The Spectroscopy and Reaction Kinetics of Coordinated Unsaturated Metal Carbonyls

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Coordinatively unsaturated metals are important chemical species with a variety of interesting and unique chemical properties. These species have been shown to be exceedingly reactive. They are important catalysts, reaction intermediates and can form oligomers and metal clusters containing multiple metal centers. Despite their importance and a great deal of interest in this area, little is known regarding details of the structure or reactivity of coordinatively unsaturated metals. Their extreme reactivity has heretofore been an impediment to detailed study of these species in the liquid phase and has virtually precluded study in the gas phase. Until recently nothing was known about the mechanism or kinetics for reactions or cluster formation in these systems.

In an effort to alter that situation we developed an apparatus and a technique which allows us to study coordinatively unsaturated metals in either phase in real time. The use of transient absorption spectroscopy has allowed us to detect and monitor coordinatively unsaturated metals. Most of our studies to date have involved excimer laser photolysis of volatile metal carbonyls to yield gas phase coordinatively unsaturated metal carbonyls or metal atoms. Most of our work has employed an apparatus that uses a line tunable CO laser, as a probe, to monitor the change in absorption of the sample following the excimer laser photolysis pulse. However, we have now integrated
a cw diode laser into the apparatus. This allows us to probe transient species in any region of the infrared and thus vastly increase the versatility of the apparatus.

To actually generate a transient spectrum the change in absorption of the probe laser is monitored at a variety of different laser frequencies with the time versus absorbance signal digitized via a transient digitizer which feeds the data to a signal averager from which it is fed to a computer. The computer takes all the frequency dependent data and assembles it into a transient absorption spectrum which can be displayed as a function of time following the photolysis pulse. Once features in the transient absorption spectrum are identified, a specific feature can be monitored as a function of time and its kinetic behavior discerned. Our current apparatus has a time response of 30 nsec, a frequency range of 350-2350 and 2900-3300 cm\(^{-1}\), and a typical detection sensitivity corresponding to \(10^9\) coordinatively unsaturated metal carbonyl molecules.

With the above technique, we have been able to obtain the first gas phase infrared spectrum of a coordinatively unsaturated metal.\(^2\) We have obtained infrared spectra in the CO stretch region for the species Fe(CO)_x (x = 2, 3, 4) and have measured the rate of reaction of Fe(CO)_x with CO and the activation energies for these reactions.\(^3\) We have made the first real time observation of and are measuring the kinetics for clustering of Fe(CO)_x species.\(^4\) We have performed similar studies for the Cr(CO)_6 system, obtaining spectra for Cr(CO)_x (x = 2, 3, 4, 5)\(^5,\)\(^6\) and have measured rates of reactions of Cr(CO)_5 with CO, CH\(_4\), N\(_2\), H\(_2\) and C\(_6\)H\(_6\).\(^7\) We have also observed a heretofore unreported clustering process in the Cr(CO)_x system. We find that all the Cr(CO)_x fragments react readily with parent. In particular, we have investigated in detail the
clustering process for the reaction of Cr(CO)$_4$ and Cr(CO)$_5$ with parent. We find that both reactions occur at a rate that is within a factor of two of gas kinetics. We assign the species initially produced via these clustering reactions to Cr$_2$(CO)$_{10}$ and Cr$_2$(CO)$_{11}$, respectively, and have recorded the first gas phase spectra for these species in the carbonyl stretch region.

We have also obtained results on the Mn$_2$(CO)$_{10}$ system. As with Cr(CO)$_6$ and Fe(CO)$_5$, we have recorded the spectra of the photoproducts identified following photolysis at 193, 249 and 351 nm. We have identified the major photoproducts and have measured the rate of reaction of Mn$_2$(CO)$_9$ with CO and the rate of reaction of two Mn(CO)$_5$ radicals to regenerate Mn$_2$(CO)$_{10}$. Interestingly, the reaction of Mn$_2$(CO)$_9$ with CO is quite slow and we are exploring the structural ramifications of this observation. The reaction of two Mn(CO)$_5$ radicals is very rapid, almost gas kinetic, and represents the first measurement of the actual rate of formation of a metal-metal bond in the gas phase.

Most recently we have been investigating the clustering process in the Fe(CO)$_5$ system in more detail. We find that only one of two isomers of Fe$_2$(CO)$_8$ forms on reaction of Fe(CO)$_3$ with Fe(CO)$_5$. Furthermore, the isomer that is produced in the gas phase has been observed to be the less stable isomer in the matrix. We believe this situation occurs because the kinetics of reaction of Fe(CO)$_3$ with Fe(CO)$_5$ is spin controlled and the isomer we observed in the gas phase, the bridged form of Fe$_2$(CO)$_8$, is a triplet while the unbridged form of Fe$_2$(CO)$_8$ is a singlet. We are working to verify this hypothesis which could have important ramifications for understanding and predicting which clustering reactions will occur in the gas phase.
We are also investigating the Fe(CO)₂(NO)₂ system where we are primarily interested in determining the relative importance of simple addition reactions versus displacement reactions. We are probing this question by looking at reactions that occur following photolysis of Fe(CO)₅ in a bath of NO molecules. Since Fe(CO)₂(NO)₂ is the only stable iron carbonyl nitrosyl we are investigating how the kinetics and branching ratios for reaction of the various Fe(CO)ₓ moieties lead to this species.

Finally, we are investigating some predictions on relative rates of reaction of metal carbonyls with various ligands which were made by Roald Hoffmann based on an inorganic analog of Woodward-Hoffmann orbital symmetry rules. Specifically we are looking at the reaction of conjugated versus unconjugated dienes with Fe(CO)₃ and Cr(CO)₄. Hoffmann predicted that the former species should react with conjugated dienes faster than with unconjugated dienes and that the latter species should behave in an opposite fashion. These predictions have never been tested because of the prior inability of experimentalists to produce specific coordinatively unsaturated metal carbonyls in a controlled fashion in the gas phase. Obviously these rules for reaction, which have been so important in the understanding of organic reaction kinetics, could also be of paramount importance in predicting rates and pathways of reactions of organometallic species.

The above work has also allowed us to formulate a hypothesis regarding the mechanism of photodissociation in these systems and provide us with insight into how to tailor the dissociation process to produce desired photoproducts. It also allows us to intelligently speculate on the timescale for dissociation.


7. T. A. Seder, S. P. Church, and E. Weitz, unpublished results.


10. R. Ryther, S. Gravelle, and E. Weitz, work in progress.

11. S. Gravelle and E. Weitz, work in progress.


13. L. van der Burgt, S. Gravelle, and E. Weitz, work in progress.


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a) Detection of Transient Organometallic Species by Fast Time-Resolved IR Spectroscopy.
   M. Poliakoff and E. Weitz
   Advances in Organometallic Chemistry 25, 277 (1986).

b) Gas Phase Infrared Spectroscopy and Recombination Kinetics for Mn(CO)₅
   Generated Via XeF Laser Photolysis of Mn₂(CO)₁₀.
   T. A. Seder, S. P. Church and Eric Weitz

   (x = 5,4,3,2) Fragments.
   T. A. Seder, S. P. Church and Eric Weitz
d) The Wavelength Dependence of Excimer Laser Photolysis of Fe(CO)$_5$ in the Gas Phase: Transient Infrared Spectroscopy and Kinetics of Fe(CO)$_x$ ($x = 4, 3, 2$) Photofragments.
T. A. Seder, A. J. Ouderkirk and Eric Weitz

e) Photodissociation Pathways and Recombination Kinetics for Gas Phase Mn$_2$(CO)$_{10}$
T.A. Seder, Stephen P. Church and Eric Weitz

f) Studies of Coordinatively Unsaturated Metal Carboxyls in the Gas Phase via Transient, Time Resolved Infrared Spectroscopy
T.A. Seder, A.J. Ouderkirk, Stephen P. Church and Eric Weitz

Associated personnel 10/1/86-9/30/86

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Papers presented relating to project area 10/1/85-9/30/86

Seminars: Purdue University 10/85
University of Wisconsin 3/86
John Hopkins University 4/86
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**Abstract**

A program involving the investigation and characterization of reactions of coordinately unsaturated organometallic species is described. The program emphasizes the measurement of rates of reaction of photolytically produced coordinately unsaturated species with the parent and rates for cluster formation. Experimental measurements are performed using a time resolved transient absorption apparatus which uses a line tunable CO laser to record spectral and kinetic information by means of probing absorptions in the CO stretch region of the infrared. Systems that have been investigated include coordinately unsaturated species generated from the Fe(CO)$_5$, Cr(CO)$_6$ and Mn$_4$(CO)$_{10}$ parents. The results of experiments with these systems are briefly discussed.

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