Reactions of Metal Atoms and Clusters in Low Temperature Matrices

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Research Scope and Objectives

The objective of this research is to study the reactions of simple molecules (e.g. CO, C_6H_6, HCl, C_2H_4) with iron atoms and small clusters in low temperature matrices. The differential behavior of Fe and Fe_n for bond cleavage and simple complex formation will be studied with a view towards modeling of catalytic processes.

Description of Research Effort

The techniques of Mössbauer and infrared spectroscopy are used to identify reaction products. Iron carbonyls, $Fe(CO_n)$, with n = 1 to 5 have been identified, and their ir and Mössbauer spectral parameters found. Iron multimers also react to form $Fe_x(CO)_y$ products.

Iron atoms and clusters react with C_2H_4 to form adducts $Fe(C_2H_4)$ and $Fe_x(C_2H_4)_x$. Only one ethylene molecule reacts per iron atom. Similar results have been found for reaction with ammonia. Benzene forms an adduct $Fe(C_6H_6)$ at low benzene concentration in the matrix, and $Fe(C_6H_6)_2$ at higher benzene ratios. There seem to be two isomers of $Fe(C_6H_6)_2$, tentatively identified as $Fe(\eta^6\text{-}C_6H_6)_2$ and $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$.

The hydrogen halides HCl, HBr, HI were all found to react with Fe atoms in 12°K matrices. The products were H-Fe-X, with iron-hydrogen stretches in the 1750 cm^{-1} region. Hydrogen fluoride did not give a bond cleavage reaction, but formed the simple adduct Fe(FH). In all of the reactions mentioned above unreacted iron atoms, and in some cases dimers, could be detected by their Mössbauer spectra. Iron atoms could even be seen in pure CO matrices.

Future Research

We have begun a study of the reactions of diazomethane with iron atoms in argon or krypton matrices. The hope is to make $Fe(CH_2)$, or $Fe_2(CH_2)$, important intermediates for many proposed mechanisms in syngas catalysis.

$$Fe + CH_2N_2 \rightarrow Fe(N_2CH_2) \xrightarrow{h\nu} Fe(CH_2) + N_2 \qquad (1)$$

Similar reactions with N_2O and HN_3 may lead to isolated FeO molecules, and FeNH.

We wish to examine cleavage reactions of HX molecules to see where the limit of reactivity is.

$$HX + Fe \rightarrow H\text{-}Fe\text{-}X \qquad (2)$$

We know that X = CH_3, NH_2, OH, CN, and C_2H gives no bond cleavage. We wish to extend to X = SH, RO, RCO_2, etc. Our present theory is that (gas phase) acid strength is the determining factor. A sufficiently strong acid, such as HCl, will react.

With the knowledge gained from studying reaction (2), an attempt will be made to cleave CH_3X bonds.

$$CH_3X + Fe \rightarrow CH_3\text{-}Fe\text{-}X \qquad (3)$$

Presumably CH_3I and CH_3Br are good candidates.