscopy and also angular resolved photoelectron spectroscopy utilizing the Wisconsin synchrotron source. The other direction is toward direct surface studies utilizing a state-of-the-art surface spectrometer currently under construction to be delivered late in 1983. These developments will significantly extend the variety of systems we are able to study and the value of the information we are able to obtain.