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Photodissociation and Photoinduced Electron Detachment in Dinuclear Metal Carbonyl Anions

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Received February 10, 1995

The photochemistry and reactivity of gas-phase metal carbonyl neutrals,² cations,³ and anions^{4,5} have been investigated extensively for their potential relevance to condensed-phase organometallic photochemistry,⁶ catalysis,⁷ and synthesis.⁸ Among the most intriguing results of these studies have been the reports of neutral metal atom loss upon low-energy (roughly 1–20 eV center-of-mass) collisional activation of the highly coordinatively unsaturated dinuclear metal carbonyl anions $\text{Cr}_2(\text{CO})_5^-$ and $\text{Fe}_2(\text{CO})_4^-$.^{4,9} This is a provocative observation because it suggests that these anions exist as completely asymmetrically coordinated dimers in which one of the metal atoms behaves like a ligand. In this Note we report on the visible and near-infrared photochemistry of the dinuclear metal carbonyl anions $\text{M}_2(\text{CO})_n^-$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$; $4 \leq n \leq 9$, depending on the metal). Electron ejection and scavenging experiments are used to establish that the “neutral metal atom loss” observed upon photoactivation of $\text{Cr}_2(\text{CO})_5^-$, $\text{Fe}_2(\text{CO})_4^-$, and $\text{Co}_2(\text{CO})_4^-$ is attributable to photoinduced electron detachment followed by dissociative attachment to the neutral metal carbonyl background gas. Since electron detachment could easily be vibrationally driven, this study provides an alternative explanation for the previous collisional activation results.

All experiments were performed with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer^{10,11} which has been described.^{12,13} The long trapping times possible with FT-

ICR and the use of optically transmissive (>80%) screens in place of the excite plates allow the study of ion photochemistry. Two photoexcitation sources were available: a pulsed Nd:YAG laser used at 1064 nm in the low-power “long-pulse” mode and a CW Ar⁺/dye laser system operated in the Rhodamine 6G tuning range (575–630 nm) with a maximum output of 1.2 W.

Dinuclear anions are generated by dissociative attachment of near-thermal electrons directly to a static background of those dinuclear neutral precursors that exist; i.e., $\text{Mn}_2(\text{CO})_9^-$ and $\text{Mn}_2(\text{CO})_8^-$ are formed from $\text{Mn}_2(\text{CO})_{10}$, $\text{Fe}_2(\text{CO})_7^-$ is formed from $\text{Fe}_2(\text{CO})_9$, and $\text{Co}_2(\text{CO})_6^-$ and $\text{Co}_2(\text{CO})_5^-$ are formed from $\text{Co}_2(\text{CO})_8$. Metal–metal bond cleavage to generate the mononuclear anions $\text{Mn}(\text{CO})_5^-$, $\text{Fe}(\text{CO})_4^-$, and $\text{Co}(\text{CO})_4^-$ competes with dinuclear anion formation even at low electron kinetic energies and typically dominates after only a slight increase in the beam voltage. (Dicobalt anion yields are <5% at all nominal beam energies.) Dinuclear chromium anions are formed by ion–molecule reactions. First, $\text{Cr}(\text{CO})_5^-$ is generated by dissociative electron attachment to $\text{Cr}(\text{CO})_6$ ¹⁴ admitted to the reaction chamber through a pulsed valve. The $\text{Cr}(\text{CO})_6$ pressure wave reaches a peak of $\sim 5 \times 10^{-5}$ Torr and is largely pumped away within 0.5 s of the pulsed valve opening. (However, sufficient $\text{Cr}(\text{CO})_6$ remains in the chamber long enough to effectively scavenge additional trapped electrons from any source.) Next, the $\text{Cr}(\text{CO})_5^-$ is photolyzed with multiple 1064 nm laser pulses to produce $\text{Cr}(\text{CO})_4^-$, which is immediately reacted with a second pulsed-valve addition of $\text{Cr}(\text{CO})_6$ to form $\text{Cr}_2(\text{CO})_8^-$. For all metals, less-saturated dimer anions can usually be prepared by visible or near-infrared photolysis of their more-saturated counterparts. Absorption cross sections for these species range from 5×10^{-19} to 1×10^{-17} cm² and are tentatively assigned as ligand field bands.

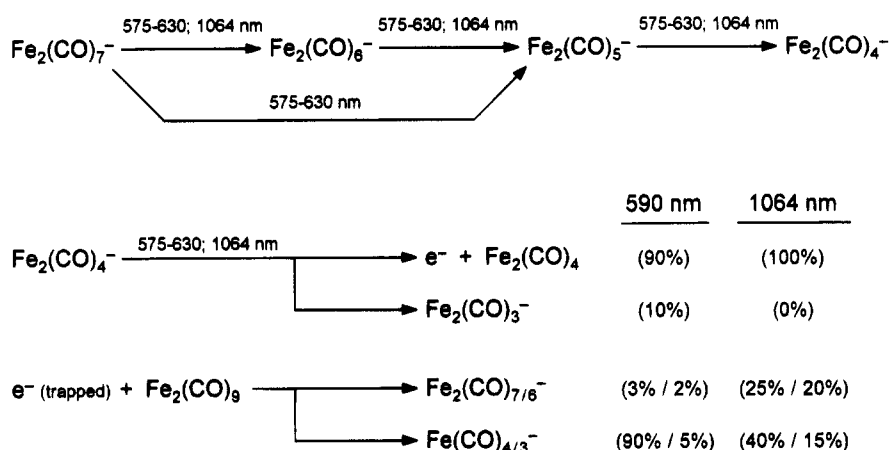
Ions are isolated using swept rf ejection pulses, and photodissociation (or photodetachment) pathways are confirmed with “double-resonance” ejection techniques or laser-fluence dependence measurements. Excess electrons are ejected from the cell when necessary using short-duration suspended trapping events.^{13,15} Up to a full 1 s is allowed for z-axis translational relaxation of the ion cloud after these events.

The diiron photochemistry shown in Scheme 1 has been chosen as representative. Sequential loss of carbonyls occurs until formation of $\text{Fe}_2(\text{CO})_4^-$, the “terminal dinuclear anion”. Photoexcitation of this ion leads mainly to electron detachment, although a small amount of competitive dissociation is also observed in the visible region. The detached electrons remain trapped in the mass spectrometer and are eventually captured by background $\text{Fe}_2(\text{CO})_9$, producing mainly $\text{Fe}(\text{CO})_4^-$. Two observations support this detachment mechanism. First, the electron attachment product intensity is significantly reduced if electrons are ejected immediately after the photoactivation

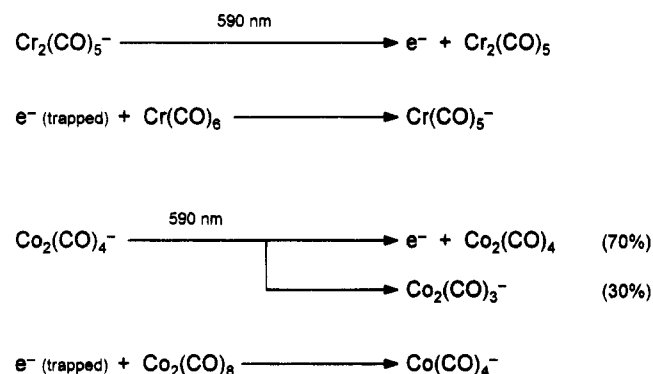
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Scheme 1



Scheme 2



event. (The product intensity is never reduced to zero because of the possibility of electron capture *during* this event.) Second, as detailed in Scheme 1, *more*-saturated dinuclear anions appear (particularly in the 1064 nm experiments), as would be expected for $\text{Fe}_2(\text{CO})_9$ scavenging low-energy electrons. The variation with photon energy of the relative intensities of the mono- and dinuclear products is discussed later.

Photodetachment is also observed (as confirmed by electron ejection) for $\text{Cr}_2(\text{CO})_5^-$ and $\text{Co}_2(\text{CO})_4^-$, as shown in Scheme 2. [True photoinduced metal–metal bond cleavage (to form $\text{Mn}(\text{CO})_5^-$) occurs in the dimanganese system, but from the more highly saturated species $\text{Mn}_2(\text{CO})_7^-$; $\text{Mn}_2(\text{CO})_6^-$ and $\text{Mn}_2(\text{CO})_5^-$ are never observed.] Unlike the diiron system, more-saturated dinuclear formation cannot be observed for dichromium because the neutral precursor is mononuclear or for dicobalt because the relative cross section for dinuclear formation is too low. Like the diiron system, dissociation competes with detachment in photoactivated $\text{Co}_2(\text{CO})_4^-$, but more strongly.

There are a few differences between these experiments and the previously-reported experiments in which apparent metal atom loss was observed.^{4,9} First, the earlier investigators used collision-induced dissociation (CID) to strip all carbonyl groups from $\text{Cr}(\text{CO})_5^-$ or $\text{Fe}(\text{CO})_4^-$, leaving the atomic metal anions Cr^- and Fe^- . These bare metal ions were then allowed to react with background $\text{Cr}(\text{CO})_6$ or $\text{Fe}(\text{CO})_5$ to form $\text{Cr}_2(\text{CO})_5^-$ or $\text{Fe}_2(\text{CO})_4^-$, respectively. While it is natural to assume that a nonsymmetrically synthesized dinuclear metal carbonyl anion might retain its asymmetry through its ultimate dissociation, the possibility of internuclear carbonyl transfer cannot be ignored. A variety of carbonyl scrambling modes (all invoking some sort of bridging carbonyl intermediate) have been observed

by ^{13}C NMR for saturated dinuclear metal carbonyls,¹⁶ and it is very likely that scrambling in these unsaturated, less-hindered complexes is even more facile. A potentially mitigating condition could be the presence of formal metal–metal multiple bonds, although this also makes it far less likely that metal atom loss is the lowest-energy dissociation pathway. Certainly, the nascent dinuclear complexes of the previous investigations must be singly bound until at least one carbonyl has transferred to the less-saturated metal center, which might be expected from steric, entropic, and bond energy considerations. For the gas phase, Wronka and Ridge¹⁷ have presented convincing kinetic evidence for iron–iron double bonds in $\text{Fe}_2(\text{CO})_n^-$ ($5 \leq n \leq 7$), and as Squires points out,⁴ the correlation they observe between the relative rate constants and the *average* electron deficiency per metal center (assuming double bonds) suggests that these anions are symmetrically substituted. There is also spectroscopic evidence for multiple bonding in Fe_2 , Co_2 , and Cr_2 neutrals.¹⁸

A potential ambiguity often exists in photoactivated experiments since it is not always known whether dissociation (or detachment) occurs from an electronically or vibrationally excited penultimate species, even though internal conversion is strongly favored by the extremely high vibrational state densities of these excited species. Here, the branching between loss of one and two carbonyls observed for the visible photodissociation of $\text{Fe}_2(\text{CO})_7^-$ suggests that a vibrationally excited intermediate is responsible at least for the loss of the second carbonyl, since no “direct” dissociation process could simultaneously remove two carbonyls. Branching was also observed between carbonyl and electron loss from photoexcited $\text{Fe}_2(\text{CO})_4^-$ and $\text{Co}_2(\text{CO})_4^-$; it is likely that these processes both proceed through a common, vibrationally excited intermediate. Vibrationally-induced electron detachment is a known phenomenon available to activated anions possessing a curve crossing with their corresponding neutral.^{19,20} (Such a process has also been invoked previously to explain transmission losses for the collision-induced dissociation of *mononuclear* metal carbonyl

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anions in a triple-quadrupole mass spectrometer.²¹) Collision experiments, however, have their own ambiguity. The collision energies reported for the previous CID experiments represent the maximum that may be deposited; the *average* energy deposited into a polyatomic ion from a neutral collision is at most a few percent of the total available center-of-mass collision energy.²² Since the threshold for apparent "neutral metal atom loss" is on the order of 1 eV, the energy regimes of the CID and photoactivated experiments are quite comparable. It appears that detachment is the lowest-energy process available to these species, and as such it ought to dominate the collisional activation behavior.

The photon energy dependence of the branching ratio between mono- and diiron formation in the $\text{Fe}_2(\text{CO})_9$ scavenging experiments is a bit troublesome, since the vibration-induced detachment model predicts that low electron kinetic energies are strongly favored.²⁰ The detachment rate decreases for higher-energy electrons because the relevant nuclei must undergo too large a change in kinetic energy and momentum upon crossing to the neutral potential surface. However, the change in electron kinetic energy required to dramatically change the dissociative electron attachment product distribution for these dinuclear metal carbonyls appears to be quite small,

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and the difference in photon energy should be large enough to allow the small changes required. (In fact, it appears that dinuclear metal carbonyls may prove useful for measuring the kinetic energy distribution of low-energy electrons, if reliable ionization cross sections can ever be obtained.)

In conclusion, vibrationally-induced electron detachment represents a much more palatable explanation than neutral metal atom loss from an asymmetrically-substituted dinuclear species for the activated processes observed for the "terminal" dinuclear anions $\text{Cr}_2(\text{CO})_5^-$, $\text{Fe}_2(\text{CO})_4^-$, and $\text{Co}_2(\text{CO})_4^-$. It remains curious that detachment occurs only from those dinuclear anions having the same number of carbonyls as their most nearly saturated mononuclear counterparts: the 17-electron $\text{Cr}(\text{CO})_5^-$ and $\text{Fe}(\text{CO})_4^-$ and the 18-electron $\text{Co}(\text{CO})_4^-$. Perhaps this is merely coincidental, but it could indicate a systematic relationship between the degree of coordinative saturation and the electron affinity of a dinuclear metal complex anion. These dinuclear complexes are not sufficiently understood at this point for such effects to be predicted *a priori*. Simple structural considerations such as the metal-metal bond order and the presence or absence of bridging carbonyls have yet to be satisfactorily addressed; a discussion of the electron affinities of these species would proceed more profitably from reasonably well-known structures.

IC950160P