

Gas-Phase Acidities of $(\text{CO})_5\text{MnH}$, $(\text{CO})_4\text{FeH}_2$, and $(\text{CO})_4\text{CoH}$

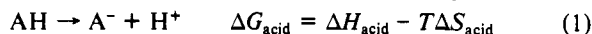
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Abstract: The gas-phase acidities of $(\text{CO})_5\text{MnH}$, $(\text{CO})_4\text{FeH}_2$, and $(\text{CO})_4\text{CoH}$ are determined by ion cyclotron resonance studies of their deprotonation by reference anions. These compounds are all extremely strong acids in the gas phase, with $\Delta H_{\text{acid}}[(\text{CO})_5\text{MnH}] = 318 \pm 4$ kcal/mol, $\Delta H_{\text{acid}}[(\text{CO})_4\text{FeH}_2] = 319 \pm 5$ kcal/mol, and $\Delta H_{\text{acid}}[(\text{CO})_4\text{CoH}] \leq 314 \pm 1$ kcal/mol. When combined with the known metal-hydrogen homolytic bond energies, the acidities determine the electron affinities, $\text{EA}[(\text{CO})_5\text{Mn}] = 2.4 \pm 0.3$ eV, $\text{EA}[(\text{CO})_4\text{FeH}] \leq 2.8 \pm 0.8$ eV, and $\text{EA}[(\text{CO})_4\text{Co}] \geq 2.3$ eV. Negative-ion mass spectra and negative-ion-molecule reactions of these complexes are discussed. The neutral hydrides dissociatively attach thermalized (298 K) electrons, with each of the hydrides showing loss of CO on the attachment. Loss of H_2 to produce $(\text{CO})_4\text{Fe}^-$ is competitive with CO loss on electron attachment to $(\text{CO})_4\text{FeH}_2$. In a process consistent with its strong gas-phase acidity, loss of an H atom to produce $(\text{CO})_4\text{Co}^-$ is competitive with detachment of CO in electron attachment to $(\text{CO})_4\text{CoH}$.

Introduction

The determination of gas-phase acidities, as defined by the free energy change of reaction 1, has led to an understanding of intrinsic substituent effects and the influence of solvation on this important molecular property.²⁻¹⁴ A classic example is from the



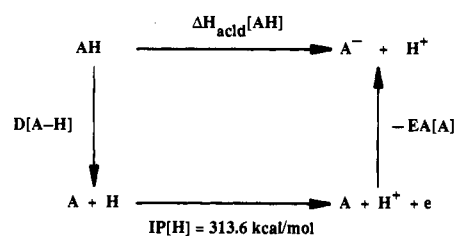
gas-phase acidities of the alcohols, which follow the order neopentyl > *tert*-butyl > isopropyl > ethyl > methyl, exactly the opposite of their solution behavior.¹³ This is interpreted as resulting from poor solvation of the anion with increasing bulkiness, which overrides the effect of alkyl group polarizability stabilizing the anionic center.^{2,13,14}

Gas-phase acidities are also important in that the enthalpy change for the acidity, $\Delta H_{\text{acid}}[\text{AH}]$, is related to the electron affinity of A, $\text{EA}[\text{A}]$, and the homolytic bond energy, $D[\text{A-H}]$, as shown in Scheme I and eq 2; determining any two of these quantities allows additional thermochemistry to be derived.

$$\Delta H_{\text{acid}}[\text{A-H}] = D[\text{A-H}] - \text{EA}[\text{A}] + 313.6 \text{ kcal/mol} \quad (2)$$

We report here the gas-phase acidities of three organometallic carbonyl hydrides, $(\text{CO})_5\text{MnH}$, $(\text{CO})_4\text{FeH}_2$, and $(\text{CO})_4\text{CoH}$,

Scheme I



determined by using the techniques of ion cyclotron resonance spectroscopy.¹⁵ Acidities of these complexes in aqueous¹⁶⁻¹⁸ and acetonitrile¹⁹ solutions have been reported; both $(\text{CO})_5\text{MnH}$ and $(\text{CO})_4\text{FeH}_2$ are weak acids, and $(\text{CO})_4\text{CoH}$ is a strong acid, being fully dissociated in aqueous solution.²⁰ Poor solvation of the bulky carbonyl anions is expected to be a major factor in determining the aqueous acidities of these complexes; it is of interest to quantify this effect. These data and the electron affinities could provide a relatively direct means of corroborating the metal-hydrogen bond dissociation energies which have been reported for $(\text{CO})_5\text{MnH}$ and $(\text{CO})_4\text{CoH}$ ²¹ and a means of determining the bond energy in $(\text{CO})_4\text{FeH}_2$.

Experimental Section

The techniques of ion cyclotron resonance (ICR) spectroscopy have been described.¹⁵ The spectrometer used in this study was built in our laboratories and utilizes a 15-in. electromagnet capable of 23.4-kG maximum field. Standard marginal oscillator detection was employed. Pressures were measured with a Schulz-Phelps-type ion gauge calibrated against an MKS Baratron Model 90H1-E capacitance manometer; the estimated uncertainty in absolute pressure is $\pm 20\%$. All electron energies are uncalibrated. All reactions were identified by double-resonance techniques;¹⁵ neutrals were not detected. These experiments were performed at ambient temperature (298 K).

Negative- and positive-ion mass spectra were recorded in the drift mode. Negative-ion mass spectra with thermalized electrons were taken in the trapping mode, and spectra were recorded following a 3-ms pulse of 70-eV electrons. The electrons were thermalized by using high pressures of CO_2 , as described in the literature.²² Pressures of the metal

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complexes were kept low ($(1-4) \times 10^{-8}$ Torr) to ensure electron thermalization before attachment and to prevent rapid reaction of the anions by cluster-forming reactions. All ion-molecule reactions reported here were studied by using the trapping mode and typically observed for 500-1000 ms following a 3-10-ms electron pulse. Reagent anions were made by electron impact on an appropriate neutral: F^- from NF_3 , Cl^- from CCl_4 , Br^- from CH_3Br , I^- from CH_3I , and $CF_3CO_2^-$ from CF_3CO_2H . Pressures of the reagent neutrals were in the range of 2-10 times the pressure of the metal carbonyl hydrides, and the electron-impact energy (typically near 5 eV) was optimized for the highest yield of each desired reagent anion. Under these conditions, the initial electron pulse produced predominantly reagent anions rather than metal-containing anions. Scattered free electrons can also be trapped in the ICR spectrometer and undergo dissociative attachment reactions with the metal carbonyl hydrides. We found that optimization of all reaction conditions (pressures of reagent and metal complexes, electron pulse length and energy, trapping voltages) proved more effective than electron ejection techniques²³ at minimizing complications from the electron attachment reactions. Furthermore, the electron attachment reactions are extremely rapid, and the free electrons are scavenged within ~ 100 ms of the initial electron pulse, while all reactions reported here were confirmed by double resonances at long reaction times. The kinetics of the reactions reported here could not be determined, since gaseous decomposition products precluded measurements of the neutral hydride pressure. Even in the event that decomposition products were not present, cluster-forming reactions between the metal anions and the parent neutral hydride and ligand displacement, ligand exchange, and nucleophilic displacement reactions involving the other neutral reagents made the reaction schemes too complex to determine accurate reaction rates. All of the proton-transfer reactions reported here are qualitatively fast (at or near the collision rate), which is indicative of exothermic proton transfer. The cluster-forming reactions appeared qualitatively slow.

Pentacarbonylhydridomanganese was prepared by reaction of $Na[(CO)_5Mn]$ with phosphoric acid.²⁴ Final purification was effected by pumping on the dry ice/acetone-cooled sample until no impurities were observed in the mass spectrum.

Tetracarbonyldihydroiron was prepared by acidification of $(CO)_4FeH^-$ as described in the literature.²⁵ The sample was purified by cooling with dry ice/acetone and pumping on the sample to remove volatile impurities. The sample of $(CO)_4FeH_2$ was stored on dry ice. A fresh sample was prepared each day by warming the stock sample to $-38^\circ C$ and vacuum-transferring the $(CO)_4FeH_2$. This sample was held at $-38^\circ C$ during the experiments. Despite all these precautions, substantial decomposition occurred, as evidenced by CO and $Fe(CO)_5$ in the mass spectra; this was attributed in large part to decomposition in the inlet system and near the hot filaments of the ICR cell.

Tetracarbonylhydridocobalt was prepared from $[Co(pyridine)_6][Co(CO)_4]_2$ as described in the literature.²⁶ $(CO)_4CoH$ was purified by several vacuum distillations from the sample held at $-45^\circ C$ and stored in dry ice. A sample bulb was prepared daily from this stock by warming it to $0^\circ C$ and vacuum-transferring the $(CO)_4CoH$. This bulb was held at $0^\circ C$ during the course of the experiments; colder baths gave insufficient vapor pressure for easy handling. The sample was degassed several times during use. Again, decomposition was extensive, with CO^+ and CO_2^+ being the most abundant ions in the positive-ion mass spectrum.

Decacarbonyldimanganese was obtained from Alfa Inorganics and used as supplied. All other reagents were used without purification, except for degassing with several freeze-pump-thaw cycles.

Results

Mass Spectra and Negative-Ion-Molecule Chemistry of $(CO)_5MnH$. The positive-ion mass spectra of $(CO)_5MnH$ recorded on our instrument agree well with those reported in the literature.^{27,28} The 70-eV negative-ion mass spectrum of $(CO)_5MnH$, taken in the drift mode at a pressure of 3×10^{-7} Torr, shows the ions $(CO)_5Mn^-$ (6%), $(CO)_4MnH^-$ (91%), and $(CO)_3MnH^-$ (3%). The spectrum is unchanged from 70 to 0.5 eV. The negative-ion spectrum with thermalized electrons (1:90 to 1:400 mixture of $(CO)_5MnH$ with CO_2) shows 100% $(CO)_4MnH^-$.

Table I. Gas-Phase Acidities of Reference Species^a

HX	$\Delta H_{acid}[HX]$	HX	$\Delta H_{acid}[HX]$
HF	371.5 ± 0.2	CF_3CO_2H	322.9 ± 4.1
HCl	333.4 ± 0.2	HI	314.4 ± 0.1
HBr	323.5 ± 0.1		

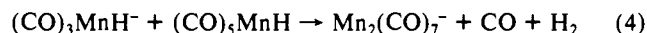
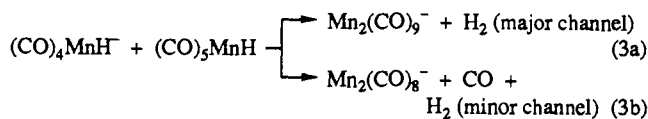
^aAll data are in kcal/mol at 298 K and are taken from ref 9. Enthalpies for HF, HCl, HBr, and HI are calculated from bond energies and electron affinities as given by Scheme 1 and eq 2. ΔG_{acid} for CF_3CO_2H (316.3 ± 1.9 kcal/mol) is determined by ion-molecule equilibrium reactions and used to determine ΔH_{acid} by eq 1, using a calculated entropy (which incurs the additional error in the enthalpy). The equilibrium method applied to HBr suggests that CF_3CO_2H may be less acidic than HBr by ~ 0.5 kcal/mol,⁹ but this is so slight that it does not change the acidity of $(CO)_5MnH$ reported here, for which CF_3CO_2H is used as a reference.

Table II. Selected Values for Gas-Phase Acidities of Metal Carbonyl Hydrides^a

complex	$\Delta H_{acid}[HX]$	complex	$\Delta H_{acid}[HX]$
$(CO)_5MnH$	318 ± 4	$(CO)_4CoH$	$\leq 314 \pm 1$
$(CO)_4FeH_2$	319 ± 5	$(CO)_4FeH$	$\geq 319 \pm 5$

^aAll data are in kcal/mol at 298 K.

A study of the negative-ion-molecule chemistry of $(CO)_5MnH$ at 4×10^{-7} Torr shows at long reaction times the formation of very small amounts of $Mn_2(CO)_9^-$ and $Mn_2(CO)_8^-$ arising from $(CO)_4MnH^-$ and of $Mn_2(CO)_7^-$ arising from $(CO)_3MnH^-$ (eqs 3a, 3b, and 4). We could not unequivocally attribute these



products to reactions with the hydride; the reactions are slow, and addition of $Mn_2(CO)_{10}$ increases the abundance of these ions dramatically. These facts suggest that these ions could be due to electron transfer with $Mn_2(CO)_{10}$, possibly present in trace amounts from decomposition of $(CO)_5MnH$.

Acidity of $(CO)_5MnH$. The negative ions $X^- = F^-$, Cl^- , and $CF_3CO_2^-$ all react with $(CO)_5MnH$ to give only the proton-transfer product $(CO)_5Mn^-$, according to eq 5. In a 10:1 mixture of



CF_3CO_2H with $(CO)_5MnH$ at a total pressure of 4.4×10^{-7} Torr, the ion intensity ratio of $(CO)_5Mn^-$ to $CF_3CO_2^-$ was 1.3:1 after a 500-ms trapping time; ion loss from reactions and trapping inefficiency is too great to allow observation of the ions at longer times. The double-resonance experiments indicate that virtually all $(CO)_5Mn^-$ observed at this time is a result of proton abstraction by $CF_3CO_2^-$ (eq 5), but no $CF_3CO_2^-$ is produced by the reverse of reaction 5. This means that the reaction is still proceeding in the forward direction and an equilibrium situation has not been achieved. A limit on the free energy change for this particular proton-transfer reaction is therefore given by $\Delta G^\circ \leq -RT \ln \{[(CO)_5Mn^-][CF_3CO_2H]/[CF_3CO_2^-][(CO)_5MnH]\}$, with the concentration ratios given by the ion intensities and the measured neutral pressures. A slight entropy change (-0.8 eu) is calculated from the rotational symmetry numbers of reactants and products and used in conjunction with the limit of ΔG° , resulting in $\Delta H \leq -1.8$ kcal/mol, that is, $\Delta H_{acid}[(CO)_5MnH] \leq \Delta H_{acid}[CF_3CO_2H] - 1.8$ kcal/mol.

For $X^- = I^-$, neither reaction 5 nor any other reaction occurs. The reverse reaction, in which $(CO)_5Mn^-$ would abstract a proton from HI to give I^- , cannot be observed on the ICR time scale ($k \leq 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$), nor is any reaction of $(CO)_5Mn^-$ with HI observed.

The acidity of $(CO)_5MnH$ is bracketed between that of HI and 1.8 kcal/mol less than that of CF_3CO_2H ; ΔH_{acid} values for the reference acids are given in Table I. A value of ΔH_{acid}

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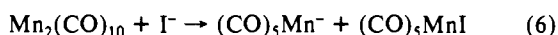
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Table III. 70-eV Positive-Ion Mass Spectral Data for (CO)₄FeH₂

<i>m/e</i>	ion	% ion current	<i>m/e</i>	ion	% ion current
169	(CO) ₄ FeH ⁺	1	85	(CO)FeH ⁺	12
168	(CO) ₄ Fe ⁺	3	84	(CO)Fe ⁺	27
140	(CO) ₃ Fe ⁺	2	68	FeC ⁺	3
113	(CO) ₂ FeH ⁺	14	56	Fe ⁺	23
112	(CO) ₂ Fe ⁺	15			

[(CO)₅MnH] = 318 ± 4 kcal/mol is chosen and is presented in Table II. The absence of additional reference species with an acidity within this range precluded further refinement of this value.²⁹

Particularly in the absence of either an equilibrium situation or observation of the back-reactions, there is concern that (C-O)₅Mn⁻ arises by reaction with any Mn₂(CO)₁₀ from decomposition of the hydride. Two pieces of evidence counter this possibility. First, although the kinetics of proton abstraction could not be determined quantitatively, the observed reactions of F⁻, Cl⁻, and CF₃CO₂⁻, as given by eq 5, are qualitatively much too fast to be attributed to reaction with any trace Mn₂(CO)₁₀ impurity. Second, we examined the reactions of the halides, including I⁻, with Mn₂(CO)₁₀. Reactions of the halides do occur, producing (CO)₅Mn⁻, as shown for I⁻ in eq 6. The fact that (CO)₅Mn⁻



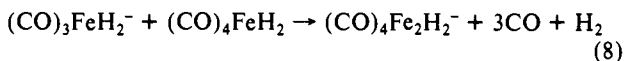
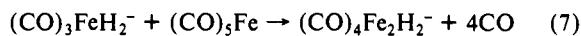
was not observed from the reaction of I⁻ with the sample of (CO)₅MnH gives some confidence that Mn₂(CO)₁₀ is not a contributor to the reactions we observed with the other X⁻ ions.

Mass Spectra and Negative-Ion-Molecule Chemistry of (C-O)₄FeH₂. The 70-eV positive-ion mass spectrum of (CO)₄FeH₂ has not been reported; the relative ion abundances from the spectrum obtained by using ICR spectroscopy are reported in Table III. Ion abundances are somewhat uncertain, as these were determined by subtracting ion intensities due to (CO)₅Fe from the observed mass spectrum; typically, ~50% of the total ion current of iron-containing ions was attributed to (CO)₅Fe. The spectra also show CO⁺ as 20–60% of the total ion current. The (CO)₄FeH₂⁺ ions are not observed (abundance <1%), nor is FeH⁺.

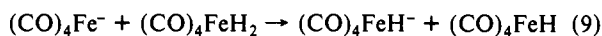
The 70-eV negative-ion mass spectrum of this sample shows the ions (CO)₄FeH⁻ (6%), (CO)₄Fe⁻ (45%), (CO)₃FeH₂⁻ (31%), and (CO)₃Fe⁻ (18%). The negative-ion mass spectrum of (CO)₅Fe under identical conditions gives the ions (CO)₄Fe⁻ (92%) and (CO)₃Fe⁻ (8%). Since there is no ion unique to (CO)₅Fe, there is no way to subtract the (CO)₅Fe contribution from the negative-ion mass spectra of (CO)₄FeH₂. Clearly, (CO)₄FeH₂ fragments much more easily to give (CO)₃Fe⁻ and is therefore expected to show a large contribution to the (CO)₄Fe⁻ intensity as well.

The negative-ion spectrum with thermalized electrons (~1:50 to 1:100 pressure ratios with CO₂, 0–80-ms trapping times) yields (CO)₄Fe⁻ (80%) and (CO)₃FeH₂⁻ (20%). The intensity of (C-O)₄Fe⁻ is so great as to indicate much of it arises from (CO)₄FeH₂ and not just from (CO)₅Fe.

At long trapping times, small amounts of (CO)₄Fe₂H₂⁻ are formed, apparently by reaction 7 and/or reaction 8.

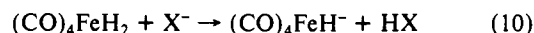


Most interestingly, (CO)₄Fe⁻ reacts by apparent proton abstraction from (CO)₄FeH₂ (reaction 9).



Acidity of (CO)₄FeH₂. The ions X⁻ = Cl⁻ and Br⁻ react with (CO)₄FeH₂ to give only the proton-transfer product (CO)₄FeH⁻

according to eq 10. For X⁻ = I⁻, neither reaction 10 nor any



reaction of I⁻ occurs. No reaction of (CO)₄FeH⁻ with HI (including the reverse of eq 10) could be observed (*k* ≤ 10⁻¹¹ cm³·molecule⁻¹·s⁻¹). Since Δ*H*_{acid}[(CO)₄FeH] is nearly the same as Δ*H*_{acid}[HBr], the reaction of CF₃CO₂⁻ with (CO)₄FeH₂ was not examined because it would not have narrowed the acidity bracketing significantly. Use of the equilibrium technique to further limit the enthalpy difference was not useful here, since (CO)₄FeH₂ decomposes so extensively that pressure measurements to determine the concentration of (CO)₄FeH₂ are meaningless.

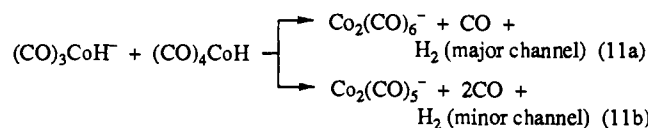
The acidity of (CO)₄FeH₂ is bracketed between that of HI and HBr (Table I) essentially in the same range as the acidity of (CO)₅MnH. A value of Δ*H*_{acid}[(CO)₄FeH₂] = 319 ± 5 kcal/mol is chosen and presented in Table II.

Mass Spectra and Negative-Ion-Molecule Chemistry of (C-O)₄CoH. The 70-eV positive-ion mass spectrum of (CO)₄CoH recorded on our instrument agrees well with that previously reported.³⁰ Our spectrum showed substantial amounts of CO (57% of the total ion current) and CO₂ (9%). These impurities do not interfere with the negative-ion chemistry, but precluded measurement of rate constants, since the actual pressure of (CO)₄CoH in the sample is unknown.

The 70-eV negative-ion mass spectrum of (CO)₄CoH shows the ions (CO)₄Co⁻ (26%), (CO)₃CoH⁻ (72%), and (CO)₂CoH⁻ (2%). This spectrum was reported previously by Saalfeld et al., but (CO)₂CoH⁻ was incorrectly identified as (CO)₂Co⁻.³⁰ The intensity of (CO)₂CoH⁻ falls with decreasing electron energy (with none detectable at 10 eV) but rises again at about 4 eV to ~22% of the total ion intensity at 3-eV electron energy. The ratio of (CO)₄Co⁻ and (CO)₃CoH⁻ does not vary significantly over these electron energies.

The negative-ion mass spectrum with thermalized electrons shows the ions (CO)₄Co⁻ (16%) and (CO)₃CoH⁻ (84%). The ratio of these products does not vary over the range of CO₂ pressures (1:50 to 1:200 pressure ratios) or trapping times (0–400 ms) investigated. Since there is no evidence for any Co₂(CO)₈ in either the positive-ion mass spectrum or the negative-ion mass spectra, the quite large intensity of (CO)₄Co⁻ indicates it can only be due to H atom loss from (CO)₄CoH.

At higher pressures of (CO)₄CoH, the ion (CO)₃CoH⁻ produces Co₂(CO)₆⁻ and, at short times, (<200 ms) a small amount of Co₂(CO)₅⁻. We attribute these reactions to eqs 11a and 11b. We



could not rule out the possibility that these dinuclear ions are due to charge transfer to Co₂(CO)₈, possibly formed in trace amounts by sample decomposition.

Acidity of (CO)₄CoH. The ions X⁻ = Cl⁻ and I⁻ react with (CO)₄CoH according to eq 12. In a mixture of (CO)₄CoH and



HI, no reaction of (CO)₄Co⁻ can be observed. The data indicate Δ*H*_{acid}[(CO)₄CoH] ≤ Δ*H*_{acid}[HI], and therefore Δ*H*_{acid}[(CO)₄CoH] ≤ 314 ± 1 kcal/mol (Tables I and II). Quantitative rates for the reactions given by eq 12 could not be determined due to the CO and CO₂ decomposition products of (CO)₄CoH. However, the qualitatively fast kinetics indicate that the (CO)₄Co⁻ product does not arise from any Co₂(CO)₈ which might possibly have been formed as a trace decomposition product in the ICR cell.

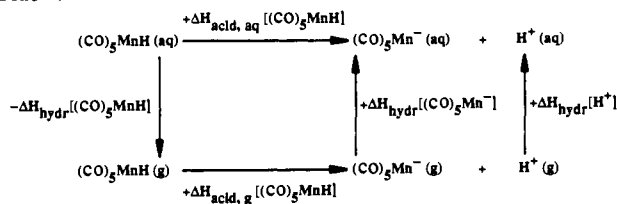
Discussion

Negative-Ion Mass Spectra and Ion-Molecule Reactions. The negative-ion mass spectra of these complexes are similar to those

(29) Meckstroth and Ridge (Meckstroth, W. K.; Ridge, D. P. *J. Am. Chem. Soc.* **1985**, *107*, 2281) studied the reactions of (CO)₅Mn⁻ in the gas phase. They did not observe reactions of the anion with the proton donors ethanol, acetic acid, methyl mercaptan, and hydrogen chloride, results consistent with the acidity of (CO)₅MnH reported in this work.

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Scheme II



reported for other metal carbonyls:²⁷⁻³² no molecular ion is observed, the predominant fragmentation occurs by loss of CO, and to a much lesser extent, loss of the σ -bonding ligand occurs. For $(\text{CO})_4\text{FeH}_2$, loss of H_2 is competitive with CO loss.

In the ion-molecule chemistry of the reactions of the metal anions with the parent neutrals, formation of dinuclear ions by $(\text{CO})_3\text{FeH}_2^-$ is similar to the chemistry observed for other transition-metal carbonyl negative ions.³² In this case, ligand loss on formation of $(\text{CO})_4\text{Fe}_2\text{H}_2^-$ is extensive and must result from a particularly strong Fe-Fe bond and/or particularly weak Fe-ligand bonds in the dinuclear species. No thermochemistry for the dinuclear anion is available to confirm this supposition. Cluster-forming reactions are common in the chemistry of unsaturated metal negative ions,³² and therefore we attribute the dinuclear ions produced by reaction of $(\text{CO})_4\text{MnH}^-$ and $(\text{CO})_3\text{MnH}^-$ to cluster-forming reactions with the parent neutral hydride (eqs 3 and 4). Since addition of $\text{Mn}_2(\text{CO})_{10}$ increases the abundance of the cluster ions, there is a possibility that traces $\text{Mn}_2(\text{CO})_{10}$ from decomposition of $(\text{CO})_5\text{MnH}$ were responsible for the observed ion products. We similarly attribute the dinuclear ions $\text{Co}_2(\text{CO})_6^-$ and $\text{Co}_2(\text{CO})_5^-$ to reaction with $(\text{CO})_4\text{CoH}$ (eq 11). These cluster ions do not contain any H atoms, suggesting that they could be the result of charge transfer to $\text{Co}_2(\text{CO})_8$, which might possibly be a trace decomposition product in $(\text{CO})_4\text{CoH}$. We were unable to verify this, as $\text{Co}_2(\text{CO})_8$ itself tends to decompose on sublimation, making it difficult to handle in the ICR spectrometer.

Gas-Phase Acidities and Solvation Effects on Acidities. Each of these carbonyl hydrides is an extremely strong acid in the gas phase, with $(\text{CO})_5\text{MnH}$ and $(\text{CO})_4\text{FeH}_2$ being comparable in acidity to HBr and HI. Even more strikingly, $(\text{CO})_4\text{CoH}$ is more acidic than HI. By contrast, $(\text{CO})_5\text{MnH}$ in aqueous solution is a very weak acid, with a $\text{p}K_{\text{a}}$ of 7.1.¹⁶ $\text{p}K_{\text{a}}$ for aqueous $(\text{CO})_4\text{FeH}_2$ is reported by different workers to be either 4.4¹⁷ or 4.0.¹⁸ Consistent with its much greater gas-phase acidity, $(\text{CO})_4\text{CoH}$ in aqueous solution has a $\text{p}K_{\text{a}}$ of <0.4,¹⁷ making it comparable in acidity to HCl and HNO_3 . The $\text{p}K_{\text{a}}$'s have also been measured in acetonitrile by Moore et al.¹⁹ and have been determined to be $\text{p}K_{\text{a}}[(\text{CO})_5\text{MnH}] = 15.1$, $\text{p}K_{\text{a}}[(\text{CO})_4\text{FeH}_2] = 11.4$, and $\text{p}K_{\text{a}}[(\text{CO})_4\text{CoH}] = 8.3$. The fact that in two solvent systems $(\text{CO})_4\text{FeH}_2$ is a stronger acid than $(\text{CO})_5\text{MnH}$ suggests that this is the likely acidity order in the gas phase, but such an effect cannot be seen within the present bracketing range.

The large difference in solution and gas-phase acidities is due mainly to poor solvation of the organometallic anions. To quantitatively illustrate this point, Scheme II shows the thermochemical cycle in which the aqueous and gas-phase enthalpies for the acidity of $(\text{CO})_5\text{MnH}$ are linked with the hydration enthalpies of $(\text{CO})_5\text{MnH}$, $(\text{CO})_5\text{Mn}^-$, and H^+ . This scheme is used to derive eq 13, from which the hydration enthalpy of $(\text{CO})_5\text{Mn}^-$

$$\begin{aligned}
 \Delta H_{\text{hydr}}[(\text{CO})_5\text{Mn}^-] &= \Delta H_{\text{acid, aq}}[(\text{CO})_5\text{MnH}] - \\
 &\Delta H_{\text{acid, g}}[(\text{CO})_5\text{MnH}] + \Delta H_{\text{hydr}}[(\text{CO})_5\text{MnH}] - \Delta H_{\text{hydr}}[\text{H}^+]
 \end{aligned} \quad (13)$$

is derived by substitution of the four known enthalpies.³³ This

substitution yields an estimate of $\Delta H_{\text{hydr}}[(\text{CO})_5\text{Mn}^-] = -35$ kcal/mol, a fairly small hydration enthalpy, which is indicative of poor solvation of the anion. The Born theory of solvation yields a relationship linking hydration enthalpy to ion radius,³⁴ which gives a solvation radius of about 4.7 Å for $(\text{CO})_5\text{Mn}^-$. This value is in surprisingly good agreement with expectations from the reported crystal structure of this anion.³⁵ A similar comparison can be made for the energetics of solvation of $(\text{CO})_4\text{FeH}^-$. An estimate for $(\text{CO})_4\text{Co}^-$ cannot be made, since both gas-phase and aqueous acidities are upper bounds.

The strong gas-phase acidities result from relatively weak metal-hydrogen bonds and high electron affinities of the metal-carbonyl radicals, evident from Scheme I and eq 2. As an example, a bond energy $D[(\text{CO})_5\text{Mn-H}] = 59$ kcal/mol has been determined from gas-phase thermochemical data.²¹ Using this value in eq 2 yields $\text{EA}[(\text{CO})_5\text{Mn}] = 2.4 \pm 0.3$ eV. It is somewhat surprising, therefore, that ICR studies by Dunbar and Hutchinson of $(\text{CO})_5\text{Mn}^-$ have indicated no "photodisappearance" of the ion when it is irradiated by photons in the range 1.55–4.1 eV.³⁶ This was interpreted as a lack of optical absorption of $(\text{CO})_5\text{Mn}^-$ within this range, since a number of metal carbonyl anions photodissociate by CO loss when irradiated.^{36,37} The calculation of a 2.4-eV electron affinity indicates also that the cross section for electron detachment must be extremely small at these energies; the vertical electron affinity must be substantially greater than the adiabatic electron affinity. This is a reflection of a sizable geometric rearrangement on electron loss from $(\text{CO})_5\text{Mn}^-$ to give the $(\text{CO})_5\text{Mn}$ radical. The crystal structure of $[\text{Ni}(1,10\text{-phenanthroline})_3]_2[\text{Mn}(\text{CO})_5]_2$ shows $(\text{CO})_5\text{Mn}^-$ to be trigonal-bipyramidal (D_{3h}).³⁵ Infrared, ESR, and optical spectra of matrix-isolated $(\text{CO})_5\text{Mn}$ show that it adopts a square-pyramidal (C_{4v}) geometry, with the IR analysis indicating the apical-equatorial angle $\sim 96^\circ$.³⁸ A large difference between the adiabatic and vertical electron affinities is evident for SF_6 , with an adiabatic electron affinity of ~ 1.05 eV³⁹ but a vertical electron affinity of ~ 3.3 eV.⁴⁰ This large difference arises from an increase of about 0.14 Å in the S-F bond distances on formation of the anion, although both the neutral and the anion are octahedral.⁴¹ Another example is afforded by $(\text{CO})_4\text{Fe}^-$, which gives a very broad photoelectron spectrum and only a very weak signal.⁴² This ion, for which the relaxation energy is expected to be more comparable to that of $(\text{CO})_5\text{Mn}^-$, undergoes competitive CO loss at the 3.408-eV irradiating energy; no vertical electron affinity was reported, and the adiabatic electron affinity is difficult to assign.

No independent thermochemical determination has been made of $D[(\text{CO})_4\text{FeH-H}]$. Data presented later in this paper can be used to determine an upper limit for the bond energy, $D[(\text{CO})_4\text{FeH-H}] \leq 70 \pm 14$ kcal/mol, which provides an upper limit

(33) Values used in eq 13: $\Delta H_{\text{acid, aq}}[(\text{CO})_5\text{MnH}] = +318$ kcal/mol, from this work, $\Delta H_{\text{acid, aq}}[(\text{CO})_5\text{MnH}] \approx +16$ kcal/mol, estimated from $\Delta G_{\text{acid, aq}}[(\text{CO})_5\text{MnH}] \approx +9.6$ kcal/mol¹⁶ and an assumed $\Delta S_{\text{acid, aq}} \approx +20$ cal/(mol·K); $\Delta H_{\text{hydr}}[(\text{CO})_5\text{MnH}] \approx +5$ kcal/mol, estimated from the solubility;¹⁶ $\Delta H_{\text{hydr}}[\text{H}^+] \approx -261.6$ kcal/mol (from data in: Marcus, Y. *Pure Appl. Chem.* **1982**, *54*, 2327. Criss, C. M.; Salomon, M. *Thermodynamic Measurements—Interpretation of Thermodynamic Data*. In *Physical Chemistry of Organic Solvent Systems*; Covington, A. K., Dickenson, T., Eds.; Plenum Press: London, 1973. Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed., Part II. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 1).

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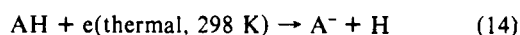
for the electron affinity, $EA[(CO)_4FeH] \leq 2.8 \pm 0.8$ eV.

A value for $D[(CO)_4Co-H] \approx 54$ kcal/mol derived from thermochemical data²¹ establishes $EA[(CO)_4Co] \geq 2.3$ eV. $(CO)_4Co^-$ is observed to "photodisappear" when irradiated; it has an optical absorption peak at 3.8 eV and a threshold at about 3.0-eV photon energy.³⁶ Attempts to identify the photoproducts in these ICR experiments were unsuccessful, but the "photodisappearance" was assumed to be due to CO loss, as for other metal carbonyls, and not to electron detachment.

The acidities of $(CO)_5MnH$ and $(CO)_4CoH$ have been calculated by McKinney and Pensak,⁴³ who find $(CO)_4CoH$ more acidic than $(CO)_5MnH$ by 6.5 kcal/mol, and by Zeigler et al.,⁴⁴ who find $(CO)_4CoH$ the more acidic by ~ 9 kcal/mol. Both calculations indicate the acidity difference is principally due to a much larger electron affinity for $(CO)_4Co$ than for $(CO)_5Mn$.

Although proton transfer from the carbonyl hydrides is rapid, none of the 18-electron anions $(CO)_5Mn^-$, $(CO)_4FeH^-$, or $(C-O)_4Co^-$ has been observed to abstract a proton from a neutral compound, including HI or another carbonyl hydride. This slow proton transfer to the anion is also the case for these and similar compounds in solution.⁴⁵ Geometric rearrangement between the neutral hydride complexes^{46,47} and the conjugate anions^{35,48,49} is considerable and would contribute to the slow reactivity. For example, $(CO)_5MnH$ has C_{4v} symmetry and has nearly octahedral coordination of the six ligands;^{46,47} $(CO)_5Mn^-$ has D_{3h} symmetry, with trigonal-bipyramidal coordination of the carbonyl ligands.³⁵ Within experimental error, the C-O and Mn-C bond distances are unchanged between the hydride and the anion. Concomitant with the effects of geometry is delocalization of the negative charge, which generally contributes to very slow proton-transfer reactions.¹¹ With $(CO)_5Mn^-$ as an example, the electron configuration of the manganese is d^8 , with the electrons back-bonding into the CO π^* orbitals. The d electrons remain essentially core electrons, and there is in fact no stereochemically active lone pair of electrons to protonate.

Dissociative Attachment of Thermalized Electrons. The absence of either equilibrium proton transfer or even any observation of proton abstraction by a closed-shell metal anion means we were unable to place a lower bound on the acidities of $(CO)_5MnH$ and $(CO)_4FeH_2$ by the observation of the back-reactions (proton abstractions by the metal anions), as is typically done in bracketing experiments. Instead, we had to assume the forward reactions (5) and (10) with I^- are endothermic, rather than being kinetically too slow to observe on the ICR time scale. In the case of $(C-O)_4CoH$, the lack of reference species with acidities less than that of HI also caused us to seek an independent method of establishing an upper limit for the acidity of this extraordinarily strong acid. These concerns prompted our examination of the reactions of the carbonyl hydrides with thermalized (298 K) electrons in order to corroborate the gas-phase acidity limits for these molecules. In particular, the observation of reaction 14 can provide limits



for the gas-phase acidity of AH.⁵⁰ The enthalpy of eq 14, ΔH_{14} , is shown by a simple thermochemical cycle to be linked to the homolytic A-H bond energy and the electron affinity of A, as given by eq 15. In eq 15, the 1.48 kcal/mol is the thermal

$$\Delta H_{14} = D[A-H] - EA[A] - 1.48 \text{ kcal/mol} \quad (15)$$

enthalpy of the electron at 298 K.⁵¹ For reaction 14 to be observed, it must be exothermic ($\Delta H_{14} \leq 0$); that is, the energy needed to break the A-H bond is compensated by the thermal energy of the electron and the exothermicity of electron attachment to A. This energetic requirement can be seen from eq 15 to be equivalent to $D[A-H] - EA[A] \leq 1.48$ kcal/mol, which, when substituted into eq 2, is equivalent to the requirement that $\Delta H_{acid}[AH] \leq 315$ kcal/mol.

Quite dramatically, $(CO)_4Co^-$ is produced as 16% of the product from capture of thermalized electrons by $(CO)_4CoH$. This dictates that $\Delta H_{acid}[(CO)_4CoH] \leq 315$ kcal/mol and is excellent corroboration of the 314 kcal/mol upper limit for the enthalpy, which was determined by the proton abstraction from $(CO)_4CoH$ by I^- (eq 12).

Neither $(CO)_5Mn^-$ nor $(CO)_4FeH^-$ is produced from the corresponding neutral by capture of thermalized electrons. This indicates that $\Delta H_{acid}[(CO)_5MnH]$ and $\Delta H_{acid}[(CO)_4FeH_2]$ are both ≥ 315 kcal/mol, again in agreement with the results of the proton transfer reactions (5) and (10). This further confirms that the proton abstractions by I^- , according to reactions 5 and 10, are not observed with $(CO)_5MnH$ and $(CO)_4FeH_2$ because they are endothermic. The reverse of reactions 5 and 10, that is, reaction of either $(CO)_5Mn^-$ or $(CO)_4FeH^-$ with HI, should be exothermic but are not observed. This lack of reaction is apparently due to kinetic factors, as discussed above in considering the geometries of the neutral hydrides and corresponding anions.

Similar analysis of the energetic requirements for the production of $(CO)_4Fe^-$ by attachment of thermal electrons to $(CO)_4FeH_2$ indicate that $D[(CO)_4Fe-H_2] \leq EA[(CO)_4Fe] + 1.48$ kcal/mol. Engelking and Lineberger attempted to determine $EA[(CO)_4Fe]$ by laser photoelectron spectroscopy⁴² and found the photoelectron spectrum of $(CO)_4Fe^-$ is very weak and quite broad; they chose a value $EA[(CO)_4Fe] = 2.4 \pm 0.3$ eV. These authors and Compton and Stockdale⁵² suggested the adiabatic $EA[(CO)_4Fe]$ is approximately equal to the first Fe-CO bond dissociation energy of $Fe(CO)_5$, $D[(CO)_4Fe-CO]$. A gas-phase kinetic study of $(CO)_5Fe$ yields the bond energy $D[(CO)_4Fe-CO] = 41.5 \pm 2$ kcal/mol (1.8 ± 0.1 eV).⁵³ This bond energy is probably a lower limit for the electron affinity of $(CO)_4Fe$. For this work, we use $EA[(CO)_4Fe] = 2.4 \pm 0.3$ eV (55 ± 7 kcal/mol), which places the limit $D[(CO)_4Fe-H_2] \leq 57$ kcal/mol. This value is not surprising: $(CO)_4FeH_2$ decomposes at temperatures above -10 °C,⁵⁴ and the isolation of $(CO)_4FeL$ in the presence of added L = PPh₃ or AsPh₃ suggests that loss of H₂ is the initial step in the decomposition.²⁵ Pearson and Mauermann have studied the kinetics of the thermal decomposition of $(CO)_4FeH_2$ in solution and found an activation energy of 26 ± 2 kcal/mol for the process yielding H₂ and $Fe(CO)_4$.⁵⁵ Sweeney has studied the reverse process, oxidative addition of H₂ to $(CO)_4Fe$, in rare-gas matrices and suggested that the process occurs with little or no activation energy.⁵⁶ These results indicate the activation enthalpy of 26 ± 2 kcal/mol corresponds to the dihydrogen binding energy $D[(CO)_4Fe-H_2] \approx 26 \pm 2$ kcal/mol, which is consistent with the upper limit of 57 kcal/mol established by the electron attachment results. Limited data for reductive elimination of dihydrogen from other transition-metal compounds show this process to be ~ 15 kcal/mol endothermic.^{21,57,58}

Each of the carbonyl hydrides shows loss of CO in the dissociative attachment of thermal electrons; no parent anion is observed. This process is that observed for a number of transition-metal percarbonyls.⁵⁹

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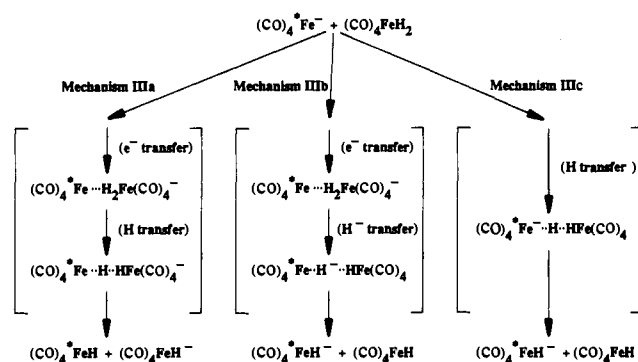
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Scheme III



Thermochemistry and Reactivity in the Iron Carbonyl Hydride System. The dihydrogen binding energy $D[(\text{CO})_4\text{Fe}-\text{H}_2]$ (26 ± 2 kcal/mol) can be used in conjunction with data presented in this paper to determine the hydride affinity of $(\text{CO})_4\text{Fe}$. $D[(\text{C}-\text{O})_4\text{Fe}-\text{H}^-] = 108 \pm 7$ kcal/mol, and the homolytic bond energy in the anion, $D[(\text{CO})_4\text{Fe}^--\text{H}] = 70 \pm 14$ kcal/mol.⁶⁰

The absence of any proton transfer to the 18-electron species makes the apparent "proton abstraction" by 17-electron $(\text{CO})_4\text{Fe}^-$ (reaction 9) particularly surprising. Since the geometric rearrangement and charge delocalization of this ion are not expected to be significantly different from those of the 18-electron species, it seems likely that this reaction does not proceed by proton transfer. Several mechanisms can be proposed for reaction 9 that do not involve proton transfer, and are shown in Scheme III. Electron transfer followed by H atom transfer has been suggested as a possible mechanism for "proton transfer" from $(\text{CO})_4\text{OsH}_2$ to $(\text{CO})_4\text{OsH}^-$ in solution;⁴⁵ this is shown for the present system in Scheme III as mechanism IIIa. Electron transfer followed by X^- transfer has been proposed as a mechanism for halogen abstraction from alkyl halides by 17-electron metal anions, including $(\text{CO})_4\text{Fe}^-$, in the gas-phase;⁶¹ a mechanism similar to this is proposed for H atom transfer in Scheme III, mechanism IIIb. Alternatively, simple H atom transfer may be the mechanism operating, as illustrated in Scheme III, mechanism IIIc. Ostensibly, proton transfer or mechanism IIIa could be distinguished from mechanism IIIb or IIIc by utilizing the isotopes of iron, as

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suggested by the $^*\text{Fe}$ label in the schemes, but this is beyond the resolution of our instrumentation.

Independently of which mechanism is operative, or even whether reaction 9 proceeds by hydrogen atom or proton transfer, the reaction still corresponds energetically to a direct proton transfer from $(\text{CO})_4\text{FeH}_2$ to $(\text{CO})_4\text{Fe}^-$. This means that the proton affinity of $(\text{CO})_4\text{Fe}^-$ is greater than that of $(\text{CO})_4\text{FeH}^-$, or $\Delta H_{\text{acid}}[(\text{CO})_4\text{FeH}] \geq \Delta H_{\text{acid}}[(\text{CO})_4\text{FeH}_2]$, as presented in Table II. This limit of $\Delta H_{\text{acid}}[(\text{CO})_4\text{FeH}] \geq 319$ kcal/mol and $\text{EA}[(\text{CO})_4\text{Fe}] = 2.4$ eV, when substituted into eq 2, give a lower bound for the homolytic bond energy of the $(\text{CO})_4\text{FeH}$ radical, $D[(\text{CO})_4\text{Fe}-\text{H}] \geq 60 \pm 12$ kcal/mol.

Reaction 9 also must be consistent with the energetics of a direct hydrogen atom transfer (Scheme III, mechanism IIIc). This dicates that the homolytic iron-hydrogen bond energy in $(\text{C}-\text{O})_4\text{FeH}^-$ is greater than that in $(\text{CO})_4\text{FeH}_2$, or $D[(\text{CO})_4\text{Fe}-\text{H}] \geq D[(\text{CO})_4\text{FeH}-\text{H}]$. This is best expressed as a limit for the neutral bond energy, $D[(\text{CO})_4\text{FeH}-\text{H}] \leq 70 \pm 14$ kcal/mol, by using the value for $D[(\text{CO})_4\text{Fe}-\text{H}]$ derived earlier in this work.

Conclusions

The transition-metal carbonyl hydrides $(\text{CO})_5\text{MnH}$, $(\text{CO})_4\text{FeH}_2$, and $(\text{CO})_4\text{CoH}$ are found to be extremely strong acids in the gas phase, with $\Delta H_{\text{acid}}[(\text{CO})_5\text{MnH}] = 318 \pm 4$ kcal/mol, $\Delta H_{\text{acid}}[(\text{CO})_4\text{FeH}_2] = 319 \pm 5$ kcal/mol, and $\Delta H_{\text{acid}}[(\text{CO})_4\text{CoH}] \leq 314 \pm 1$ kcal/mol. Strong gas-phase acidities are undoubtedly very common for organometallic hydrides because of the weak metal-hydrogen bonds and moderately high electron affinities of the corresponding radicals.⁶² The acidities are combined with the known metal-hydrogen bond energies to determine the electron affinities, $\text{EA}[(\text{CO})_5\text{Mn}] = 2.4 \pm 0.3$ eV, $\text{EA}[(\text{CO})_4\text{FeH}] \leq 2.8 \pm 0.8$ eV, and $\text{EA}[(\text{CO})_4\text{Co}] \geq 2.3$ eV. When exothermic, deprotonation of the hydrides is a rapid reaction. Protonation of the anion formed is much slower, by at least 1–2 orders of magnitude, even when the process is appreciably exothermic. The neutral hydrides dissociatively attach thermalized (298 K) electrons, with each of the hydrides showing the loss of CO in the attachment; $(\text{CO})_4\text{FeH}_2$ also loses H_2 on attachment, to produce $(\text{CO})_4\text{Fe}^-$. In a process consistent with its strong gas-phase acidity, $(\text{CO})_4\text{CoH}$ also loses H on attachment, producing $(\text{CO})_4\text{Co}^-$. Extensions of this work, including measurements of acidities as a function of metal and ligand variation, are in progress.⁶³

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Registry No. $(\text{CO})_5\text{MnH}$, 16972-33-1; $(\text{CO})_4\text{FeH}_2$, 12002-28-7; $(\text{CO})_4\text{CoH}$, 16842-03-8.

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