

Properties of Ions and Radicals Derived from
Decacarbonyldimanganese,
Decacarbonylmanganerhenium, and Decarbonyldirhenium
by Electron Attachment and Protonation in the Gas Phase

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Abstract: $\text{Mn}_2(\text{CO})_{10}$, $\text{ReMn}(\text{CO})_{10}$, and $\text{Re}_2(\text{CO})_{10}$ attach thermal electrons in the gas phase and lose either a CO or an $\text{M}(\text{CO})_5$ radical. The extent of $\text{M}(\text{CO})_5$ loss decreases in the order $\text{Mn}_2(\text{CO})_{10} > \text{ReMn}(\text{CO})_{10} > \text{Re}_2(\text{CO})_{10}$. No $\text{M}(\text{CO})_5$ loss is observed for $\text{Re}_2(\text{CO})_{10}$, and both $\text{Mn}(\text{CO})_5$ and $\text{Re}(\text{CO})_5$ are lost from $\text{ReMn}(\text{CO})_{10}$. Assuming that there is no energy barrier for charge transfer between $\text{Re}(\text{CO})_5$ and $\text{Mn}(\text{CO})_5^-$ leads to the conclusion that $D(\text{Re}(\text{CO})_5-\text{Mn}(\text{CO})_5) \leq \text{EA}(\text{Mn}(\text{CO})_5) \approx \text{EA}(\text{Re}(\text{CO})_5)$. HCl and other acids fail to transfer a proton at an observable rate to $\text{Mn}(\text{CO})_5^-$, $\text{Re}(\text{CO})_5^-$, $\text{Mn}_2(\text{CO})_9^-$, $\text{ReMn}(\text{CO})_9^-$, and $\text{Re}_2(\text{CO})_9^-$. Assuming this is because the proton transfers are endothermic leads to the conclusion that the proton affinities of the unreactive negative ions are less than that of Cl^- . Combining the conclusions about the radical electron affinities with proton affinity and bond strength data from the literature gives $\text{EA}(\text{Re}(\text{CO})_5) = \text{EA}(\text{Mn}(\text{CO})_5) \approx 2.43 \pm 0.21$ eV. The gas-phase electron-attachment processes are found to closely resemble the reactions of radiolytically produced solvated electrons. The proton affinities of $\text{Mn}_2(\text{CO})_{10}$, $\text{ReMn}(\text{CO})_{10}$, and $\text{Re}_2(\text{CO})_{10}$ are found to be 774 ± 13 , 794 ± 6 , and 805 ± 5 kJ/mol, respectively. Comparison with proton affinities of $\text{M}(\text{CO})_5\text{CH}_3$ species suggests that substituting a methyl group for $\text{M}(\text{CO})_5$ in the $\text{M}_2(\text{CO})_{10}$ has very little effect on the proton affinity.

The group 7 metal carbonyls, $\text{Mn}_2(\text{CO})_{10}$, $\text{ReMn}(\text{CO})_{10}$, and $\text{Re}_2(\text{CO})_{10}$, constitute the simplest series of polynuclear metal carbonyl periodic congeners. The $\text{M}(\text{CO})_5$ radicals are isolobal¹ with the methyl radical so the decacarbonyls might be considered to be inorganic alkane analogues. Investigation of the validity of the analogy and the periodic behavior of metal clusters are among the purposes of a number of photolytic and radiolytic studies of these compounds.²⁻⁴

Reported here are investigations of the behavior of these species under ionizing conditions in the gas phase. In particular the decomposition resulting from attachment of thermal electrons to the metal carbonyls, the reactivity of the resulting metal carbonyl anions with neutral proton donors, and the reactivity of the neutral metal carbonyls with cationic proton donors are described. A principal reagent generated by radiolysis is the solvated electron, so the dissociative electron attachment results should be helpful in characterizing important primary processes in radiolysis. The acid-base behavior of the anion fragments could also be helpful in characterizing radiolytic processes in protic solvents. Gas-phase ionic acid-base behavior of the three carbonyls is also of interest because little data of that kind are available on periodic families of polynuclear metal carbonyls.

Experimental Section

These studies were done by using an ion cyclotron resonance spectrometer with a frequency scanned capacitance bridge detector which has been previously described.⁵ Reactions were identified by double resonances⁶ and by variation of the mass spectrum with pressure. The pressure measurements were made with a standard ionization gauge.

$\text{Mn}_2(\text{CO})_{10}$ was purchased from Ventron, Alfa Division, and $\text{Re}_2(\text{CO})_{10}$ was purchased from Strem Chemicals, Inc. Both samples could be used as received. $\text{ReMn}(\text{CO})_{10}$ was prepared by published procedures⁷ and purified by sublimation. The compounds were introduced into the spectrometer through leak valves, and pressures as high as $(2-4) \times 10^{-6}$ torr could readily be obtained. Commercial samples of acetic acid, methyl mercaptan, hydrogen chloride, methanol, ethanol, isopropyl alcohol, and *tert*-butyl alcohol could also be used as received.

Negative Ions

Negative ion mass spectra obtained at 80 and 5 eV are given in Table I. Ionization by secondary electrons caught by the trapping potential is important at both energies, but the extent of fragmentation indicates that energetic electrons are responsible for some of the ionization. To determine results of dissociative

Table I. Relative Intensities of Negative Ions in the Mass Spectrum of $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}, \text{Re}$) Obtained by 80 and 5 eV Electron Impact

stoichiometry	nominal mass (m/z)	relative intensity, %	
		80 eV	5 eV
$\text{Mn}(\text{CO})_4^-$	167	1	<i>a</i>
$\text{Mn}(\text{CO})_5^-$	195	100	100
$\text{Mn}_2(\text{CO})_4^-$	222	12	<i>a</i>
$\text{Mn}_2(\text{CO})_5^-$	250	2	<i>a</i>
$\text{Mn}_2(\text{CO})_6^-$	178	4	<i>a</i>
$\text{Mn}_2(\text{CO})_7^-$	306	14	<i>a</i>
$\text{Mn}_2(\text{CO})_8^-$	334	80	60
$\text{Mn}_2(\text{CO})_9^-$	362	93	63
$\text{Mn}(\text{CO})_5^-$	195	40	21
$\text{Re}(\text{CO})_5^-$	327	15	8
$\text{ReMn}(\text{CO})_7^-$	438	6	6
$\text{ReMn}(\text{CO})_8^-$	466	36	38
$\text{ReMn}(\text{CO})_9^-$	494	100	100
$\text{Re}_2(\text{CO})_5^-$	512	4	<i>a</i>
$\text{Re}_2(\text{CO})_6^-$	540	5	<i>a</i>
$\text{Re}_2(\text{CO})_7^-$	568	5	<i>a</i>
$\text{Re}_2(\text{CO})_8^-$	596	11	6
$\text{Re}_2(\text{CO})_9^-$	624	100	100

^aNot measurable.

attachment of the thermal electrons it is necessary to add excess pressures of an inert collision gas as discussed below. The most

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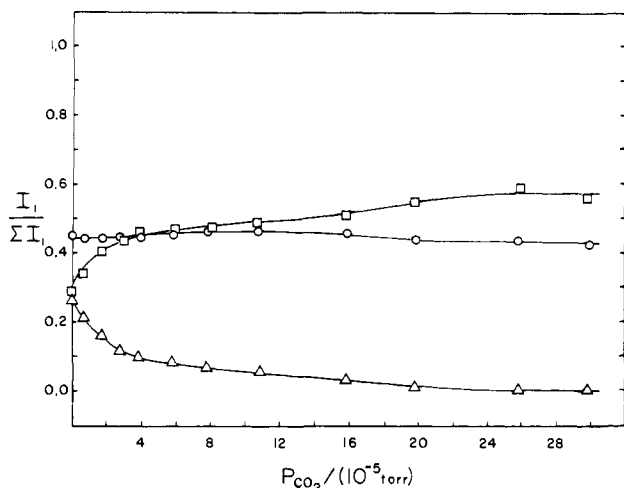


Figure 1. Relative intensity of negative ions in $\text{Mn}_2(\text{CO})_{10}$ at an ionizing electron energy of 4 eV as a function of CO_2 pressure: $\text{Mn}_2(\text{CO})_8^-$ (Δ), $\text{Mn}(\text{CO})_5^-$ (\circ), and $\text{Mn}_2(\text{CO})_9^-$ (\square).

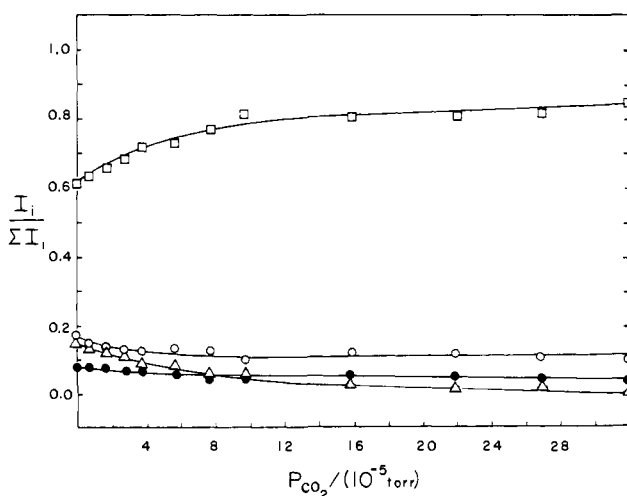


Figure 2. Relative intensity of negative ions in $\text{ReMn}(\text{CO})_{10}$ at an ionizing electron energy of 4 eV as a function of CO_2 pressure: $\text{ReMn}(\text{CO})_8^-$ (Δ), $\text{Re}(\text{CO})_5^-$ (\bullet), $\text{Mn}(\text{CO})_5^-$ (\circ), and $\text{ReMn}(\text{CO})_9^-$ (\square).

striking feature of the data in Table I is the difference between $\text{Re}_2(\text{CO})_{10}$ and the other two carbonyls. Even at high electron energy there is no discernible cleavage of the Re-Re bond, while formation of $\text{M}(\text{CO})_5^-$ species is a major process in both $\text{Mn}_2(\text{CO})_{10}$ and $\text{ReMn}(\text{CO})_{10}$. This probably reflects the difference in metal-metal bond strength among the three species. It also may reflect the M-CO bond strength and the electron affinities of the fragments. The effects of these factors may be better analyzed in terms of the thermal electron attachment results.

The effects of adding a collision gas to thermalize a beam of electrons entering the ion cyclotron resonance cell at a nominal energy of 4 eV are shown in Figures 1-3. The nominal pressure of the $\text{M}_2(\text{CO})_{10}$ compound was $\sim 2 \times 10^{-6}$ torr in each of these experiments. CO_2 is a particularly effective collision gas having low-lying transient negative ion states which dissociate into a slow electron and vibrationally excited CO_2 .⁸ The fragmentation pattern initially changes rapidly with CO_2 pressure as the electrons are thermalized. At higher CO_2 pressures the higher energy fragments such as $\text{M}_2(\text{CO})_8^-$ disappear and the relative abun-

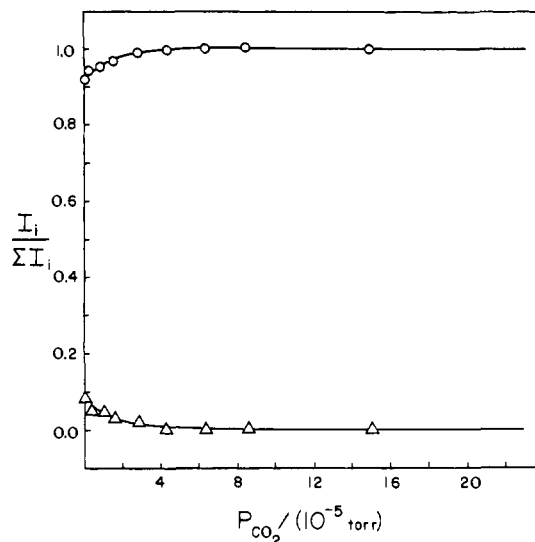
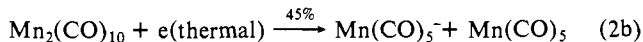
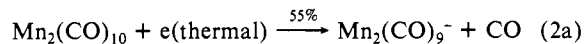


Figure 3. Relative intensity of negative ions in $\text{Re}_2(\text{CO})_{10}$ at an ionizing electron energy of 4 eV as a function of CO_2 pressure: $\text{Re}_2(\text{CO})_8^-$ (Δ) and $\text{Re}_2(\text{CO})_9^-$ (\circ).

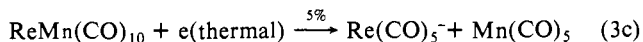
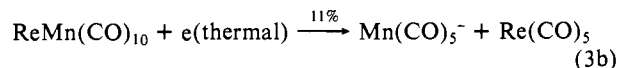
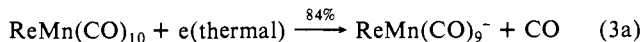
dances of the fragments remain constant with further increase in pressure. The spectra were taken in the drift mode with an observation time of approximately 10 ms. Double resonance and the variation of ion abundance with metal carbonyl pressure revealed no ion-molecule reactions in these systems. Addition of CCl_4 to a nominal pressure equal to that of $\text{Mn}_2(\text{CO})_{10}$ gave a Cl^- signal about twice that of the total negative ion signal from the metal carbonyl independent of CO_2 pressure above CO_2 pressures of 1×10^{-5} torr. This suggests that the metal carbonyls have electron attachment cross sections comparable to that of CCl_4 . The relative abundances of the fragments observed at high CO_2 pressures can thus be taken as the result of attachment of thermal electrons to the metal carbonyls. In $\text{Re}_2(\text{CO})_{10}$ the only process at higher pressures is loss of CO (eq 1). The product



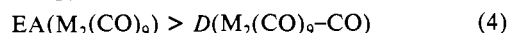
of (1) was observed with a signal-to-noise ratio greater than 100, so unobserved minor channels are less than 1%. In $\text{Mn}_2(\text{CO})_{10}$, however, cleavage of the Mn-Mn bond remains competitive with loss of CO at the highest pressures, as shown in eq 2. In Re-



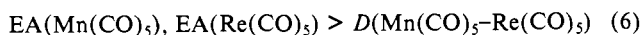
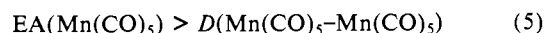
$\text{Mn}(\text{CO})_{10}$ both processes are competitive at high pressure also, but cleavage of the metal-metal bond is not the dominant process. The high-pressure distribution is given in eq 3.



If we assume that the high-pressure product distributions in reactions 1-3 are the result of the attachment of thermal electrons and reflect the thermochemistry of the competing processes, several conclusions are possible. First, in all three cases the electron affinity (EA) of $\text{M}_2(\text{CO})_9$ ($\text{M} = \text{Mn}, \text{Re}$) is greater than the bond strength (D) of $\text{M}_2(\text{CO})_9\text{-CO}$ (eq 4). From the cleavage of the



metal-metal bonds in reactions 2b, 3b, and 3c, we conclude



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Table II. Bond Dissociation Energies and Activation Enthalpies of Bond Homolysis for $M_2(CO)_{10}$ ($M = Mn, Re$)

compound, $M_2(CO)_{10}$	$D(M-M)$, kJ/mol	ΔH^\ddagger for M-M bond homolysis, ^c kJ/mol
$Mn_2(CO)_{10}$	94 ± 13^a	153.8 ± 1.6
$ReMn(CO)_{10}$	210 ± 10^b	162.8 ± 0.8
$Re_2(CO)_{10}$	187 ± 5^b	165.5 ± 0.8

^a The value of ΔE_{298}^\ddagger for $Mn_2(CO)_{10} \rightarrow 2Mn(CO)_5$ from data in ref 10. ^b The value of ΔE_T^\ddagger for $Mn_2(CO)_{10} \rightarrow 2Mn(CO)_5$ where T is unspecified but probably between 300 and 500 K from ref 11. ^c Activation enthalpies for homolytic fission of M-M bonds from ref 15.

A simple explanation for the failure to observe cleavage of the Re-Re bond in reaction 1 would be that such a process is endothermic. This leads to the conclusion that

$$EA(Re(CO)_5) < D(Re(CO)_5-Re(CO)_5) \quad (7)$$

The product yield of reaction 1 could be kinetically determined, however. If decomposition of excited $Re_2(CO)_{10}^-$ formed by electron attachment is a statistical process, loss of CO might dominate even if Re-Re bond cleavage is energetically accessible. The preference for CO loss persists even at higher electron energies. At 80 eV loss of multiple CO molecules is observed (Table I), but Re-Re bond cleavage is not. At higher energies resonant, nonstatistical processes and decompositions producing only neutral fragments are possible. In addition, at higher energies much of the ionization is the result of secondary electrons caught in the trap. Interpretation of the high-energy results is, therefore, difficult. These difficulties in evaluating the role of kinetic effects in determining the fragmentation pattern should be kept in mind as we explore the consequences of expression 7.

From the formation of both $Mn(CO)_5^-$ products in reaction 3 we conclude

$$EA(Mn(CO)_5) \approx EA(Re(CO)_5) \quad (8)$$

Calculations suggest that $Mn(CO)_5^-$ has a structure very similar to that of $Mn(CO)_5$, and very little energy is required to make the structures identical.⁹ The structures of $Re(CO)_5$ and $Re(CO)_5^-$ should therefore also be nearly identical. Under these circumstances charge exchange between $Mn(CO)_5^-$ and $Re(CO)_5$ should have no activation energy barrier. The fact that both $Mn(CO)_5^-$ and $Re(CO)_5^-$ occur suggests that the charge exchange is thermoneutral, hence eq 8. Comparing eq 5 and 6 with eq 7 and using eq 8 gives

$$D(Mn(CO)_5-Mn(CO)_5), D(Re(CO)_5-Mn(CO)_5) < EA(Mn(CO)_5) \approx EA(Re(CO)_5) < D(Re(CO)_5-Re(CO)_5) \quad (9)$$

Assigning quantitative electron affinities using expression 9 requires values for the M-M strengths in the decacarbonyls. Values of the bond strengths are listed in Table II. Also listed in Table II are activation enthalpies for condensed phase homolysis of the M-M bonds in the decacarbonyls. The Mn-Mn bond strength comes from measurements of the temperature dependence of the equilibrium constant for the gas-phase dissociation of $Mn_2(CO)_{10}$ to $Mn(CO)_5$.¹⁰ This result is in quite good agreement with the difference between the measured appearance potential of $Mn(CO)_5^+$ from $Mn(CO)_{10}$ and the ionization potential of $Mn(CO)_5$.¹¹ The Re-Mn bond strength is the measured appearance potential of $Mn(CO)_5^+$ from $ReMn(CO)_{10}$ less the measured ionization potential of $Mn(CO)_5$.¹¹ The Re-Re bond strength is the measured appearance potential of $Re(CO)_5^+$ from $Re_2(CO)_{10}$ less the estimated ionization potential of $Re(CO)_5$.¹¹ The correlation between these bond strengths and the activation enthalpies for bond homolysis is not particular good. The activation enthalpies should be greater than or equal to the bond strengths since the activation enthalpies for the reverse reactions

are at least zero. In addition, the Mn-Mn bond strength has been calculated by the extended Hückel method to be 166 kJ/mol.¹² We conclude that these bond strengths from the literature should be used only in a tentative way. The bond strengths in Table II are actually inconsistent with expression 9 since $D((CO)_5Re-Mn(CO)_5) > D((CO)_5Re-Re(CO)_5)$. It is only necessary to assume errors of 0.1 to 0.2 eV in the measured bond strengths to reverse that situation, however. If such errors are assumed, then an electron affinity of ~ 198 kJ/mol or 2.1 eV for both $M(CO)_5$ species is consistent with expression 9. The observation of both reactions 3b and 3c suggests the lower limit on the electron affinities. The failure of $Re(CO)_5^-$ to form on electron attachment to $Re_2(CO)_{10}$ suggests the upper limit on the electron affinities. As discussed above, however, the failure to observe $Re(CO)_5^-$ cannot be interpreted unambiguously. Under these circumstances the only conclusion we make with some confidence is

$$EA(Mn(CO)_5) \approx EA(Re(CO)_5) \geq D(Mn(CO)_5-Re(CO)_5) \approx 2.0 \text{ eV} \quad (10)$$

The anions formed from the $M_2(CO)_{10}$ compounds were exposed to the following protic acids in the gas phase: ethanol, acetic acid, methyl mercaptan, and hydrogen chloride. No reactions were observed with any of these species. The slowest reaction which could have been observed was ca. $0.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. There could be a kinetic barrier to proton transfer, but if not, this result indicates that

$$PA(M(CO)_5^-), PA(M_2(CO)_{10}^-) < PA(H^+) = 1395 \text{ kJ/mol}^{12} \quad (11)$$

where PA = proton affinity and $M = Mn, Re$. This is consistent with the recently reported value $PA(Mn(CO)_5) = 1331 \pm 13 \text{ kJ/mol}$.¹³

Recently values of 57 to 64 kcal/mol (238 to 268 kJ/mol) have appeared for $D(Mn(CO)_5-H)$.¹⁴ An extended Hückel calculated value of $D(Mn(CO)_5-H) = 270.7 \text{ kJ/mol}$ has also been reported.¹² Taking the Mn-H bond strength as $253 \pm 15 \text{ kJ/mol}$ and using the reported proton affinity of $Mn(CO)_5^-$ ¹³ allows one to calculate the electron affinity of $Mn(CO)_5$. Equating the sum of the enthalpy changes for the individual steps in eq 12 with that of the overall process gives eq 13 where IP(H) is the ionization potential

$$Mn(CO)_5-H \rightarrow Mn(CO)_5^- + H^+ \rightarrow Mn(CO)_5 + e + H^+ \rightarrow Mn(CO)_5 + H \quad (12)$$

$$D(Mn(CO)_5-H) = PA(Mn(CO)_5^-) + EA(Mn(CO)_5) - IP(H) \quad (13)$$

of the hydrogen atom. The resulting value of $EA(Mn(CO)_5)$ is $234 \pm 20 \text{ kJ/mol}$ ($2.43 \pm 0.21 \text{ eV}$). If, consulting expression 8, we take $234 \pm 15 \text{ kJ/mol}$ as the electron affinity of $Re(CO)_5$, then eq 11 and expressions analogous to eq 12 and 13 imply that $D(Re(CO)_5-H) < 318 \text{ kJ/mol}$. This electron affinity (234 kJ/mol) is consistent with expression 10, but it is inconsistent with the last inequality in expression 9. That is, electron attachment to both $ReMn(CO)_{10}$ and $Re_2(CO)_{10}$ to form $Re(CO)_5^-$ is exothermic if $D(Re(CO)_5-Re(CO)_5) = 187 \text{ kJ/mol}$,¹¹ $D(Re(CO)_5-Mn(CO)_5) = 210 \text{ kJ/mol}$, and $EA(Re_2(CO)_{10}) = 234 \pm 15 \text{ kJ/mol}$. Electron attachment to the metal carbonyls to produce $Re(CO)_5^-$ is endothermic only if there is an overall error in the electron affinity and metal-metal bond strength of 51 kJ/mol (0.53 eV). If there are no such errors, then as discussed above the most probable explanation for the failure of $Re(CO)_5^-$ to result from electron attachment to $Re_2(CO)_{10}$ is that cleavage of the M-M bond is not facile enough to compete with a very facile M-CO bond cleavage.

It is curious that metal-metal bond cleavage does not compete with M-CO bond cleavage in $Re_2(CO)_{10}$. The Re-Mn bond is stronger than the Re-Re bond (Table II), yet only the former breaks on electron attachment. If the absence of observable M-M

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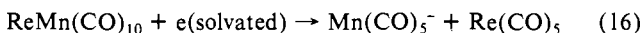
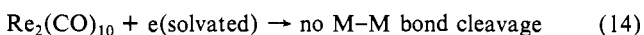
(14) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 190-192 and references therein.

bond cleavage in the $\text{Re}_2(\text{CO})_{10}$ is the result of very facile CO loss, then CO loss should dominate even more the cleavage of the stronger M–M bond in $\text{ReMn}(\text{CO})_{10}$. This is more particularly the case since Mn–CO bonds are generally weaker than Re–CO bonds.^{11,15} A more probable explanation is that the M–M bond in $\text{ReMn}(\text{CO})_{10}$ is the same or lesser strength as the M–M bond in $\text{Re}_2(\text{CO})_{10}$. This is supported by the activation energies for bond heterolysis (Table II) and by the force constants for the M–M stretch ($f_{\text{M-M}} = 0.82, 0.81, \text{ and } 0.59$ in $\text{Re}_2(\text{CO})_{10}$, $\text{ReMn}(\text{CO})_{10}$, and $\text{Mn}_2(\text{CO})_{10}$, respectively¹⁶).

Data on electron affinities of $\text{Fe}(\text{CO})_n$ and $\text{Ni}(\text{CO})_n$ radicals are available. They give the electron affinities of $\text{Fe}(\text{CO})_n$ as $2.4 \pm 0.3, 1.8 \pm 0.2, 1.22 \pm 0.02, 1.26 \pm 0.02, \text{ and } 0.164 \pm 0.035$ eV for $n = 4, 3, 2, 1, \text{ and } 0$.¹⁷ The electron affinities of $\text{Ni}(\text{CO})_n$ are $1.077 \pm 0.013, 0.643 \pm 0.014, \text{ and } 0.804 \pm 0.012$ eV for $n = 3, 2, \text{ and } 1$.¹⁸ The value of $\text{EA}(\text{M}(\text{CO})_5) = 234 \pm 20$ kJ/mol (2.43 ± 0.21 eV) for $\text{M} = \text{Mn, Re}$ is the same as $\text{EA}(\text{Fe}(\text{CO})_4)$ but more than twice $\text{EA}(\text{Ni}(\text{CO})_3)$. This does not suggest a simple periodic trend. The adiabatic and vertical electron affinities of these species may be quite different.^{17,18} The electron affinity given above for the $\text{M}(\text{CO})_5$ radicals is derived from thermochemical data and the thermal electron attachment product distributions. This should give a thermodynamic (adiabatic) electron affinity.

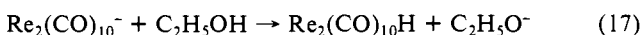
Comparison to Radiation Chemistry

It is interesting to compare reactions 1–3 with the results of radiolysis of the $\text{M}_2(\text{CO})_{10}$ compounds in solution. Reactions 14–16 indicate the metal–metal bond cleavage products observed spectroscopically in the pulsed radiolysis of ethanol solutions of $\text{M}_2(\text{CO})_{10}$ ^{3,4} ($\text{M} = \text{Mn, Re}$). We note that this reflects the



relative importance of the metal cleavage processes in the gas-phase thermal electron-attachment reactions. There is no metal cleavage in reaction 1, $\text{Mn}(\text{CO})_5^-$ is an important product in reaction 2, and $\text{Mn}(\text{CO})_5^-$ is more important than $\text{Re}(\text{CO})_5^-$ in reaction 3. This supports the postulated role of the solvated electron in the radiochemistry.

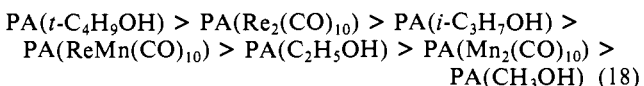
In the radiation chemistry of $\text{Re}_2(\text{CO})_{10}$, reaction 17 is thought to play a role.³ The evidence does not distinguish between



$\text{Re}_2(\text{CO})_9^-$ and $\text{Re}_2(\text{CO})_{10}^-$ as the reagent ion. This appears to contradict the gas-phase results which suggest that at least $\text{Re}_2(\text{CO})_9^-$ is a weaker base than $\text{C}_2\text{H}_5\text{O}^-$. However, the relative basicity of the ions should be highly modified by the solvent. The $\text{C}_2\text{H}_5\text{O}^-$ ion is much more susceptible to stabilization by a polar hydrogen bonding solvent than larger metal carbonyl anions.

Proton Affinities

Proton transfer was observed from a number of protonated species to the $\text{M}_2(\text{CO})_{10}$ species. If it is assumed that the observed proton transfer reactions are exothermic and those that failed to occur at an observable rate are endothermic, the following order of proton affinities is obtained.



From this order the numerical proton affinities for the decarbonyl compounds in Table III were assigned by using proton affinities of the alcohols from the literature.¹⁹ The values for

Table III. Proton Affinities and Hydrogen Atom Bond Strengths in $\text{M}_2(\text{CO})_{10}$ and $\text{M}(\text{CO})_5\text{CH}_3$ ($\text{M} = \text{Mn, Re}$)

compound, $\text{M}_2(\text{CO})_{10}$	proton affinity, kJ/mol	ionization potential, eV	bond energy $D(\text{M}_2(\text{CO})_{10}^+-\text{H}),$ kJ/mol
$\text{Mn}_2(\text{CO})_{10}$	774 ± 13^a	8.46 ± 0.03^b	279 ± 16
$\text{ReMn}(\text{CO})_{10}$	794 ± 6^a	8.14 ± 0.01^b	267 ± 7
$\text{Re}_2(\text{CO})_{10}$	805 ± 5^a	8.06^c	271 ± 5
$\text{Mn}(\text{CO})_5\text{CH}_3$	774 ± 13^d	8.3 ± 0.1^d	268 ± 13^d
$\text{Re}(\text{CO})_5\text{CH}_3$	782 ± 8^d	8.5 ± 0.1^d	289 ± 13^d

^a On the basis of present results and proton affinities for $t\text{-C}_4\text{H}_9\text{OH}$ (810 kJ/mol), $i\text{-C}_3\text{H}_7\text{OH}$ (800 kJ/mol), $\text{C}_2\text{H}_5\text{OH}$ (788 kJ/mol), and CH_3OH (761 kJ/mol) from ref 19. ^b Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* 1977, 9, Suppl. 1. ^c Hall, M. B. *J. Am. Chem. Soc.* 1975, 97, 2057–2065. ^d From data in ref 14 adjusted to a proton affinity scale based on $\text{PA}(\text{NH}_3) = 853.5$ kJ/mol from ref 19.

$\text{Mn}(\text{CO})_5\text{CH}_3$ and $\text{Re}(\text{CO})_5\text{CH}_3$ are based on data given by Stevens and Beauchamp.¹⁴ It is interesting to note that replacing $\text{Mn}(\text{CO})_5$ with the isolobal CH_3 in $\text{Mn}_2(\text{CO})_{10}$ has little, if any, effect on the proton affinities. Replacing $\text{Re}(\text{CO})_5$ with the isolobal CH_3 in $\text{Re}_2(\text{CO})_{10}$ has only a small effect. This suggests that the hydrogen atom in the protonated dimetal decarbonyls is terminally bonded to the metal and not bridging. The values of $D(\text{M}_2(\text{CO})_{10}^+-\text{H})$ given in Table III were obtained from the proton affinity data by using the ionization potentials for the decarbonyls and the hydrogen atom. As indicated in the table, the hydrogen atom bond strengths are comparable to those reported for protonated $\text{Mn}(\text{CO})_5\text{CH}_3$ and $\text{Re}(\text{CO})_5\text{CH}_3$,¹⁴ which also suggests that the hydrogen atom bonding is similar in the dimetal decarbonyls and the methyl metal pentacarbonyls.

The proton affinities increase somewhat, but not dramatically, as rhenium atoms replace manganese atoms in the dimetal decarbonyls. This reflects a change in ionization potential more than a change in bonding to the hydrogen atom as shown by the values for $D(\text{A}^+-\text{H})$ and $\text{IP}(\text{A})$ in Table III. It is interesting that the $D(\text{A}^+-\text{H})$ values in Table III vary between 267 and 289 kJ/mol. As noted above, the reported values of $D(\text{Mn}(\text{CO})_5-\text{H})$ are near that range, varying from 238 to 271 kJ/mol. This suggests that the M–H bonding in the protonated species is similar to that in $\text{Mn}(\text{CO})_5\text{H}$; that is that the H atom is terminally bonded to the metal.

Summary and Conclusions

The extent of M–M bond cleavage vs. M–CO bond cleavage on thermal electron attachment decreases in the order $\text{Mn}_2(\text{CO})_{10} > \text{ReMn}(\text{CO})_{10} > \text{Re}_2(\text{CO})_{10}$. The M–M bond in $\text{ReMn}(\text{CO})_{10}$ cleaves to give both $\text{Re}(\text{CO})_5^-$ and $\text{Mn}(\text{CO})_5^-$, but $\text{Mn}(\text{CO})_5^-$ is predominant. No M–M bond cleavage occurs in $\text{Re}_2(\text{CO})_{10}$. These results indicate that the electron affinities of $\text{Re}(\text{CO})_5$ and $\text{Mn}(\text{CO})_5$ are nearly equal and are greater than $D(\text{Re}(\text{CO})_5-\text{Mn}(\text{CO})_5)$. From values for $\text{PA}(\text{Mn}(\text{CO})_5^-)$ and $D(\text{Mn}(\text{CO})_5-\text{H})$ in the literature $\text{EA}(\text{Mn}(\text{CO})_5) = 2.43 \pm 0.21$ eV is assigned. From the present results $\text{EA}(\text{Re}(\text{CO})_5) \approx 2.4 \pm 0.2$ eV then follows. The failure of the Re–Re bond to cleave on electron attachment apparently results from the greater facility of CO loss rather than the endothermicity of the metal–metal bond cleavage. The cleavage of the Re–Mn bond in $\text{ReMn}(\text{CO})_{10}$ on electron attachment suggests that the Re–Mn bond is weaker than the Re–Re bond in $\text{Re}_2(\text{CO})_{10}$. The failure of HCl and other acids to donate a proton to the $\text{M}(\text{CO})_5^-$ and $\text{M}_2(\text{CO})_9^-$ species suggests that the proton affinities of these species are less than that of Cl^- .

Gas-phase thermal electron attachment gives the same M–M cleavage processes as reaction of the solvated electron in condensed-phase radiolysis. Both processes give $\text{Mn}(\text{CO})_5^-$ from $\text{Mn}_2(\text{CO})_{10}$, more $\text{Mn}(\text{CO})_5^-$ than $\text{Re}(\text{CO})_5^-$ in $\text{ReMn}(\text{CO})_{10}$, and no M–M bond cleavage in $\text{Re}_2(\text{CO})_{10}$. The radiolysis of $\text{Re}_2(\text{CO})_{10}$ is thought to produce an anion containing two rhenium atoms and nine or ten carbonyls. In the gas phase $\text{Re}_2(\text{CO})_9^-$ is

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the only observed product. In the condensed phase the $\text{Re}_2(\text{C}-\text{O})_{9,10}^-$ is thought to extract a proton from the solvent, ethanol. In the gas phase $\text{Re}_2(\text{CO})_9^-$ does not extract a proton from alcohols. Ethanol may be a stronger acid toward $\text{Re}_2(\text{CO})_9^-$ in condensed phase because the conjugate base, $\text{C}_2\text{H}_5\text{O}^-$, is very effectively solvated in protic solvents.

The proton affinities of the dimetal decacarbonyls increase slightly on going from $\text{Mn}_2(\text{CO})_{10}$ to $\text{ReMn}(\text{CO})_{10}$ to $\text{Re}_2(\text{CO})_{10}$. Substituting a methyl group for $\text{Re}(\text{CO})_5$ or $\text{Mn}(\text{CO})_5$ has only

small effects. The hydrogen atom is probably bonded terminally to one of the metals in the protonated $\text{M}_2(\text{CO})_{10}$ species.

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Registry No. $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; $\text{ReMn}(\text{CO})_{10}$, 14693-30-2; $\text{Re}_2(\text{CO})_{10}$, 14285-68-8.

Vibrational Circular Dichroism of *trans*-1,2-Dideuteriocyclobutane. Experimental and Computational Results in the Mid-Infrared

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Abstract: We have measured the VCD of *trans*-1,2-dideuteriocyclobutane in the mid-IR and have compared it to the results of fixed partial charge and localized molecular orbital calculations. For a force field optimized from the ab initio results of Banhegyi et al., we find good agreement between calculated and experimental results for the FPC but not for the LMO model. Other force fields and charge configurations were also investigated with the general result that optimized force fields gave superior results due to better representation of both the modes and their frequency distributions.

In recent years vibrational circular dichroism (VCD) has become technologically feasible in the near- and mid-IR.^{1,2} The utility of such measurements is dependent on the development of theoretical models which can reliably represent the relationship between VCD spectra and molecular structure. Two such models, the fixed partial charge³ (FPC) and localized molecular orbital⁴ (LMO) models, have proven to be computationally useful in several recent studies which compared calculations with experimental VCD spectra in the near-IR region⁵ ($\nu > 2000 \text{ cm}^{-1}$). We have recently analyzed these two models in detail with respect to their ability to reproduce the C-H and C-D stretching VCD of *trans*-1,2-dideuteriocyclobutane.⁶ These results indicated that both models gave qualitatively the same VCD but did differ in the order of magnitude of the predicted VCD. However, the $\Delta A/A$ ratios calculated were about the same with each model. The major factor that we found to be necessary in that work for good agreement with experiment was the obtaining of a force field which correctly reproduced the relative frequency spacings of the overlapped modes. The various force fields we used did not significantly alter the calculated rotational strengths of individual stretching modes but did alter their interfering VCD overlap. Our best results were obtained with a new force field derived from the ab initio results of Banhegyi, Fogarasi, and Pulay⁷ (hereafter BFP) by optimizing to best reproduce the frequencies of several isotomers.⁸

Cyclobutane has several advantages for such a comparative test of theoretical models. Its small size, lack of heteroatoms, and known geometry⁹ combine to simplify calculational work. Furthermore, the force fields that are now available, refined to fit the isotopic variants,⁸ provide a necessary ingredient for both models.^{3,4} We have previously reviewed the successes and failures of the FPC and LMO models.⁶ In short, it is clear that the C-H and C-D stretching modes of a pure hydrocarbon should provide a best possible case for both. The presence of two conformers

in *trans*-1,2-dideuteriocyclobutane (with deuteriums equatorial or axial to the ring) additionally provides some cancellation of coupled-oscillator-type effects that are thought to dominate VCD of previously analyzed six-member ring systems.¹⁰ This coupling will occur between all pairs of local oscillators¹¹ and can give rise to significant VCD when the transition dipole moments are large and the modes involved are strongly coupled.¹²

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