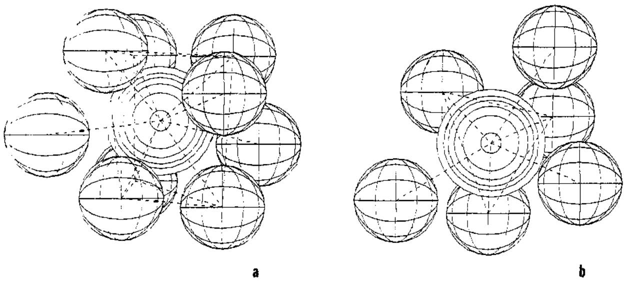

Figure 16. Space filling representation of $Cl(H_2O)_9^-$ complex. Hatched spheres correspond to water molecules with van der Waals radii of 1.4 Å. (a) Complete complex; (b) complex with top triangle removed.

Conclusions

In conclusion, we have shown that simulation results on ionic hydration can be analyzed by using elementary pattern recognition techniques and that the mean water positions in the hydration complexes can be interpreted in terms of elementary geometric polyhedra. The nature of the polyhedral structure depends significantly on the type of ion in the complex. In some cases the results are different from those expected or predicted from chemical intuition but correspond to types seen in crystal hydrate structures of various ions. Pattern recognition methods thus appear to be a useful procedure for the analysis of simulation results on fluids and provide a convenient and accessable means of considering geometrical aspects of the organization of solvent molecules in solvation shells. Most importantly, the solvent mean positions are rigorously defined on the statistical state of the fluid-phase system.

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Registry No. H_2O, 7732-18-5; Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7; F^-, 16984-48-8; Cl^-, 16887-00-6.

Photochemistry of Gas-Phase $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$: Mass Spectrometric Evidence for a Dinuclear Primary Photoproduct

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Abstract: The photochemistries of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ following excitation at 337 nm in the region of their $\sigma^* \leftarrow \sigma$ bands are investigated under collision-free conditions. Results suggest that in addition to the $M(CO)_5$ photofragments previously reported in the molecular beam study of Freedman and Bersohn, partially decarbonylated dimetal photofragments are also produced. Thus, in the gas phase, as in solution, both dissociative CO loss and M–M bond scission appear to be primary photochemical processes in the dimetal decacarbonyl systems.

The decacarbonyldimetal complexes of manganese and rhenium were among the first metal–metal bonded systems to be subjected to a detailed photochemical investigation.[1,2] These molecules, in which the two $M(CO)_5$ subunits are joined solely by a metal–metal single bond, provide ideal systems with which to examine the competition between metal–metal and metal–ligand bond reactivity in the excited state chemistry of transition-metal carbonyl complexes. Early condensed-phase studies indicated that excitation of the allowed $\sigma^* \leftarrow \sigma$ transitions,[3] which reduce the formal metal–metal bond order from one to zero, results in clean, quantum efficent homolytic cleavage to 17-electron $M(CO)_5$ radicals.[1,2] This contrasts with the thermal decomposition pathway in the ground electronic state, which is dominated by dissociative loss of carbonyl ligands.[4]

However, recent investigations have disclosed a more complex pattern of photochemical behavior for the $M_2(CO)_{10}$ systems, involving at least two primary photoproducts whose relative yields appear to be highly sensitive to environmental effects. Flash photolysis and chemical studies suggest that CO loss[5-7] or isomerization[8] can compete with M–M bond cleavage in solution, and quantum yields as high as 30% have been estimated for the former process.[6,7] The appearance of both mononuclear and dinuclear species within 25 ps after excitation suggests that both are primary photoproducts.[5] In rigid alkane or rare gas matrices, on the other hand, only M_2-containing decarbonylated photofragments are observed upon photolysis of $Mn_2(CO)_{10}$[6] and other M–M bonded systems.[9] This has been attributed to a solvent cage effect on the efficiency of formation of solvent-separated $M(CO)_n$ species.[6,9a] In the gas phase, where such environmental perturbations are absent, dissociation of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ has been reported to result solely in metal–metal bond cleavage.[10]

In view of recent evidence for competing photochemical pathways in solution following one-photon near-UV excitation of dinuclear carbonyl complexes, and the results of multiphoton

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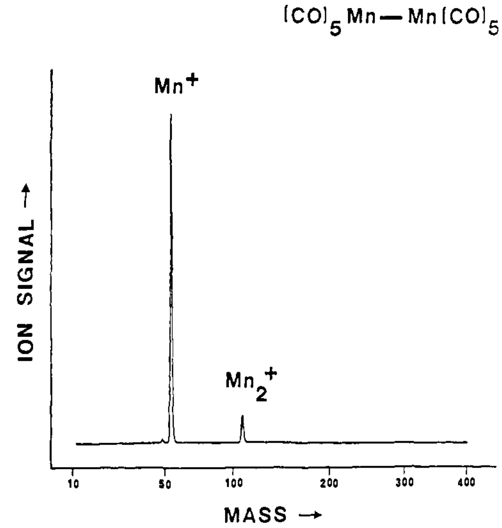

Figure 1. Multiphoton ionization (MPI) time-of-flight mass spectrum of gas-phase $Mn_2(CO)_{10}$ sublimed at 60 °C and excited at 337 nm into its intense $\sigma^* \leftarrow \sigma$ band (λ_{max} 342 nm, ϵ 21 400 L/mcm in isooctane solution at 300 K).[2] At 600 ns after photolysis, the photoproducts were ionized at 442 nm and 1×10^8 W/cm^2. The weak signal observed at a slightly shorter time of flight than the main Mn^+ peak is due to Mn^+ produced by the earlier 337-nm pulse, and its intensity was observed to vary as the third power of that of the 337-nm beam.

gas-phase experiments on the group 7[11,12] as well as other[12-14] carbonyl compounds in which photofragments retaining the initial nuclearity have been observed, we have reinvestigated the one-photon gas-phase photochemistry of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. Results described below suggest that in the gas phase, as in fluid and rigid solutions, both loss of CO (with retention of the metal-metal bond) and metal-metal bond scission occur as primary photochemical processes following $\sigma^* \leftarrow \sigma$ excitation.

Experimental Section

The apparatus used in these studies has been described in detail previously.[14] In the experiments reported here, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, purchased from Strem Chemicals, were sublimed at 55–100 °C and introduced into a vacuum chamber maintained below 1×10^{-5} torr. The samples were excited at 337 nm into the region of their $\sigma^* \leftarrow \sigma$ transitions by 5-ns, 130–250-μJ pulses from a Lambda Physik K 600 N_2 laser. To obtain the mass spectra shown below, the photoproducts were multiphoton ionized 0.6 μs after photolysis by 10-ns, 250-μJ pulses from an excimer-pumped dye laser (Lambda Physik EMG101/FL2000) operated at 442 nm. The resulting ions were mass analyzed by a home-built time-of-flight mass spectrometer. The counterpropagating N_2 and dye laser beams were focussed by 8- and 10-in. focal-length lenses, respectively, and spatially overlapped in the ionization region of the mass spectrometer, whose axis was orthogonal to the laser beam paths. This scheme introduces a conceptual simplification over that employed in our previous report[14] in that the initial excitation and the multiphoton ionization are accomplished by separate laser beams. The same ionization laser flux of 1×10^8 W/cm^2 was employed in both the $Mn_2(CO)_{10}$ and the $Re_2(CO)_{10}$ experiments, and its 442-nm wavelength was chosen to be nonresonant with electronic transitions of both the parent molecules and the bare metal atoms.

Results and Discussion

Figures 1 and 2 display the time-of-flight mass spectra of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ excited at 337 nm and multiphoton ionized at 442 nm. Both systems are observed to yield bare atomic and diatomic metal ions. Carbonyl-containing species are apparently unstable with respect to dissociation under the multiphoton ionization (MPI) conditions employed here and do not give rise to detectable ion signals. The 337-nm, 5-ns pulse, which preceded the 442-nm, 10-ns pulse by 0.6 μs, did not itself produce significant ion signal intensities (see Figure 1). When the 337-nm beam was blocked, however, signal intensities of both the M^+ and the M_2^+ species decreased by about an order of magnitude. At the laser fluxes employed, ion signal intensities varied linearly with the intensity of the 337-nm beam, suggesting that the initial excitation was mainly a one-photon process. These considerations indicate that most of the ions detected in these experiments originate from molecules which have undergone one-photon excitation at 337 nm. Thus, by selecting a wavelength for the MPI process that is not readily absorbed by the parent molecules, we are able to selectively mass analyze those molecules that have previously been electronically excited, even though these may constitute a very small fraction of the molecules in the ionization region. This represents a considerable advantage of the multiphoton ionization technique[15] over the relatively indiscriminate electron impact ionization method for mass spectrometric studies of unimolecular photoreactions.

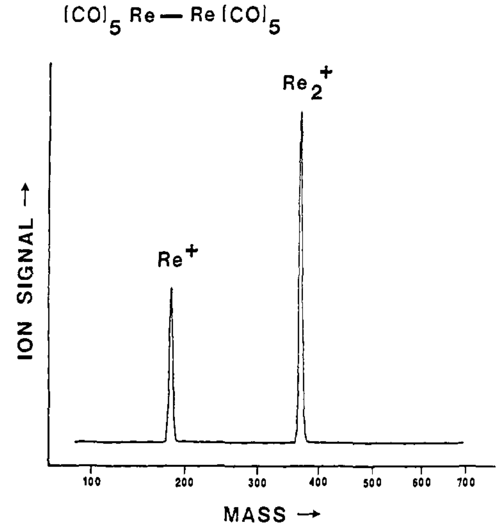

Figure 2. MPI mass spectrum of gas-phase $Re_2(CO)_{10}$ sublimed at 100 °C and excited at 337 nm into the low-energy tail of its intense $\sigma^* \leftarrow \sigma$ band (λ_{max} 313 nm, ϵ = 15 500 L/mcm in isooctane solution at 300 K).[2] Photoproducts were ionized at 442 nm, 1×10^8 W/cm^2.

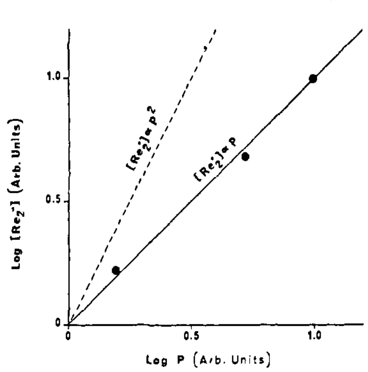

Figure 3. Dependence of Re_2^+ signal intensity on the sample number density in the photolysis region. Lines show the expected pressure dependences of products of direct unimolecular dissociation and ionization ($[Re_2^+] \propto P$) and of binary reaction ($[Re_2^+] \propto P^2$). The sample number density was controlled by varying the source temperature between 55 and 100 °C. The relative sample pressures were determined from the intensity of the Re^+ signal, which comprised ~80% of the total ion signal under the photolysis conditions employed. $Re_2(CO)_{10}$ was photolyzed at 337 nm and multiphoton ionized at 458 nm, 10^9 W/cm^2.

The intensities of the M_2^+ ion signals were found to scale linearly with the number densities of the sample molecules. This result, which is illustrated in Figure 3 for the $Re_2(CO)_{10}$ system, eliminates the possibility that the dimetal species detected arose

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from ion–molecule or other binary reactions.[16,17]

The detection of Mn_2^+ and Re_2^+ under these conditions thus demonstrates that $\sigma^* \leftarrow \sigma$ excitation of gas-phase $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ yields some species which retain the metal–metal bond, but which are not identical with the unphotolyzed species, as demonstrated by the greatly enhanced ion signals observed for the photolyzed molecules. The delay between the photolysis and the ionization laser pulses sets a lower limit of 0.6 μs on the lifetimes of these species under collision-free conditions.[18] Since the lifetimes of the initially prepared excited singlets of the parent molecules are 10^{-11} s or less,[5,10] these cannot be the species detected. In view of solution-phase results for $Mn_2(CO)_{10}$ which indicate that solvated $Mn_2(CO)_9$ is generated within 25 ps after near-UV excitation[5] with a quantum yield of about 0.3,[6,7] the most likely assignments for the primary photoproducts which eventually give rise to the M_2^+ ion signals detected in the present study are partially decarbonylated dinuclear complexes. Other possible assignments for these species include the vibrationally hot parent molecules in their ground electronic states populated by interanl conversion from the prepared singlets, or low-lying excited singlet or multiplet states of the $M_2(CO)_{10}$ systems. However, these species do not appear to be as likely to be detected by the delayed ionization laser pulse in view of the efficient decomposition pathways expected for highly excited ground states of metal carbonyl complexes[19] and the lack of any evidence for relatively long-lived low-lying excited states in the *non*emissive $M_2(CO)_{10}$ systems.[1] The $M_2(CO)_{10}$ isomer previously suggested to be a primary photoproduct in the manganese system[8a] also does not appear to be a probable precursor to the molecular ions detected in these epxeriments, since the absence of a direct metal–metal bond in the proposed isomer renders fragmentation to a bare metal dimer during the MPI process unlikely.

In the gas phase, the loss of more than one carbonyl ligand has been demonstrated to occur following one-photon near-UV excitation of mononuclear transition-metal carbonyl complexes.[19,20] Average metal–ligand bond strengths in the systems studied here have been determined calorimetrically to be 23.9 kcal/mol for $Mn_2(CO)_{10}$ and 44.7 kcal/mol for $Re_2(CO)_{10}$.[21] This suggests that while the most likely dirhenium photofragment following excitation at 337 nm (84.8 kcal/mol of photons) is $Re_2(CO)_9$, possible photoproducts for the dimanganese complex include Mn_2-containing species that have lost up to three carbonyl ligands. It is noteworthy that the detection of the bare dimetal ions reported here shows, surprisingly, that the metal–metal bonds can survive the absorption of sufficient energy to dissociate not only one but all ten carbonyl ligands from the parent molecule and subsequently form neutral or ionic fragments. Assuming that the decarbonylation process occurs largely in the neutral rather than the ionic ladder,[22] the average metal–ligand bond strengths noted above suggest that this process requires the absorption of at least three 442-nm photons for $Mn_2(CO)_{10}$ and at least six for $Re_2(CO)_{10}$ after the initial 337-nm excitation.

Unfortunately, the relative yields of mononuclear and dinuclear neutral photoproducts cannot quantitatively be estimated from the M^+ and M_2^+ signal intensities, due to the unknown MPI cross sections of the different fragments and to the likelihood that a substantial number of M_2-containing photoproducts fragment to mononuclear species in the ionization process. However, we note that the qualitative trend suggested in Figures 1 and 2 of a greater yield of M_2^+ relative to M^+ ions for $Re_2(CO)_{10}$ than for $Mn_2(CO)_{10}$ is consistent with the greater strength of the metal–metal bond in the third row (30.6 kcal/mol) than in the first row (16.0 kcal/mol) complex.[21] In a separate set of experiments, we have observed a parallel trend among the $M_3(CO)_{12}$ systems (M = Fe Ru, Os) excited at 385 nm, whose MPI mass spectra display an increased preservation of the metal cluster core as the series progresses to heavier members of the iron triad.[14,23]

In summary, these results suggest that the excitation of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ at 337 nm under collision-free conditions produces some partially decarbonylated primary photoproducts that retain the metal–metal bond. Thus, dissociative CO loss appears to provide an alternate primary photoprocess to the M–M bond scission reaction previously demonstrated by Freedman and Bersohn to occur in the gas phase following near-UV excitation of these systems.[10]

Acknowledgment. Financial support from the National Scienc Foundation and the National Institutes of Health is gratefull acknowledged. We thank Dr. Frank Wang for discussion of th work presented here.

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Re_2(CO)_{10}$, 14285-68-8.

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[16] Remarkably efficient reactions of atomic metal ions with metal carbonyl complexes have been observed for the $M_2(CO)_{10}$ systems (ref 11) and for $Fe(CO)_5$ (ref 17) at pressures as low as 4–5 × 10^{-7} torr. In both studies, the abundances of ion–molecule reaction products were observed to vary as the square of the sample density.

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[18] The experimental conditions employed in these studies are not well suited to probing the lifetime of the primary photoproduct by varying the delay between the "pump" and "probe" laser beams, due to the complexities introduced by the movement of the photoproduct out of the small (~1 × 10^{-3} cm^2) active area of the focussed MPI laser beam with increasing delay times.

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[22] This is suggested by the atomic ion signal enhancement general observed for metal carbonyl systems when the MPI laser is resonant wi atomic transitions and by the lack of observable ion signal for highly carb nylated fragments in metal carbonyl MPI experiments. For a review of Ml mechanisms in organometallic and other systems, see ref 15b.

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