Funding Request for Noble Gas–Transition Metal Interactions

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Abstract

This is a request for funding a chemical kinetic study of noble gas coordination to organometallic centers. Recent advances in high speed infrared spectroscopy have opened up new opportunities to enhance a wealth of information already accumulated in low temperature matrix studies. In this proposal, reaction conditions will be at room temperatures, where organometallic complexes will be dissolved in supercritical noble gas solutions.

Introduction

Noble gases have sustained plasmas for the past few decades, but who would have ever thought that these so called “inert” substances could eventually stabilize transition metal complexes and serve as catalysts in selective chemistry applications. According to James Martin, at North Carolina State University, noble gas chemistry may impact the next century of science as dramatically as the electron influenced this century. If this proposal is funded, you have a ground level opportunity to participate in the noble gas frontier.

Literature

Let’s start by reviewing some of the relevant literature in the field of noble gas interactions with transition metal centers. Perutz and Turner used photolysis of group 6 hexacarbonyls, $M(CO)_6$, where M=Cr, Mo, and W, under low temperature matrix conditions, to generate $M(CO)_5$ metal centers which interacted with traditionally inert substances like: CF_4, SF_6, CH_4, Ar, Kr, and Xe. The interaction was characterized by a blue shift in λ_{max} of the visible absorption band of the metal center, with a stronger interaction creating a greater shift[1].

Although low temperature matrix isolation methods gave the noble gas–transition metal field momentum, the solid state nature of the material made it difficult to do in situ chemical kinetic studies. To overcome this obstacle, people tried gas and liquid phase studies, using one or both of two infra red techniques, fast fourier transformation IR(FTIR) and fast time resolved IR(TRIR). However, the gas phase compounds under study must have high vapor pressures, which limited the work to group 6 hexacarbonyls, $M(CO)_6$, and liquid studies required cryogenic noble gas temperatures which made the equipment rather cumbersome[2].

To overcome these barriers, the latest trend in noble gas–transition metal chemistry occurs at room temperature in supercritical solvent environments. If you have any recollection of phase diagrams, I’m talking about moving to the right of the critical point, at temperatures and pressures above critical conditions, where the boundary between liquid and vapor no longer exists. In such an environment, fluids become a “curious hybrid” between liquid and gas, allowing virtually infinite solubility of a wide variety of substances. Additionally, the solvent density can be varied over a wider range than conventional solvents[2].

A typical experiment might involve a noble fluid as a solvent, plus a transition metal, like $M(CO)_6$, and other reactants, such as CO, to serve as solutes. Photochemical removal of a single carbonyl group from the transition metal to create an unstable 16 electron intermediate still prevails from the crude beginnings. The researchers then track the reaction kinetics, watching for the appearance and subsequent degradation of noble gas–transition metal complexes, using FTIR and/or TRIR spectroscopically, until the carbonyl group returns.

To illustrate these principles, I wanted to focus your attention on recent results published by Sun et al. Figure 1 shows both infrared spectrums, (a)FTIR and (b) TRIR traces, for $CpRe(CO)_3$ in supercritical(sc) Xe in the presence of CO. The FTIR curve is used primarily as a base line to insure purity and consistency from experiment to experiment. The TRIR curve gives real time snapshots of the reaction in progress as evidenced by the data produced 1 microsecond after photolysis. Because TRIR is measured relative to the FTIR, the “parent” peaks of the unphotolized solution go negative, and the new species created after photolysis become positive peaks on the trace. The parent and new specie peaks positions are compared to historical data from matrix experiments to indentify compounds[3].

Once a specific compound has been identified, a particular peak intensity will directly convey its concentration in the TRIR mode, as seen in figure 2, where (a) represents $CpRe(CO)_2Xe$, the stabilized noble gas–transition metal complex, (b) corresponds to $CpRe(CO)_3$, the initial reactant and final product, and (c) directly follows from the second order rate equation:

$$CO + CpRe(CO)_2Xe \rightarrow CpRe(CO)_3 + Xe$$

$$r = k_2[CO][CpRe(CO)_2Xe].$$

Upon removal of a carbonyl group, research has shown that the typical 16 electron intermediate only lasts for less than a picosecond before it becomes stabilized by the solvent[10]. A pulsed Nd:YAG laser, $\lambda = 266$ or 355 nm, initiates the photochemical reactions[3].

Now that I’ve explained the basic procedures for conducting experiments, I want to show you some startling results from the Sun et al. paper detailed in figure 3, which lists various noble gas–transition metal compounds and their second order reaction rate constants. As you go through the group 6 metal carbonyl substances stabilized in Kr and Xe, all of them are on the order of 10^6 to 10^8 dm^3/mol.s. If you move over to group 7 metal aromatic carbonyl substances, Kr stability is consistent with group 6 reaction rates, but Xe stands alone with a reactivity of 4.8 x 10^3 dm^3/mol.s. In fact, the authors point out that its reactivity is a little more than twice that of $CpRe(CO)_3$ stabilized in n–heptane, at 2 x 10^3 dm^3/mol.s, and alkane groups have historically shown substantially better stabilization[3].

Before I launch into my research proposal, I wanted to draw your attention to figure 4, which demonstrates another clever trick the Sun et al. team pursues, to partially address the question of whether the organometallic truly coordinates with the noble gas. Realizing the large disparity between second order reaction constants in the $CpRe(CO)_3$ case, they put trace amounts of Xe in a supercritical Kr solution. Figure 4 illustrates how curve (a), the Kr complex peaks out early on, because it is in excess, but curve (b), the Xe complex rises and prevails over the 1.5 microsecond time scale, because it is a more stable species. This mimics the following reaction sequence[3]:

$$CpRe(CO)_3 \rightarrow CpRe(CO)_2 + CO \tag{1}$$

$$CpRe(CO)_2 + Kr \rightarrow CpRe(CO)_2Kr \tag{2}$$

$$CpRe(CO)_2Kr + Xe \rightarrow CpRe(CO)_2Xe + Kr \tag{3}$$

Proposal

My research proposal addresses the issue of why is there such a large disparity between second order reaction constants in $CpRe(CO)_3$ for Xe versus Kr stabilization. The proposal is primarily experimental, in collaboration with the Sun et al. research group. I propose to use their techniques to explore the following alternative organometallic species in Xe and Kr supercritical solutions:

group 6	group 7
(Benzene)$Cr(CO)_3$	$HRe(CO)_5$
(Benzene)$Mo(CO)_3$	$FRe(CO)_5$
(Benzene)$W(CO)_3$	$ClRe(CO)_5$

If you do an electron count, all of these species start out as 18 electron transition metals, which become 16 electron intermediates upon photolysis of one carbonyl group. My hunch is that some type of Agostic behavior could be playing itself out in the experiments done so far. If you go back to figure 3, with the organometallics tried, all the group 6 metals are purely carbonyls, whereas all the group 7 metals contain cyclopentane groups. Why not reverse the situation and see what happens. Perhaps Xe somehow coordinates to the metal center in a different manner than Kr, due to the size difference and induces an Agostic interaction. Typically Agostic conditions appear under the following circumstances: 1) early transition metals, 2) electron deficient species, and 3) C–H atom proximity. Agostic behavior occurs when the transition metal is bonded to either a carbon or a hydrogen on an organic ligand, and the neighboring carbon or hydrogen gets “sucked” into proximity by the transition metal, hungry for electrons.

The group 6 metalorganic series has been chosen to induce Agostic behavior, whereas, the group 7 metalorganic series attempts to inhibit such an interaction. Although the $HRe(CO)_5$ might suffice in the latter group, people might argue whether the CO and H ligands rearrange or recombine upon photolysis, so I tried a few different halogen ligands to preserve electron counts. According to James Martin, a close associate, Agostic behavior has been seen in boron hydride ligands as well. If you look at electronegativities for all three elements, they are as follows:

Element	Electronegativity
Boron	2.0
Carbon	2.5
Hydrogen	2.2

Clearly, these electronegativities fall in a very narrow range. By taking advantage of the higher electronegativity in flourine and chlorine, hopefully the Agostic behavior will be suppressed in the group 7 series.

So, a total of 12 different experiments (6 metalorganics solvated in 2 supercritical noble gases) will be carried out over the next two years to fulfill the research contract. One could envision future experiments further down the line upon completion of this contract. Changing organic ligands on group 6 and group 7 metalorganics to probe potential Agostic behavior, or exporing group 8 metal series with supercritical noble gases.

Conclusion

Some researchers have seen no interaction between CpCo(CO) and cyclohexane[4], but Cp*Rh(CO)[5,6] and Cp*Ir(CO)[7] react with alkane solvents to form C–H activated products. Grevels has reported a lifetime of less than 10 microseconds for $Fe(CO)_4$(cyclohexane)[8]. Perutz also found C–H activated products following photolysis of Os metalorganics in methane doped Ar lattices[9]. By using pure supercritical noble gases in these cases as solvents, C–H activated products might be avoided and transition metal–noble gas stabilization explored. One could even imagine the possibility of doping the supercrical noble gas solutions with reactants in which the noble gas stablization provides selective chemistry with the transition metal complexes.

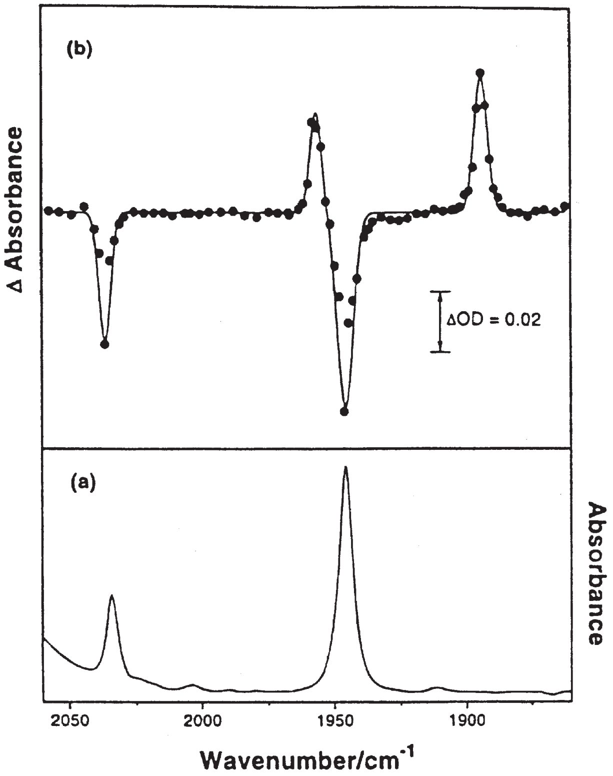

Figure 1: (a) FTIR spectrum

(b) TRIR difference spectrum

$M(CO)_5L$	temp/°C	k_2/mol^{-1} dm^3 s^{-1}
$Cr(CO)_5(Xe)$	25	8.4×10^6
$Cr(CO)_5(Kr)$	32	4.7×10^8
$Mo(CO)_5(Xe)$	25	1.1×10^7
$Mo(CO)_5(Kr)$	30	4.3×10^8
$W(CO)_5(Xe)$	25	2.0×10^6
$W(CO)_5(Kr)$	25	7.5×10^7
$CpRe(CO)_2(Xe)$	25	4.8×10^3
$CpRe(CO)_2(Kr)$	25	8.1×10^6

Figure 3: Second order rate constants

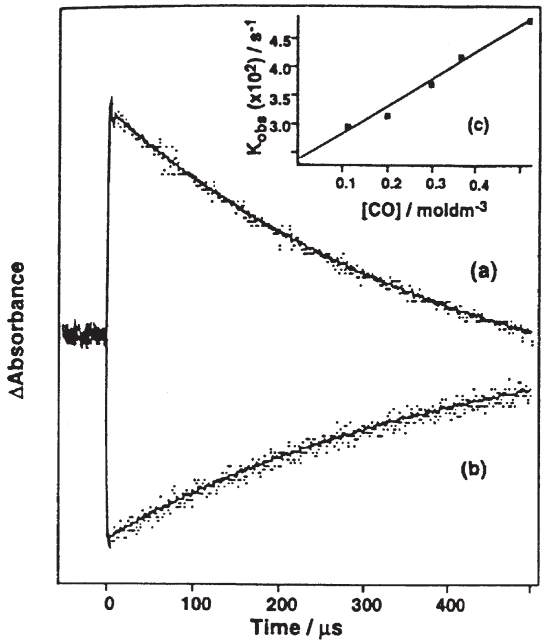

Figure 2: (a) TRIR degradation of $CpRe(CO)_2Xe$

(b) TRIR restoration of $CpRe(CO)_3$

(c) kinetic curve

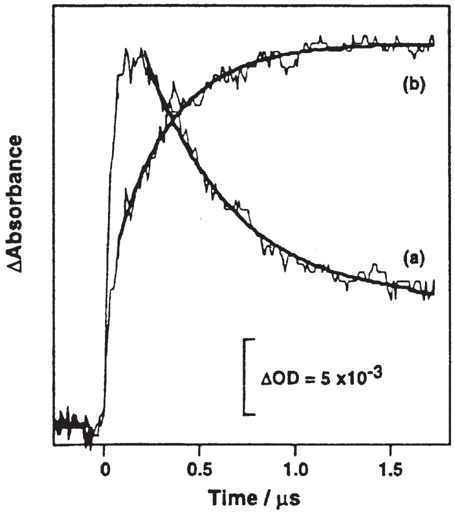

Figure 4: (a) TRIR consumption of $CpRe(CO)_2Kr$

(b) TRIR generation of $CpRe(CO)_2Xe$

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