

Anion Affinities of Transition-Metal Carbonyls. A Thermochemical Correlation for Iron Tetracarbonyl Acyl Negative Ions

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Abstract: Relative binding energies of $\text{Fe}(\text{CO})_5$ to a series of gaseous anions, including H^- , OH^- , CH_3O^- , F^- , CH_3CO_2^- , and Cl^- , have been determined from gas-phase ion-molecule reactions in a flowing afterglow apparatus at 300 ± 2 K. Qualitative evidence is presented which shows that attachment of an anion to $\text{Fe}(\text{CO})_5$ in the gas phase directly produces an iron tetracarbonyl acyl negative ion. The measured anion binding energies vary over a 40 kcal mol⁻¹ range of magnitudes and exhibit linear correlations with both the proton affinities $\text{PA}(\text{X}^-)$ and acetyl cation affinities ($D[\text{CH}_3\text{CO}^+-\text{X}^-]$) of the negative ions: $D[(\text{CO})_4\text{FeCO}-\text{X}^-] = 0.66\text{PA}(\text{X}^-) - 206$ kcal mol⁻¹ and $D[(\text{CO})_4\text{FeCO}-\text{X}^-] = 0.59D[\text{CH}_3\text{CO}^+-\text{X}^-] - 80.3$ kcal mol⁻¹, respectively. These correlations may be used in combination with established anion thermochemistry to estimate heats of formation for a large variety of iron tetracarbonyl acyl anions. The relationship of these data to homogeneous catalysis mechanisms and nucleophilic addition reactions involving transition-metal complexes in solution is discussed.

The thermochemical data base for transition-metal compounds is currently undergoing an explosive growth.¹⁻⁴ This growth is inspired, in part, by the burgeoning field of organometallic chemistry, as well as by the expanding interests in homogeneously catalyzed synfuel production.⁵⁻⁹ Gas-phase studies of metal ions have made major contributions to inorganic thermochemistry in recent years. Through systematic investigations of the properties and reactivity of gas-phase metal ions, useful new thermodynamic data such as metal-hydrogen and metal-carbon bond energies,^{1,10-13} electron affinities,¹⁴ ionization potentials,¹⁵ and metal ion heats of formation¹⁶ have been derived. Gas-phase ion-molecule reactions involving neutral transition-metal complexes have featured strongly in many of these studies. For example, the occurrence or non-occurrence of a binary gas-phase ion-molecule reaction often may be used in assigning limits on certain thermochemical properties for the species involved. This approach lies at the heart of the well-known and much-employed acidity

or basicity bracketing technique, wherein the direction of proton transfer between the neutral and ion of interest establishes a proton affinity hierarchy.^{17,18} When this approach is applied to transition-metal complexes, heterolytic and homolytic metal-hydrogen bond strengths may be determined.^{1,12,19}

We have been applying this kind of approach to obtaining thermochemical information in our studies of gas-phase nucleophilic addition reactions of negative ions with transition-metal carbonyls.²⁰⁻²² As with their condensed-phase counterparts, these gas-phase reactions often yield anionic metal-acyl complexes as products (eq 1).^{5,23-26} Metal-acyls are chemically significant



species in that they are frequently proposed as key intermediates in catalytic processes as well as in a host of inorganic and organic syntheses. For example, metal-hydroxycarbonyls, (metallo-carboxylic acids) such as $(\text{CO})_4\text{FeCO}_2\text{H}^-$, have been postulated as intermediates in water-gas shift catalysis,²⁷⁻³⁰ and metal-formyl complexes such as $(\text{CO})_4\text{FeCHO}^-$ commonly intercede in metal-catalyzed reductions of CO and CO₂ by H₂.^{5,31,32} Furthermore, many metal-acyls of the structure $(\text{CO})_4\text{FeC}(\text{O})\text{R}^-$ have been produced from reactions between alkyl halides and $\text{Fe}(\text{CO})_4^{2-}$ in the presence of CO,³³ as well as by nucleophilic addition of

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carbanions to $\text{Fe}(\text{CO})_5$.³⁴ Iron-acyl derivatives such as these have been used as versatile synthetic intermediates for the production of unsymmetrical ketones and α -diketones from alkyl, aryl, and acyl halides.³⁵ Therefore, information on the intrinsic properties, reactivity, and, particularly, the *thermochemistry* of transition metal-acyls is of practical significance. In this paper we describe our measurements of the energetics for gas-phase anion binding to $\text{Fe}(\text{CO})_5$ ("anion affinities") for a series of negative ions generated in a flowing afterglow apparatus at 300 K. These new data, and the iron tetracarbonyl acyl anion heats of formation derived from them, have enabled the discovery of a useful correlation between $\text{Fe}(\text{CO})_5$ anion affinities and those for several other reference acids. We demonstrate here the scope and applicability of this correlation and show how it may be used to estimate gas-phase heats of formation for a wide variety of anionic iron-acyl complexes.

Experimental Section

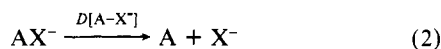
All experiments were carried out at 300 ± 2 K in a flowing afterglow apparatus which has been described in detail previously.^{20a}

The apparatus consists of a 100 cm \times 7 cm i.d. flow reactor interposed between an electron impact ion source and a quadrupole mass spectrometer which is located behind a 0.5 mm sampling orifice in a nose cone. Helium buffer gas, which thermalizes the ions and carries the plasma through the flow reactor, was maintained at a pressure of 0.40 torr and a typical flow rate of 180 STP $\text{cm}^3 \text{ s}^{-1}$ by a Roots blower. The primary reactant ions, NH_2^- and OH^- , were generated by electron impact on NH_3 and a $\text{N}_2\text{O}/\text{CH}_4$ mixture, respectively. These ions were allowed to react with one or more neutral compounds added further downstream to produce the required anion-transfer agents which were subsequently reacted with $\text{Fe}(\text{CO})_5$. The bimolecular rate constants and product branching ratios cited in this work were determined by standard methods^{36,37} which employed a movable neutral inlet. The neutral reactant flow rates were measured by monitoring a pressure increase with time in a calibrated volume.

All reagent gases were obtained from commercial suppliers and were of the following purities: He (99.995%), NH_3 (99.99%), N_2O (99.0%), $\text{C}_2\text{H}_4\text{F}_2$ (98.0%), H_2S (99.5%), SO_2 (99.98%), PF_3 (99.0%), MeSH (99.5%), CO_2 (99.5%). Liquid samples were also obtained from commercial sources and were used without further purification except for multiple freeze-pump-thaw cycles to remove noncondensable impurities.

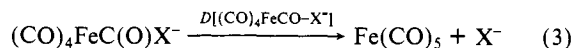
General Considerations

Before proceeding with a description of the results, we must first establish a few definitions. An "anion affinity" of a neutral compound is defined as the enthalpy of dissociation of a negative ion-molecule complex to the corresponding free anion and neutral. For example, eq 2 corresponds to the X^- affinity of neutral A, where AX^- may be an electrostatically bound cluster ion or a



covalently bonded species. A large number of anion affinities have been determined. McMahon, Kebarle, and others have measured and compiled extensive lists of gas-phase halide ion affinities for a wide variety of neutral compounds.³⁸⁻⁴¹ These studies have

provided an excellent experimental data base for developing theories about Lewis acidity, ion solvation, and hydrogen bonding.⁴²⁻⁴⁴ Most investigations have focused on a single, fixed reference ion and the energetics of its binding to a series of neutral molecules. The present approach differs somewhat in that we are specifically interested in a single neutral species ($\text{Fe}(\text{CO})_5$) and its affinity for a series of different anions. Equation 3 defines the anion affinity of $\text{Fe}(\text{CO})_5$. Here we presume the negative



ion/ $\text{Fe}(\text{CO})_5$ complexes to be covalent adducts wherein the anion is attached directly to carbon to produce an 18-electron iron tetracarbonyl acyl negative ion. Evidence supporting this view has been presented previously,²⁰ and additional discussion relating to this question is provided in the present work.

An anion affinity for a neutral compound may be obtained by a number of different methods, including direct equilibrium measurements, bracketing techniques, and thermodynamic cycles based on observed ion-molecule reactions. An equilibrium constant for a reaction in which a negative ion is transferred from one neutral compound to another provides a measure of the relative free energy of anion binding by the two molecules. Entropies for anion transfer are usually either small and negligible or estimable from statistical mechanics.^{38a} Therefore, relative anion affinities may be directly determined. Extensive anion affinity ladders may be constructed from measurements for many such equilibria, and an absolute scale is established when an absolute anion binding energy for one constituent of the ladder becomes available—the so-called "anchor". Equilibrium constants for gas-phase anion transfers may be determined by direct assay or from kinetic measurements for forward and reverse reactions.

Bracketing techniques offer a useful alternative when direct equilibration cannot be achieved due to competing side reactions, unfavorable kinetics, or the absence of stable neutral components.^{17,18} The central requirement for all affinity bracketing methods is that the occurrence or non-occurrence of a gas-phase reaction be determined by thermodynamic, as opposed to kinetic, factors. Therefore, in the present case we require reference ions and neutral compounds with established thermochemistry which can be shown independently to rapidly transfer or accept the anion of interest when reaction is exoergic.

Finally, absolute limits on anion-binding energies often may be extracted from the outcome for more complex reactions than simple anion transfer, provided a suitable thermodynamic cycle can be constructed and supporting thermochemical data are available.⁴²

Results

In the following sections we describe the results of our measurements of the binding energies of $\text{Fe}(\text{CO})_5$ to H^- , OH^- , F^- , CH_3O^- , CH_3CO_2^- , and other ions, using the methods discussed above.

Hydride Ion. We recently reported a determination of the $\text{Fe}(\text{CO})_5$ hydride affinity ($\text{HA} = D[(\text{CO})_4\text{FeCO-H}^-]$) along with the corresponding $\Delta H_f^\circ[(\text{CO})_4\text{FeCHO}^-]$ and discussed the relevance of these data to hydride reductions by iron-formyls in solution.²¹ The determination utilized reference anions possessing known hydride-neutral bond energies derived from gas-phase acidities in conjunction with a bracketing approach in which a thermodynamic threshold for bimolecular hydride transfer to $\text{Fe}(\text{CO})_5$ was established. From qualitative and quantitative experiments involving hydride donor anions that spanned a 40 kcal mol^{-1} range in hydride affinity, we established that the H^- binding energy for $\text{Fe}(\text{CO})_5$ lies between that for $\text{CH}_2=\text{C}(\text{CN})\text{CH}_3$ ($\text{HA} = 56.1 \pm 2.5$ kcal mol^{-1}) and $\text{CH}_2=\text{CHCN}$ ($\text{HA} = 57.6 \pm 2.5$ kcal mol^{-1}). We thus assigned a value of 56.1 ± 4 kcal mol^{-1} to

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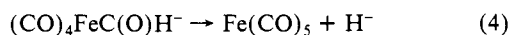
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Table I. Fluoride Affinity Bracket for Fe(CO)₅

neutral (A)	anion (AF ⁻)	fluoride affinity ^a of (A)	(AF ⁻) transfers F ⁻ to Fe(CO) ₅	(CO) ₄ FeC(O)F ⁻ transfers F ⁻ to (A)
SO ₂	SO ₂ F ⁻	43.8	no	yes
PF ₃	PF ₄ ⁻	40.2	yes	yes
CF ₃ CH ₂ OH	CF ₃ CH ₂ OH·F ⁻	39.1	yes	no
H ₂ S	H ₂ S·F ⁻	34.6	yes	no

^aIn units of kcal mol⁻¹, ref 38a.

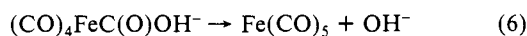
HA(Fe(CO)₅), eq 4. From this bond energy a value for ΔH_f[(CO)₄FeCHO⁻,g] = -194.4 ± 4 kcal mol⁻¹ was calculated.



$$\Delta H = D[(\text{CO})_4\text{FeCO-H}^-] = 56.1 \pm 4 \text{ kcal mol}^{-1}$$

Hydroxide Ion. We also recently established a lower limit for the OH⁻ binding energy of Fe(CO)₅ from the observed occurrence of reaction 5.^{20a} Using measured values of the OH⁻ hydration HO(H₂O)₄⁻ + Fe(CO)₅ → (CO)₄FeC(O)OH⁻ + 4H₂O (5)

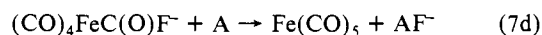
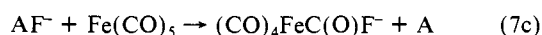
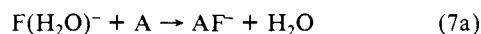
enthalpies and entropies from high-pressure mass spectrometry (HPMS) measurements,⁴⁵ plus a calculated entropy contribution to eq 6 of 32.80 eu,⁴⁶ we estimate that ΔH(6) ≥ 53.1 kcal mol⁻¹. This value is slightly larger than the previously reported limit^{20a} (>50 kcal mol⁻¹) since a more rigorous estimation of ΔS_{trans} was



$$\Delta H = D[(\text{CO})_4\text{FeCO-OH}^-] \geq 53.1 \text{ kcal mol}^{-1}$$

employed.⁴⁶ We also noted in the earlier work that the relatively rapid rate measured for reaction 5 could suggest that the next higher cluster, HO(H₂O)₅⁻, might also react analogously and, therefore, that the OH⁻/Fe(CO)₅ binding energy is likely to be even greater. The structural assignment for the product of eq 5 as the covalent iron-hydroxycarbonyl anion shown, as opposed to an electrostatically bound cluster ion or isomeric metalloformate anion, was based on its inactivity toward binary neutral switching reactions and its H/D exchange behavior, respectively.

Fluoride Ion. Accurate fluoride affinities for numerous Brønsted and Lewis acids have been determined by using ion cyclotron resonance^{38,40} and high-pressure mass spectrometry.³⁹ These measurements provide excellent reference data for determining the fluoride affinity of Fe(CO)₅ by both bracketing and equilibrium methods. We have examined an extensive series of binary fluoride transfer reactions, both from F⁻ donor anions to Fe(CO)₅ and from (CO)₄FeC(O)F⁻ to neutral fluoride acceptors. Fluoride donor anions were produced in the upstream quarter of the flow reactor from reactions between the corresponding neutral compound and F(H₂O)⁻ (*m/z* 37). This latter ion was generated by reaction between CH₃CHF₂ and OH⁻ in the presence of traces of water.⁴⁷ Downstream addition of either Fe(CO)₅ (eq 7b) or a neutral reference compound possessing a known fluoride affinity^{38a} (eq 7a) provided primary reactant anions for the bracketing experiments summarized in Table I. Fluoride transfer to Fe(CO)₅ (eq 7c) is observed for AF⁻ = (F⁻·H₂S), (F⁻·HO-

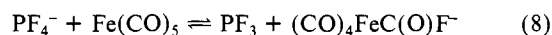


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(46) Estimated entropy is given by ΔS_{trans} + ΔS_{rot}. These values were calculated by standard statistical formulae, except the inertial term in ΔS_{rot} has been neglected (ref 38a). An internal rotational symmetry number of 3 is assumed for the anion/Fe(CO)₅ adducts, i.e., attachment of the negative ion to an axial carbonyl ligand.

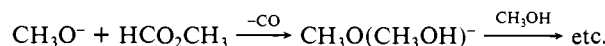
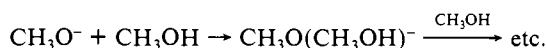
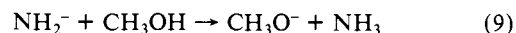
(47) The reaction of HO⁻ with CH₃CHF₂ in our flowing afterglow produces F(H₂O)⁻ as the major product with traces of F⁻ and F(H₂O)₂⁻ also observed. These products probably arise from a β-elimination reaction in the fluorocarbon followed by expulsion of fluoroethylene from the product complex. Subsequent association of F(H₂O)⁻ with traces of water in the system produces F(H₂O)₂⁻. See ref 38a.

CH₂CF₃), and PF₄⁻, while no F⁻ transfer is observed to occur from SO₂F⁻. Moreover, F⁻ transfers from (CO)₄FeCOF⁻ to SO₂ and PF₃ (eq 7d), but not to CF₃CH₂OH nor H₂S. From these results it is established that the fluoride affinity of Fe(CO)₅ lies between that for SO₂ (43.8 kcal mol⁻¹) and CF₃CH₂OH (39.1 kcal mol⁻¹) and is very close to that for PF₃ (40.2 kcal mol⁻¹).^{38a} The occurrence of fluoride transfer in both directions (eq 7c and 7d) with the PF₄⁻/PF₃ system enabled a direct study of the equilibrium reaction 8.



We chose to determine the equilibrium constant, K(8), from measurements of the forward and reverse reaction rates rather than by direct assay since the latter method requires the simultaneous measurement of two neutral flow rates—an experimental capability which we do not possess at present. Both the forward and reverse reactions in eq 8 are clean, second-order processes which produce a single ionic product as shown. Five measurements of each rate coefficient at 300 ± 2 K gave *k_f* = 6.68 ± 0.14 × 10⁻¹⁰ cm³ s⁻¹ and *k_r* = 3.13 ± 0.8 × 10⁻¹¹ cm³ s⁻¹. This leads to a value for K(8) = *k_f*/*k_r* = 21.3 ± 1.0, which corresponds to ΔG(8) = -1.82 ± 0.03 kcal mol⁻¹. To convert this to an enthalpy, the entropy contribution to reaction 8 needs to be estimated. Using the simple statistical mechanics formulations given by McMahon,^{38a} we compute ΔS(8) = 3.83 eu.⁴⁶ Thus, at 25 °C, ΔH(8) = -0.67 kcal mol⁻¹. Combining this with the absolute fluoride affinity measured for PF₃^{38a} yields D[(CO)₄FeCO-F⁻] = 40.9 ± 3 kcal mol⁻¹. The conservative uncertainty interval assigned to this value takes into account the probable uncertainty in the absolute fluoride affinity scale.^{38a} From this bond energy, a value for ΔH_f[(CO)₄FeCOF⁻,g] = -273.4 ± 3 kcal mol⁻¹ may be calculated.

Alkoxide Ions. As part of a larger study of solvated ion reactions with metal carbonyls,⁴⁸ we have examined the reactions of CH₃O(CH₂OH)_{*n*}⁻, *n* = 1-3, with Fe(CO)₅. Recent HPMS measurements of the CH₃O(CH₂OH)⁻ binding energy⁴⁹ along with the observed reactivity of this and higher clusters with Fe(CO)₅ in our flow reactor permit an estimate of a lower limit to D[(CO)₄FeCO-OCH₃]. Methoxide/methanol cluster ions are produced in the upstream end of the flow tube by coaddition of a relatively high concentration of CH₃OH (ca. 0.05 STP cm³ s⁻¹) along with traces of methyl formate, HCO₂CH₃, to an initial reactant ion stream of NH₂⁻. Proton transfer produces CH₃O⁻, which subsequently undergoes rapid termolecular association with excess methanol to yield CH₃O(CH₂OH)_{*n*}⁻ cluster ions up to *n* = 3.⁵⁰ The methyl formate serves to enhance the rate of cluster ion formation via the well-known Riveros reaction (eq 9).⁵¹



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(49) Caldwell, G.; Kebarle, P., private communication.

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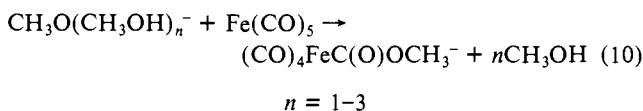
(51) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057.

Table II. Estimation of Solvation Enthalpies and Entropies for $\text{CH}_3\text{O}(\text{CH}_3\text{OH})_n^-$ Cluster Ions

cluster	$-\Delta H_{n-1,n}$ (kcal/mol) for $n = 1-3$			$-\Delta S_{n-1,n}$ (eu) for $n = 1-3$		
	1	2	3	1	2	3
$\text{HO}(\text{H}_2\text{O})_n^-$ ^a	25.0	17.9	15.1	20.8	21.2	24.8
$\text{F}(\text{H}_2\text{O})_n^-$ ^b	23.3	16.6	13.7	17.4	18.7	20.4
$\text{CH}_3\text{O}(\text{CH}_3\text{OH})_n^-$ ^c	21.8 ^d	(15.6)	(13.2)	21.8 ^d	(22.2)	(26.0)

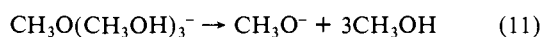
^aReference 45. ^bReference 39c. ^cEstimated values in parentheses, see text. ^dExperimental values, ref 49.

Each of the cluster ions formed in this way rapidly reacted with $\text{Fe}(\text{CO})_5$ to yield the iron-methoxycarbonyl ion as the sole product (eq 10). Bimolecular rate coefficients were determined for each

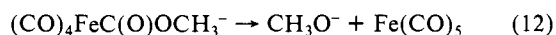


reactant ion and are 1.7×10^{-9} , 1.3×10^{-9} , and 1.1×10^{-9} $\text{cm}^3 \text{s}^{-1}$ for $n = 1, 2$, and 3 , respectively. Comparison of these rates with the corresponding Langevin collision rates⁵² indicates that CH_3O^- is transferred from the solvates to $\text{Fe}(\text{CO})_5$ on essentially every encounter.

A lower limit to the methoxide ion affinity of $\text{Fe}(\text{CO})_5$ ($D[(\text{CO})_4\text{FeCO}-\text{OCH}_3^-]$) may be inferred from the occurrence of CH_3O^- transfer from the $n = 3$ cluster ion. While the required solvation enthalpies and entropies for $\text{CH}_3\text{O}(\text{CH}_3\text{OH})_3^-$ have not been measured experimentally, they may be estimated with reasonable accuracy from other data. Kebarle and co-workers have recently determined $\Delta H_{0,1}$ and $\Delta S_{0,1}$ for formation of $\text{CH}_3\text{O}(\text{CH}_3\text{OH})^-$ to be -21.8 ± 1.0 kcal mol⁻¹ and -21.8 ± 3.0 eu, respectively.⁴⁹ Furthermore, the first three hydration enthalpies and entropies for OH^- ⁴⁵ and F^- ^{39c} are also known from HPMS measurements. If we assume that the successive decreases in $\Delta H_{n-1,n}$ and increases in $\Delta S_{n-1,n}$ for $\text{HO}(\text{H}_2\text{O})_n^-$ and $\text{F}(\text{H}_2\text{O})_n^-$, $n = 1-3$, cluster ions will be followed in a proportionate manner for $\text{CH}_3\text{O}(\text{CH}_3\text{OH})_n^-$, $n = 1-3$, clusters, then the desired thermochemical data may be estimated. Table II summarizes these data and the resulting estimated values for the $\text{CH}_3\text{O}(\text{CH}_3\text{OH})_n^-$ cluster ions. The sum of the solvation enthalpies and entropies (eq 11) and an estimated entropy contribution to eq 12 of 31.6 eu⁴⁶ may be combined to evaluate a lower limit to $D[(\text{CO})_4\text{FeCO}-\text{OCH}_3^-]$



$$\Delta H = 50.6 \text{ kcal mol}^{-1}; \Delta S = 70.0 \text{ eu}$$

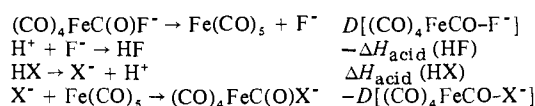


$$\Delta H = D[(\text{CO})_4\text{FeCO}-\text{OCH}_3^-] \geq 39.1; \Delta S = 31.6 \text{ eu}$$

$D[(\text{CO})_4\text{FeCO}-\text{OCH}_3^-] \geq 50.6 \text{ kcal mol}^{-1} - (300 \text{ K})(70.0 \text{ eu} - 31.6 \text{ eu})/1000 = 39.1 \text{ kcal mol}^{-1}$. From this, an upper limit for $\Delta H_f[(\text{CO})_4\text{FeCO}_2\text{CH}_3^-]$ $\leq -246.8 \text{ kcal mol}^{-1}$ may be derived. As with the $\text{HO}(\text{H}_2\text{O})_n^-$ clusters, the observed rapid reaction of the $\text{CH}_3\text{O}(\text{CH}_3\text{OH})_3^-$ ion suggests that the next higher cluster may react as well, and that the methoxide affinity of $\text{Fe}(\text{CO})_5$ is actually somewhat greater than the present estimate.⁵³

Bounds on additional alkoxide, thioalkoxide, and related ion affinities of $\text{Fe}(\text{CO})_5$ can be established from several other ion-molecule reactions that we have observed. For example, the iron-acyl fluoride ion, generated by the procedures described in the previous section, undergoes binary exchange reactions in the

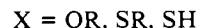
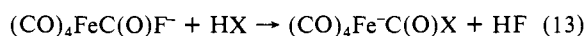
Scheme I

**Table III.** Anion Affinities of $\text{Fe}(\text{CO})_5$ Derived from Equation 14

Neutral (HX)	ΔH_{acid}^- (HX) ^{a,b}	does anion exchange occur	$D[(\text{CO})_4\text{FeCO}-\text{X}^-]$ inference ^a
H_2S	353.5	yes	≥ 23.1
MeSH	359.0	yes	≥ 28.6
$\text{CF}_3\text{CH}_2\text{OH}$	364.4	yes	≥ 34.0
$\text{MeOCH}_2\text{CH}_2\text{OH}$	372.5	no	≤ 42.1
<i>t</i> -BuOH	373.3	no	≤ 42.9
<i>n</i> -BuOH	374.0	no	≤ 43.6
<i>i</i> -PrOH	374.1	no	≤ 43.7
<i>n</i> -PrOH	374.7	no	≤ 44.3
EtOH	376.1	no	≤ 45.7
MeOH	381.4	no	≤ 51.0
H_2O	390.7	no	≤ 60.3

^aIn units of kcal mol⁻¹. ^bReference 18.

presence of certain alcohols, thiols, and H_2S (eq 13). Since the fluoride affinity for $\text{Fe}(\text{CO})_5$ and $\Delta H_f[(\text{CO})_4\text{FeC}(\text{O})\text{F}^-]$ have



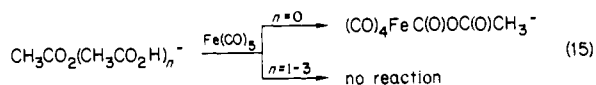
been established previously, the occurrence or non-occurrence of eq 13 can be used to derive limits on the X^- binding energies of the acyl anion products. Scheme I illustrates the pertinent thermochemical equations, and eq 14 gives the resulting expression for $D[(\text{CO})_4\text{FeCO}-\text{X}^-]$, assuming $\Delta S(13) \approx 0$. A lower limit for this quantity is established when reaction 13 is observed, and an upper limit is obtained when it is not—provided that the outcome is thermodynamically and not kinetically determined.

$$D[(\text{CO})_4\text{FeCO}-\text{X}^-] \geq D[(\text{CO})_4\text{FeCO}-\text{F}^-] + \Delta H_{\text{acid}}(\text{HX}) - \Delta H_{\text{acid}}(\text{HF}) \quad (14)$$

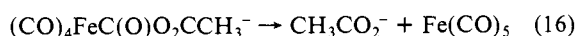
$$D[(\text{CO})_4\text{FeCO}-\text{X}^-] \geq \Delta H_{\text{acid}}(\text{HX}) - 330.4 \text{ kcal mol}^{-1}$$

The results for a series of these reactions, and the corresponding thermochemical inferences are summarized in Table III.

Acetate Ion. Using the same approach as that described for OH^- and CH_3O^- , we can estimate the acetate ion affinity of $\text{Fe}(\text{CO})_5$ from the observed reactivity of $\text{CH}_3\text{CO}_2(\text{CH}_3\text{CO}_2\text{H})_n^-$ clusters. Cluster ions of this type are readily fashioned in the flow reactor by introducing a high concentration of $\text{CH}_3\text{CO}_2\text{H}$ into a NH_3^- reactant ion stream. Rapid proton abstraction followed by sequential association of the resulting acetate ion with excess acid produces abundant cluster ions, $\text{CH}_3\text{CO}_2(\text{CH}_3\text{CO}_2\text{H})_n^-$, up to $n = 3$. Downstream addition of $\text{Fe}(\text{CO})_5$ results in moderately fast decay of the unsolvated CH_3CO_2^- ion signal, m/z 59 ($k = 1.35 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, $k_{\text{obsd}}/k_1 = 0.07$),⁵² while the cluster ions appear to be unreactive ($k \leq 10^{-13} \text{ cm}^3 \text{ s}^{-1}$), eq 15. We formulate the product of the former reaction as a covalently-bonded (metalloanhydride) anion in analogy with the other iron tetracarbonyl acyl ions described in the previous sections.²³



Kebarle and co-workers have measured the $\text{CH}_3\text{CO}_2(\text{CH}_3\text{CO}_2\text{H})^-$ solvation enthalpy and entropy to be $\Delta H_{0,1} = -27.0$ kcal mol⁻¹ and $\Delta S_{0,1} = -26.2$ eu, respectively.⁴⁹ Combining these data with an estimated entropy for eq 16 of 34.6 eu⁴⁶ yields the following expression: $D[(\text{CO})_4\text{FeCO}-\text{O}_2\text{CCH}_3^-] \leq 27.0 \text{ kcal mol}^{-1}$



$-(300 \text{ K})(26.2 \text{ eu} - 34.6 \text{ eu})/1000 = 29.5 \text{ kcal mol}^{-1}$. Thus, an upper limit of 29.5 kcal mol⁻¹ to the acetate ion affinity of $\text{Fe}(\text{CO})_5$

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(53) For a pertinent discussion of the interplay between dynamic and thermochemical factors in nucleophilic substitution reactions involving these cluster ions, see ref 50 and: Henchman, M.; Paulson, J. F.; Hierl, P. M. *J. Am. Chem. Soc.* **1983**, 105, 5510.

Table IV. Comparison of Anion Affinities (kcal mol⁻¹)

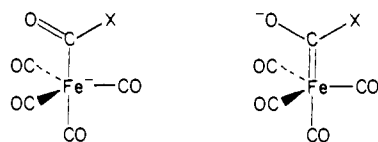
X ⁻	D[(CO) ₄ FeCO-X ⁻]	PA(X ⁻) ^a	D[CH ₃ CO ⁻ -X ⁻] ^b
H ⁻	56.1 ± 4	400.4	231.3
HO ⁻	53.1 ≤ x ≤ 60.3	390.7	227.5
MeO ⁻	39.1 ≤ x ≤ 51.0	381.4	222.5
EtO ⁻	≤45.7	376.1	217.5
<i>n</i> -PrO ⁻	≤44.3	374.7	216.6
<i>n</i> -BuO ⁻	≤43.6	374.0	215.7
<i>t</i> -BuO ⁻	≤42.9	373.3	215.4
MeOCH ₂ CH ₂ O ⁻	≤42.1	372.5	214.2
F ⁻	40.9 ± 3	371.3	203.5
CF ₃ CH ₂ O ⁻	≥34.0	364.4	200.9
MeS ⁻	≥28.6	359.0	
HS ⁻	≥23.1	353.5	181.7
CH ₃ CO ₂ ⁻	≤29.5	348.5	172.1

^aReference 18. ^bDetermined from eq 18.

may be assigned from the reactivity depicted in eq 15. From this, a lower limit on $\Delta H_f[(CO)_4FeC(O)O_2CCH_3^-] \geq -323.0$ kcal mol⁻¹ is calculated.

Discussion

Table IV presents a complete summary of the derived limits and absolute values of Fe(CO)₅ binding energies for 13 negative ions. The anion affinities span a nearly 40 kcal mol⁻¹ range of magnitudes and encompass a diverse set of atomic, diatomic, and polyatomic ion types. In keeping with our earlier studies of the (CO)₄FeCO₂H⁻ ion,²⁰ we assign covalently bonded iron tetracarbonyl acyl structures to the negative ion products described in the previous sections. The binding energies listed in Table IV are generally quite large (up to ~60 kcal mol⁻¹)—larger than what can be reasonably expected for simple electrostatic binding. For example, although the large polarizability of Fe(CO)₅ (28 Å³)⁵⁴ could account for substantial ion-induced dipole attractive forces, such forces do not become large enough to match the experimental binding energies until the negative ion is within 3–4 Å of the polarization center (ignoring repulsion).⁵⁵ Moreover, Dedieu has computed an ab initio SCF potential energy surface for the reaction between H⁻ and Fe(CO)₅, which shows that direct attachment to an axial CO occurs *without activation*.⁵⁶ Therefore, considering the large electrostatic attraction forces initially operating along with the absence of a barrier preventing covalent attachment to CO, we see no reason to believe that the Fe(CO)₅/negative ion complexes would not spontaneously collapse to the proposed iron–acyls. Moreover, direct attachment of a negative ion to iron seems highly unlikely since this would produce unprecedented, and presumably unstable, 20-electron complexes. Metal–formyls, hydroxycarbonyls, alkoxycarbonyls, and metal–acylfluorides which are analogous to many of the acyl ions postulated in this study are well-known species in solution.^{5,23–26} Nucleophilic addition to Fe(CO)₅ under nondissociative conditions is believed to generally favor axial CO attack.⁵⁷ The resulting negative charge can be viewed as delocalized over the entire complex, with particularly high electron density on the acyl oxygen atom by virtue of 3d_π(Fe) – 2p_π(CO) conjugation.^{26a} The



observation of F⁻ transfer from (CO)₄FeC(O)F⁻ to both SO₂ and PF₃ deserves special comment. In our previous work, we noted that hydride transfer from (CO)₄FeCHO⁻ to neutral acceptor molecules was not observed; even in cases where transfer was

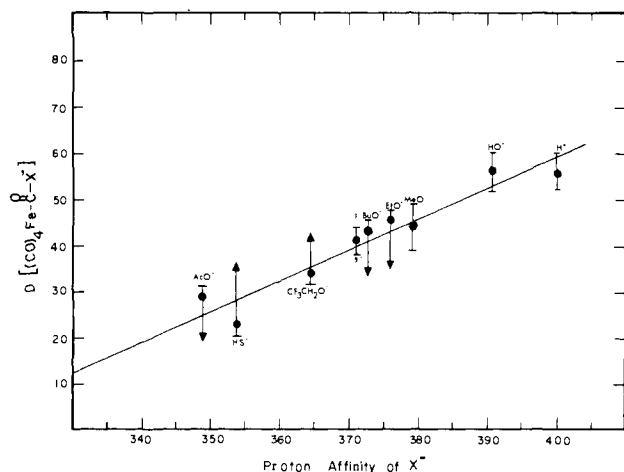


Figure 1. Plot of proton affinity vs. measured Fe(CO)₅ binding energies for negative ions (kcal mol⁻¹).

estimated to be thermodynamically favorable.²¹ We attributed this to a kinetic barrier to H⁻ transfer arising from unfavorable charge localization requirements in the iron–formyl complex. That is, the formyl C–H⁻ bond is a relatively strong one (56.1 kcal mol⁻¹), and the low electronegativity of hydrogen may inhibit appreciable hydride-character buildup in the CHO moiety as would ultimately be required for H⁻ transfer to another molecule. To avoid violating microscopic reversibility, we must assume that the kinetic barrier impeding H⁻ transfer *from* (CO)₄FeCHO⁻ to neutral acceptors must not correspond to the same transition state as that for H⁻ transfer *to* Fe(CO)₅, i.e., a more complex reaction surface than a simple single or double well potential is implicit in our view. In contrast to H⁻, fluoride ion may be considered to be a better “leaving group” for transfer from (CO)₄FeC(O)F⁻, since it is both more electronegative and a weaker base than H⁻, and possesses lone-pair electrons which may enable Lewis acid–base interactions with the acceptor molecule. Thus, the barrier to F⁻ transfer from this acyl ion is lessened.

The Fe(CO)₅ anion affinities in Table IV may be directly compared with several other series of negative ion affinities involving different reference acids. Cross-comparisons of experimental and theoretical affinity data for anions, cations, metal ions, and other ion–molecule complexes have yielded valuable information about chemical bonding, charge distributions, and ion–neutral interactions.^{38e,58–62} The simplest reference acid for which complete data are available to compare with our D[(CO)₄FeCO-X⁻] values is the proton. The anion affinity of a proton is, of course, simply the gas-phase acidity of the corresponding acid HX, or PA(X⁻).¹⁸ The 13 anions in Table IV are listed in order of decreasing basicity, and the corresponding proton affinities are given in column two. A plot of D[(CO)₄FeCO-X⁻] vs. PA(X⁻) is shown in Figure 1, where the upper or lower limits on certain of the Fe(CO)₅ anion affinities are represented by open-ended intervals. A good linear correlation is evident in which the bounded and half-bounded data define the linear relationship given by eq 17. Thus, within the accuracy of this correlation, the

$$D[(CO)_4FeCO-X^-] = 0.66PA(X^-) - 206 \text{ kcal mol}^{-1} \quad (17)$$

binding energy of a negative ion to Fe(CO)₅ can be predicted from its thermodynamic basicity. That is, the *relative* energies of anion attachment to either a proton or an iron-bound carbonyl ligand are proportional.

(58) Brown, H. C. “Boranes in Organic Chemistry”; Cornell University Press: Ithaca, NY, 1972; Part 2.

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Table V. Chloride Affinity Bracket for Fe(CO)₅

neutral (A)	anion (ACl ⁻)	chloride affinity ^a of (A)	(ACl ⁻) transfers Cl ⁻ to Fe(CO) ₅	(CO) ₄ FeCOCl ⁻ transfers Cl ⁻ to (A)
CH ₃ OH	CH ₃ OH·Cl ⁻	16.8	no	
H ₂ O	H ₂ O·Cl ⁻	14.4	no	yes
CH ₃ COCH ₃	CH ₃ COCH ₃ ·Cl ⁻	14.1	no	yes
C ₆ H ₅ Cl	C ₆ H ₅ Cl·Cl ⁻	13.6	yes	no
C ₆ H ₆	C ₆ H ₆ ·Cl ⁻	9.9	yes	no

^a In units of kcal/mol⁻¹, ref 38c.

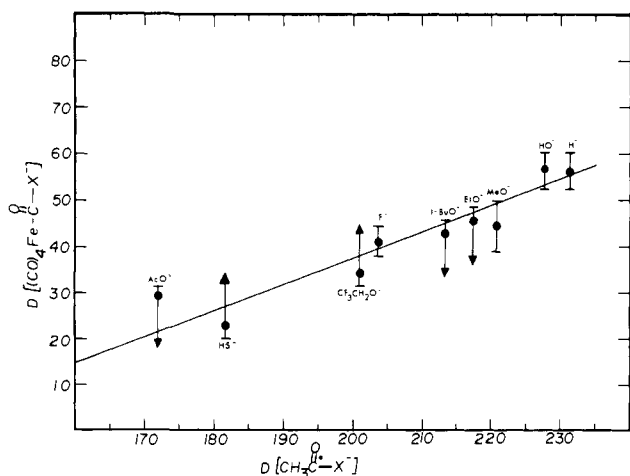
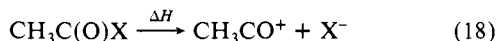


Figure 2. Plot of heterolytic bond energies for acetyl compounds vs. measured binding energies of the corresponding negative ions to Fe(CO)₅ (kcal mol⁻¹).

A similar correlation is evident between Fe(CO)₅ anion affinities and heterolytic bond energies for the corresponding acetyl derivatives, i.e., the anion affinities of the acetyl cation (eq 18). Here, the model more closely approximates the Fe(CO)₅ system in that



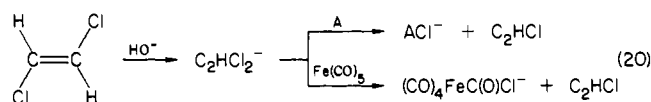
$$\Delta H = D[\text{CH}_3\text{CO}^+ - \text{X}^-] = \Delta H_f(\text{CH}_3\text{CO}^+) + \Delta H_f(\text{X}^-) - \Delta H_f(\text{CH}_3\text{C}(\text{O})\text{X})$$

negative ion bonding to a linear CO results in a trigonal acyl product. The required data are readily obtained from known heats of formation for anions,¹⁸ acetyl cation (CH₃CO⁺),⁶³ and the neutral acetyls.⁶⁴ Heterolytic bond energies defined in this way are also given in Table IV, and a plot of these data vs. Fe(CO)₅ anion affinities is presented in Figure 2. Again, a reasonably good linear correlation can be seen, at least within the uncertainties inherent in our D[(CO)₄FeCO-X⁻] data. The equation of the best straight line fitting these data is given in eq 19.

$$D[(\text{CO})_4\text{FeCO-X}^-] = 0.59D[\text{CH}_3\text{CO}^+ - \text{X}^-] - 80.3 \text{ kcal mol}^{-1} \quad (19)$$

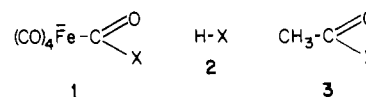
In order to further test the scope and validity of these apparent correlations, we measured the chloride ion affinity of Fe(CO)₅ ex post facto, for comparison with the values predicted from eq 17 and 19. Using PA(Cl⁻) = 333.4 kcal mol⁻¹¹⁸ and eq 17, we calculate D[(CO)₄FeCO-Cl⁻] = 14.0 kcal mol⁻¹, while using D[CH₃CO⁺-Cl⁻] = 160.6 kcal mol⁻¹⁶³ and eq 19 we arrive at a value of 14.5 kcal mol⁻¹. For our experimental determination, an adequate number of chloride affinities for Lewis and Brønsted acids were available from a recent study by McMahon and co-workers to provide a good reference data base.^{38c} Chloride donor anions were produced in the upstream end of the flow reactor from

reactions between the (M-H)⁻ ion of *trans*-1,2-dichloroethylene⁶⁵ and the reference neutral of interest (eq 20). Similarly, the iron-acyl chloride ion could be generated by Cl⁻ transfer from



C₂HCl₂⁻ to Fe(CO)₅. Downstream addition of either Fe(CO)₅ to a reference chloride donor ion or addition of a reference neutral to (CO)₄FeCOCl⁻ allowed a determination of the Cl⁻ affinity ordering from the observed direction of chloride transfer. The results are summarized in Table V. Chloride transfer to Fe(CO)₅ can be observed from (C₆H₆·Cl⁻) and (C₆H₅Cl·Cl⁻), but not from either (CH₃COCH₃·Cl⁻) or (H₂O·Cl⁻). Furthermore, (CO)₄FeC(O)Cl⁻ transfers Cl⁻ to H₂O and CH₃COCH₃, but not to either C₆H₅Cl or C₆H₆. From this behavior it is established that the chloride affinity of Fe(CO)₅ lies between that of acetone (14.1 kcal mol⁻¹) and chlorobenzene (13.6 kcal mol⁻¹).^{38c} We therefore assign a value of 13.9 ± 3 kcal mol⁻¹ which is in excellent agreement with the chloride affinity predicted from eq 17 and 19. Thus, either the proton or acetyl cation affinity of a negative ion may serve as a good predictor of its binding energy with Fe(CO)₅.

The apparent success of these correlations is somewhat surprising in that bonding in metal-acyl anions, **1**, Brønsted acids, **2**, and neutral acetyls, **3**, differs significantly with respect to charge distribution resonance interactions and, possibly, steric effects



within the acid-base complexes. For example, intramolecular hydrogen bonding within ion **1** is conceivable when X = OH or SH which cannot take place in **2**. Similarly, π-type resonance interactions involving lone-pair substituents attached to the carbonyl may be operative in **1** and **3**, but not in **2**. However, four different π-donor atom types (Cl, O, S, F) all fit on the same correlation line as hydrogen. Evidently such differences among the reference acids are not large enough to appear in the thermodynamic trends illustrated by Figures 1 and 2. That is, more refined measurements for a broader class of anions may be necessary to expose subtle differences among reference acids when large binding energies (170–400 kcal mol⁻¹) are compared to smaller ones (10–60 kcal mol⁻¹).

Equations 17 and 19 can be used to estimate the Fe(CO)₅ binding energy to virtually any negative ion for which the proton affinity or acetyl cation affinity is known. Heats of formation for the corresponding iron tetracarbonyl acyl negative ions may then be calculated from eq 21. Representative thermochemical data calculated for a variety of gas-phase metal acyl ions are

$$\Delta H_f[(\text{CO})_4\text{FeC}(\text{O})\text{X}^-] = \Delta H_f[\text{X}^-] + \Delta H_f[\text{Fe}(\text{CO})_5] - D[(\text{CO})_4\text{FeCO-X}^-] \quad (21)$$

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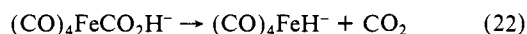
(65) The C₂HCl₂⁻ ion derived from *trans*-1,2-dichloroethylene has a measured proton affinity of 364 ± 4 kcal mol⁻¹ and is believed to be a vinyl carbanion, as opposed to a chloride/acetylene cluster. From observed Cl⁻ transfers from this ion, an upper limit to the chloride affinity of chloroacetylene of 9 kcal mol⁻¹ is established. This value is consistent with the proton affinity estimate. Lane, K. R.; Squires, R. R., to be published.

Table VI. Calculated Heats of Formation of Iron Tetracarbonyl Acyl Anions (kcal mol⁻¹)

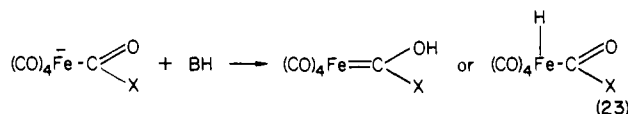
anion (X ⁻)	PA(X ⁻) ^a	D[CH ₃ CO ⁺ -X ⁻] ^b	D[(CO) ₄ FeCO-X ⁻] ^c	ΔH _f [(CO) ₄ FeCO-X ⁻ ,g] ^d
CH ₃ ⁻	416.6	241.9	62.4	-202.4
NH ₂ ⁻	403.6	240.9	61.8	-207.9
H ⁻	400.4	231.3	56.2	-194.5
C ₆ H ₅ ⁻	398.8	230.6	55.8	-175.9
NMe ₂ ⁻	396.1		55.4 ^e	-202.4
HO ⁻	390.7	227.5	53.9	-259.7
C ₆ H ₅ CH ₂ ⁻	379.4	206.3	41.4	-188.7
MeO ⁻	381.4	222.5	51.0	-256.5
EtO ⁻	376.1	217.5	48.0	-266.6
CF ₃ ⁻	375.6		41.8 ^e	-371.9
<i>n</i> -PrO ⁻	374.7	216.6	47.5	-272.4
<i>n</i> -BuO ⁻	374.0	215.7	47.0	-277.4
<i>t</i> -BuO ⁻	373.3	215.4	46.8	-286.9
MeOCH ₂ CH ₂ O ⁻	372.5	214.2	46.1	-299.7
F ⁻	371.3	203.5	39.8	-272.3
CH ₃ C(O)CH ₂ ⁻ (C)	368.8	199.0	37.4 ^e	-259.2
CF ₃ CH ₂ O ⁻	364.4	200.9	38.2	-424.7
MeS ⁻	354.9		28.2 ^e	-213.4
CH ₃ C(O ⁻)CH ₂ ⁻ (O)	354.9		28.2 ^e	-250.0
HS ⁻	353.5	181.7	26.9	-217.0
CN ⁻	353.1		27.0 ^e	-180.3
CH ₃ CO ₂ ⁻	348.5	172.1	21.2	-214.7
N ₃ ⁻	344.0 ^f		21.0 ^e	-146.0

^aReference 18. ^bEquation 18. ^cEquation 19, use of eq 17 gives nearly identical values. Estimated uncertainty ±5 kcal/mol. ^dEquation 21, ΔH_f(X⁻,g) taken from ref 18; ΔH_f(Fe(CO)₅,g) = -173.0 ± 1.5 kcal/mol, ref 64. ^eEquation 17. ^fReference 69.

presented in Table VI. These bond energies and heats of formation may be used in a number of different ways as mechanistic tools for investigating nucleophilic addition reactions involving Fe(CO)₅ in the gas phase and in solution. For example, using the upper limit on ΔH_f[(CO)₄FeCO₂H⁻,g] established in our previous work,^{20a} we were able to bound the decarboxylation energy of this ion (eq 22) at ≥-17 kcal mol⁻¹. This is an important reaction since it had long been believed to occur spontaneously



in the course of water-gas shift catalysis by Fe(CO)₅ in alkaline solution.^{27,28} However, recent studies by Ford and co-workers suggest that it is a bimolecular process requiring a proton-bearing Lewis base.⁶⁶ Using the new data for (CO)₄FeCO₂H⁻ from Table VI, along with a value for ΔH_f[(CO)₄FeH⁻,g] = -178.3 ± 6 kcal mol⁻¹ from the gas-phase acidity of (CO)₄FeH₂,^{19b} we calculate a final value for ΔH(22) = -12.7 kcal mol⁻¹. As another illustration of the utility of these data, the heats of formation for iron-acyl anions may be combined with proton affinity measurements to derive estimates of the heats of formation for a variety of known or postulated homogeneous catalysis intermediates such as iron hydroxycarbene^{5,67} and hydridoacyls^{5,8,31,68} (eq 23). Measurements of this type are currently in progress and will be



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reported in a separate paper. Finally, iron tetracarbonyl acyl anions are produced as the initial intermediates in gas-phase nucleophilic addition reactions of negative ions with Fe(CO)₅. Many of these reactions produce products by decarbonylation of the initially "hot" iron-acyl adducts, and the data derived in the present study have been invaluable for rationalizing the extent of CO loss observed in each particular case.²²

Conclusion

Measurements of the Fe(CO)₅ binding energies for a series of gaseous negative ions have been carried out by using a variety of kinetic and thermodynamic methods. Binary anion transfer reactions between Fe(CO)₅ and several different types of donor species are observed from which relative anion binding energies may be deduced. Iron pentacarbonyl undergoes rapid reactions with many solvated anion clusters by complete solvent displacement to produce Fe(CO)₅-anion adducts. Evidence is presented which supports a structural assignment for the negative ion-Fe-(CO)₅ adducts as iron tetracarbonyl acyl complexes in which covalent attachment of the anionic nucleophile to a carbonyl ligand has occurred. The measured anion binding energies, D-[(CO)₄FeCO-X⁻], are found to vary over a 40 kcal mol⁻¹ range and to correlate with both the proton affinities, PA(X⁻), and acetyl cation affinities, D[CH₃CO⁺-X⁻], of the negative ions. These correlations may be used in conjunction with established anion thermochemistry to derive estimates of bond energies and heats of formation for a wide variety of iron tetracarbonyl acyl anion complexes.

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