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Gas-Phase Reactions of $Cr(CO)_5^-$, $Fe(CO)_4^-$, and $Ni(CO)_3^-$ with Organic Electrophiles

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Abstract: Rate constants and product distributions for reactions of the title anions with 15 organic electrophiles as measured by Fourier transform ion cyclotron resonance techniques are reported. The electrophiles are all aromatic or olefinic compounds with electronegative substituents. The reaction efficiencies defined as the overall rate constant divided by the collision rate (k/k_c) vary from unity to unmeasurable (upper limit 10^{-3} or less). For each anion reactivity drops rapidly as the electron affinity (EA) of the electrophile drops below some critical range values. The critical range (eV) is 0.62–0.91, 1.01–1.29, and 1.29–1.44 for $Ni(CO)_3^-$, $Cr(CO)_5^-$, and $Fe(CO)_4^-$, respectively. Eight cases were examined where the EA of the electrophile was below the critical range, and no reactivity was observed for any of those cases. Twenty-four cases were examined where the EA of the electrophile is above the critical range, and in all of those cases reaction was efficient $(k/k_c > 0.10)$. Reactivity was observed for the four cases where the EA of the electrophile was in the critical range, but the efficiency was lower $(k/k_c < 0.05)$. In most cases where any reaction was observed displacement of one or more CO ligands was the dominant process. Exothermic charge transfer competes with ligand substitution in the $Ni(CO)_3^-$ reactions, but only with tetracyanoethylene is charge transfer a significant product for $Cr(CO)_5^-$ and $Fe(CO)_4^-$. These results are interpreted in terms of a mechanism for ligand substitution involving incipient charge transfer within a collision complex to produce a 16-electron metal center which then undergoes substitution. The ligand substitution results are compared to previous results on the reactions of the title ions both in the gas phase and in solution. Products of subsequent reactions of the initial products are described. It is suggested that oxidative addition to the metal of carbon–halogen and in one case carbon–carbon bonds (i.e., the decarbonylation of benzophenone) plays a role in this chemistry. One sequence of reactions is described that appears to involve formation of a carbon–carbon bond (i.e., the coupling of two 4-nitrophenyl groups in reactions of 1-bromo-4-nitrobenzene).

Introduction

Because of their significance in a variety of interesting and important processes,[1,2] the substitutional lability of 17-electron metal complexes has been the subject of a number of studies.[1-9]

Ligand substitution at a 17-electron metal center by an associative mechanism involves a 19-electron transition state which might be expected to be energetically unfavorable. Nevertheless, there is substantial evidence that many 17-electron metal complexes have a high degree of substitutional lability. It has been found that 17-electron radicals can react 10^6–10^{10} times faster than analogous 18-electron complexes.[3]

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In the case of the extensively studied[1,4,5] nucleophilic substitution reactions of 17-electron neutral and cationic complexes, substitution proceeds through a 19-electron transition states formed in associative nucleophilic attack of the ligand at the metal center.[6,7] Delocalizing electron density onto a ligand and ring slippage of polyhapto ligands are among the mechanisms by which the hyperelectronic transition state can be avoided.[7] If such a mechanism for delocalizing electrons from the metal onto resident ligands is inaccessible, substitution can be slow.[8] Consistent with the necessity of forming an associative complex, substitutional lability in the neutral and cationic systems tends to increase with the nucleophilicity of the attacking ligand.[9] A dramatic example is the reaction of $Mn(CO)_5$ with triphenylphosphine which proceeds with a rate constant of 1.7×10^7 M^{-1} s^{-1} corresponding to ca. 15% of the diffusion-controlled rate.[6]

There have been fewer reports of ligand substitution reactions of 17-electron radical anions. Krusic and San Filippo used electron spin resonance (ESR) methods to observe substitution of CO in $Fe(CO)_4^-$ by maleic anhydride and other activated olefins.[10] The maleic anhydride reaction was also observed in the gas phase.[10,11]

Other gas-phase studies of ligand substitution in 17-electron radical anions include an early ion cyclotron resonance (ICR) study by Corderman and Beauchamp.[12] They found that $CpCo(CO)^-$ reacts with NO and PF_3 by ligand substitution. McDonald, Schell, and McGhee used flowing afterglow techniques to observe reactions of $Fe(CO)_4^-$ with CF_3X (X = I, Br) and CCl_3Y (Y = Cl, Br) where the dominant product is halogen atom transfer.[13] McDonald and Schell report observing ligand substitution reactions of $Fe(CO)_4^-$, $Cr(CO)_5^-$, and $Mn(CO)_4H^-$ with PF_3, NO, SO_2, $(CF_3)CO$, and tetracyanoethylene (TCNE).[14] They also report that a number of 17-electron anionic complexes with ligands such as NO, C_3H_5, and C_5H_5 that can change their hapticities undergo ligand substitution.[15] Jones, McDonald, Schell, and Ali report halogen atom transfer reactions of haloalkanes with a number of 17-electron transition-metal anions including $Ni(CO)_3^-$ and $Cr(CO)_5^-$.[16]

We report here the results of a study of the gas-phase reactions of the 17-electron radical anions $Cr(CO)_5^-$, $Fe(CO)_4^-$, and $Ni(CO)_3^-$ with a series of organic electrophiles including a number of substituted benzenes and quinones, maleic anhydride, and tetracyanoethylene. This study takes advantage of the ICR technique which makes it possible to examine reactions of ions with neutrals of low volatility under single collision conditions.

The present study increases very substantially the number of systems in which $Fe(CO)_4^-$ and $Cr(CO)_5^-$ have been observed to react efficiently. A preliminary report on the $Cr(CO)_5^-$ results has previously appeared.[17] It appears that ligand substitution reactions of $Ni(CO)_3^-$ have not been previously reported, and we find that it reacts extensively with the organic electrophiles examined. Charge transfer competes with ligand substitution for most of the ligands that react with $Ni(CO)_3^-$. The $Ni(CO)_3^-$ chemistry also includes examples of reactions in which cleavage and formation of C–C bonds occurs and examples of diastereomerically specific reactions.

Experimental Section

The experiments were done using an FTMS-2000 ion cyclotron resonance spectrometer (Extrel FTMS, Madison, WI).[18,19] The metal

Figure 1. The ion cyclotron resonance signals (arbitrary units) of $Cr(CO)_5^-$ (□) and $Cr(CO)_4(maleic\ anhydride)^-$ (×) as a function of trapping time after an initial 4-eV, 5-ms electron beam pulse. The solid lines are a fit of the data to the kinetic model implicit in eqs 1 and 2.

carbonyls and three of the organic compounds (maleic anhydride, 1,4-benzoquinone, and nitrobenzene) were introduced into the vacuum chamber through a batch inlet system. The remaining organic compounds were introduced into the chamber using a solid sample probe. The pressure in the vacuum chamber was held constant by maintaining a constant pressure in the batch inlet reservoir or by holding the probe temperature constant. Ionization resulted from a nominal 4-eV electron beam which was pulsed on for 5 ms to initiate a typical experiment. The electron beam is parallel to a 3-T magnetic field and passes along the central axis of a 2-in. cubic cell. Ions are confined to the cell by the magnetic field and a -2-V trapping potential applied to two cell plates perpendicular to the magnetic field. After a variable delay a mass spectrum is obtained by exciting the cyclotron motion of the ions and detecting the resulting signal. The excitation voltage is applied between two opposing cell plates parallel to the magnetic field. The signal is detected by the remaining pair of opposing cell plates. At a typical metal carbonyl pressure of 1×10^{-7} Torr the total ion signal increased for about 0.1 s as a result of electron attachment of secondary electrons caught in the trap during the electron beam pulse. The total ion signal then remained constant at longer times, indicating efficient trapping and detection.

Pressures of the organic compounds were determined by assuming that the total ion signal in a positive ion spectrum increases linearly with sample pressure and with ionization cross section. It was further assumed that the ionization cross section can be obtained from the molecular polarizability using the results of Bartmess and Georgiadis[20] and that the polarizability can be obtained using the method of Miller and Savchik.[21] It was then possible to use a known rate constant as a standard for our pressure measurements. The rate constants used were those for the reaction of CH_3CO^+ with CH_3COCH_3 ($k = 2.2 \times 10^{-9}$ cm^3 s^{-1})[22] and the reaction of CH_3O^+ with CH_3OH ($k = 2.0 \times 10^{-9}$ cm^3 s^{-1}).[23] This calibration procedure gave reproducible and consistent results. We estimate that the uncertainty in this procedure gives an uncertainty in the absolute rate constants of ±30%. Relative values of the rate constants for similar compounds should be more accurate.

Results

Typical data are shown in Figure 1 for the reaction of $Cr(CO)_5^-$ with maleic anhydride. The points represent intensities of the $Cr(CO)_5^-$ and $Cr(CO)_4C_4H_2O_3^-$ signals. The lines are fit to the

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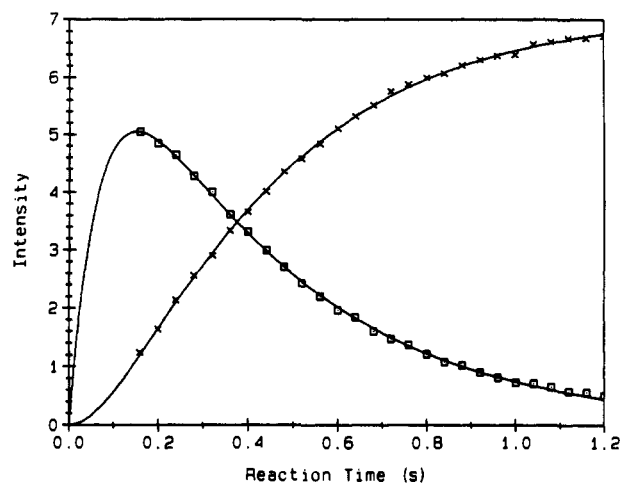
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Table I. Rate Constants and Branching Ratios for Reactions of Cr(CO)$_5^{-a}$ with Ligands

ligand	EA (eV)[b]	k (10^{-10} cm^3 s^{-1})[c]	k/k_c[d]	$-$CO	$-$2CO	$-$4CO	$-$5CO	CT[e]
hydroquinone	<0	<7 × 10^{-5}	<8 × 10^{-6}					
anthracene	0.57	<0.01	<0.01					
benzophenone	0.62	<0.01	<5 × 10^{-4}					
1,3-DCB[f]	0.91	<0.05	<2 × 10^{-3}					
nitrobenzene	1.01	0.79	4.3 × 10^{-2}	0.85		0.15		
1-Br-2-NB[f,g]	1.16	0.86	4.4 × 10^{-2}	0.36	0.27			
phthalic anhydride	1.21	3.2 × 10^{-3}	1.3 × 10^{-4}	1.00				
1-Br-4-NB[f,g]	1.29	2.9	0.20	0.25	0.66			
maleic anhydride	1.44	7.8	0.40	1.00				
1,3-dinitrobenzene	1.65	3.7	0.17	0.08	0.92			
1,4-naphthoquinone	1.81	1.5	0.12	0.15	0.85			
1,4-benzoquinone	1.91	9.0	0.98		1.00			
1,4-dinitrobenzene	2.00	1.2	0.13		1.00			
2,3,5,6-Cl$_4$BQ[f]	2.78	2.4	0.24		0.31	0.28	0.41	
tetracyanoethylene	3.17	3.5	0.39	0.05	0.32			0.63

^{a} EA (Cr(CO)$_5^-$) > 2.26 eV (ref 30). ^{b} Ligand electron affinities from ref 25. ^{c} k is the total bimolecular rate constant. Estimated uncertainty is ±30%. ^{d} k_c is the capture collision rate calculated from formulas in ref 26. ^{e} CT = charge transfer. ^{f} DCB = dicyanobenzene; BrNB = bromonitrobenzene; Cl$_4$BQ = tetrachlorobenzoquinone. ^{g} Br atom abstraction is 0.37 and 0.09 of the total reaction for 1-bromo-2-nitro- and 1-bromo-4-nitrobenzene, respectively.

Table II. Rate Constants and Branching Ratios for Reactions of Fe(CO)$_4^{-a}$ with Ligands

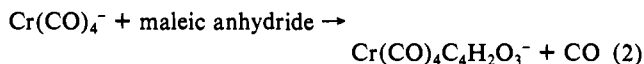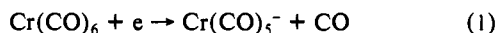| ligands	k (10^{-10} cm^3 s^{-1})[b]	k/k_c[c]	ligand substitution			
			$-$CO	$-$2CO	$-$4CO	CT[d]
1-Br-2-NB[e]	<1 × 10^{-4}	<7 × 10^{-6}				
phthalic anhydride	<6 × 10^{-5}	<2 × 10^{-4}				
1-Br-4-NB[e]	<6 × 10^{-5}	<4 × 10^{-6}				
maleic anhydride	10.1	0.46	1.00			
1,3-dinitrobenzene	2.0	0.10		1.00[f]		
1,4-naphthoquinone	1.4	0.11	0.94	0.06		
1,4-benzoquinone	8.0	0.85	0.14	0.86		
1,4-dinitrobenzene	2.5	0.26		1.00[f]		
2,3,5,6-Cl$_4$BQ[e]	3.6	0.35			1.00	
tetracyanoethylene	3.2	0.34		0.60		0.40

^{a} EA(Fe(CO)$_4$) = 2.4 ± 0.3 eV (ref 28). ^{b} k is the overall bimolecular rate constant. Estimated uncertainty is ±30%. ^{c} The capture collision rate k_c is calculated by the method of ref 26. ^{d} CT = charge transfer. ^{e} BrNB = bromonitrobenzene; Cl$_4$BQ = tetrachlorobenzoquinone. ^{f} Neutral products correspond in mass to CO + CO$_2$.

Table III. Rate Constants and Branching Ratios for Reactions of Ligands with Ni(CO)$_3^{-a}$

ligands	k (10^{-10} cm^3 s^{-1})[b]	k/k_c[c]	$-$CO	$-$2CO	$-$3CO	CT[d]
anthracene	<9 × 10^{-3}	<7 × 10^{-4}				
benzophenone	0.062	0.0027	1.00			
1,3-DCB[e]	2.6	0.18	1.00			
nitrobenzene	10.3	0.53	0.86			0.14
1-Br-2-NB[e,f]	7.4	0.35			0.92	0.05
phthalic anhydride	5.8	0.22	0.66	0.10		0.24
1-Br-4-NB[e]	5.7	0.36	0.11	0.22	0.61	0.06
maleic anhydride	26	1.16	0.25	0.50		0.25
1,4-benzoquinone	14	1.12[g]		0.76		0.24
2,3,5,6-Cl$_4$BQ[e]	3.7	0.35	0.15	0.18	0.08	0.59
tetracyanoethylene	4.8	0.50		0.17	0.07	0.76

^{a} EA(Ni(CO)3) = 1.077 ± 0.13 eV (ref 29). ^{b} k is the overall bimolecular rate constant. Estimated uncertainty is ±30%. ^{c} The capture collision rate k_c is calculated by the method in ref 26. ^{d} CT = charge transfer. ^{e} DCB = dicyanobenzene; BrNB = bromonitrobenzene; Cl$_4$BQ = tetrachlorobenzoquinone. ^{f} Br atom abstraction is 0.03 of the total reaction for 1-bromo-2-nitrobenzene. ^{g} Calculated using k_c obtained from a model that includes the ion–quadrupole interaction (ref 27).

data using the simplex method[24] assuming sequential pseudo-first-order processes:

$$Cr(CO)_6 + e \rightarrow Cr(CO)_5^- + CO \qquad (1)$$

$$Cr(CO)_4^- + \text{maleic anhydride} \rightarrow$$
$$Cr(CO)_4 C_4 H_2 O_3^- + CO \quad (2)$$

Electrons are not observed directly in the instrument so only ion concentrations are included in the fit of the model. The fit is typical as is the fact that the decay is exponential over at least 3 half-lives. This suggests the absence of a kinetically distinct population of excited ions. Similar data were obtained for reactions of Fe(CO)$_4^-$ and Ni(CO)$_3^-$ formed by electron attachment to Fe(CO)$_5$ and Ni(CO)$_4$, respectively.

The rate constants, reaction efficiencies, and branching ratios for the reactions of Cr(CO)$_5^-$, Fe(CO)$_4^-$, and Ni(CO)$_3^-$ with a series of organic electrophiles are listed in Tables I–III. Table I lists the electron affinities of the ligands from a recent review by Kebarle and Chowdhury.[25] The collision rate k_c values in the table are calculated from equations given by Su and Chesnavich.[26] In the case of the reaction of Ni(CO)$_3^-$ with benzoquinone, k_c was calculated from a model that includes the ion–quadrupole interaction.[27] The electron affinities of Fe(CO)$_4$ and Ni(CO)$_3$ are 2.4 ± 0.3 eV[28] and 1.077 ± 0.013 eV,[29] respectively. A lower

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Table IV. Summary of Sequential Substitution Reactions of $Cr(CO)_5^-$

ligands	products[a] Cr(CO)$_n$L$^-$	Cr(CO)$_n$L$_2^-$	CrL$_3^-$
1,4-naphthoquinone	0.74 ($n = 3$)	0.20 ($n = 2, 0$)	0.06
1,4-benzoquinone	0.57 ($n = 3$)	0.15 ($n = 1, 2, 0$)	0.27
1,4-dinitrobenzene	0.66 ($n = 1$)	0.34 ($n = 0$)	
2,3,5,6-Cl$_4$BQ	0.14 ($n = 0, 1, 3$)	0.86 ($n = 0$)	
tetracyanoethylene	0.24 ($n = 3$)	0.53 ($n = 0$)	0.23

[a] Primary products are in the first column, secondary products are in the second column, and tertiary products are in the third column. The ratios of the primary and sequential reaction products are given at time $t \approx 5t_{1/2}$. $t_{1/2}$ = half-life for $Cr(CO)_5^-$ reaction.

Table V. Summary of Sequential Substitution Reactions of $Fe(CO)_4^-$

ligands	products[a] Fe(CO)$_n$L$^-$	Fe(CO)$_n$L$_2^-$	FeL$_3^-$
1,3-dinitrobenzene	0.07 ($n = 1$)	0.93 ($n = 0$)	
1,4-naphthoquinone	0.29 ($n = 1$)[b]	0.71 ($n = 1$)[b]	
1,4-benzoquinone	0.04 ($n = 1$)	0.96 ($n = 1$)	
1,4-dinitrobenzene	0.06 ($n = 1$)[b]	0.74 ($n = 0$)[b]	0.20[b]
2,3,5,6-Cl$_4$BQ	0.17 ($n = 0$)	0.83 ($n - 0$)	
tetracyanoethylene	0.11 ($n = 1$)	0.42 ($n = 0$)	0.47

[a] Primary, secondary, and tertiary products are in the first, second, and third columns, respectively. The numbers represent relative intensities of ion signals at a reaction time $t \approx 5t_{1/2}$ where $t_{1/2}$ is the half-life of the $Fe(CO)_4^-$ reaction. [b] The primary product is $Fe(CO)(NOC_6H_4NO_2)^-$. Secondary and tertiary products are formed by adding L = dinitrobenzene.

Table VI. Summary of Sequential Substitution Reactions of $Ni(CO)_3^-$

ligands[a]	products[a,b] Ni(CO)L$^-$	NiL$_2^-$
maleic anhydride	0.18	0.82
1,4-benzoquinone	0.22	0.78
2,3,5,6-Cl$_4$BQ	0.53	0.47
tetracyanoethylene	0.36	0.64

[a] See text for a discussion of sequential reactions of benzophenone and 1-bromo-2-nitrobenzene. [b] Primary and secondary products are in the first and second columns, respectively. The numbers represent relative ion intensities of ion signals at a reaction time $t \approx 5t_{1/2}$ where $t_{1/2}$ is the half-life of the $Fe(CO)_4^-$ reaction.

limit of 2.26 eV has been reported for the electron affinity of $Cr(CO)_5$.[30]

As noted in the tables there are a few instances when the reactions observed do not correspond to simple ligand substitution or charge transfer. The two bromonitrobenzene isomers react with $Cr(CO)_5^-$ to give Br atom transfer as a minor product. The 1-bromo-2-nitrobenzene reaction with $Ni(CO)_3^-$ gives 3% Br atom transfer. The 1,3- and 1,4-dinitrobenzenes give displacement of one CO and one CO_2 as the products of their reaction with $Fe(CO)_4^-$

$$Fe(CO)_4^- + \text{dinitrobenzene} \rightarrow$$
$$Fe(CO)_2(NO_2C_6H_4NO)^- + CO_2 + CO \quad (3)$$
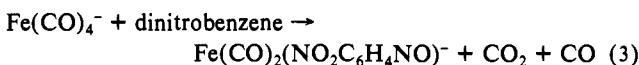
In a number of instances subsequent reactions of the initial products are observed. Usually these reactions are ligand substitutions, but there are interesting exceptions. The ligand substitution products present at long time are summarized in Tables IV–VI.

In two cases the primary products of reactions of $Ni(CO)_3^-$ undergo exceptional subsequent reactions. The primary product of reaction with benzophenone, $Ni(CO)_2(\text{"benzophenone"})^-$, loses CO in what appears to be a decomposition activated by a collision

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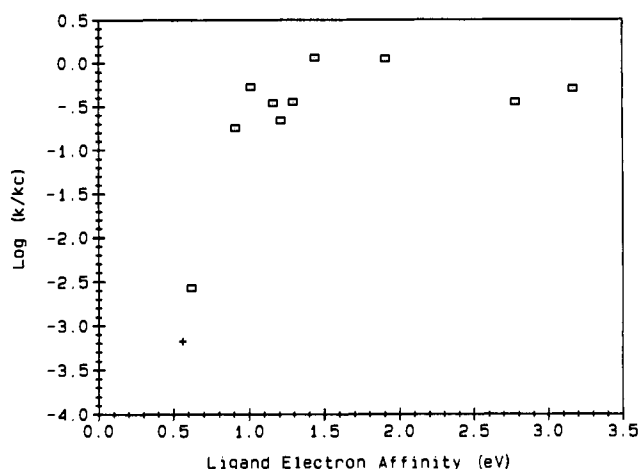
Figure 2. Efficiencies of the reactions of $Ni(CO)_3^-$ with electrophilic ligand molecules as a function of the EA of the ligand.
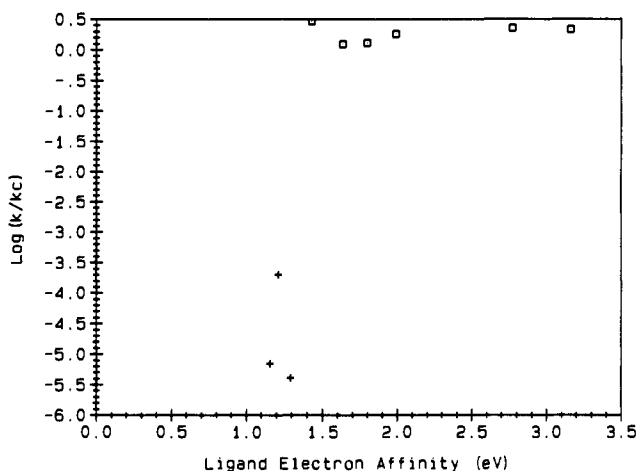
Figure 3. Efficiencies of the reactions of $Fe(CO)_4^-$ with electrophilic ligand molecules as a function of the EA of the ligand.

at thermal energies with a third body. A primary product of the reaction with 1-bromo-2-nitrobenzene, $Ni(\text{"bromonitrobenzene"})^-$, reacts with a second molecule of 1-bromo-2-nitrobenzene to give $NiBr_2^-$. Both of these reactions are described in more detail in a separate section of the discussion below.

Discussion

Overall Reactivity. The efficiency of reaction of $Ni(CO)_3^-$ and $Fe(CO)_4^-$ is plotted against the electron affinity of the organic electrophilic reactant in Figures 2 and 3, respectively. The overall behavior of both ions is essentially similar to that of $Cr(CO)_5^-$.[17] The ions react efficiently with species of high electron affinity, but reactivity drops rapidly for species with electron affinities below some critical range of values. For $Ni(CO)_3^-$ that range is 0.62 eV (benzophenone) to 0.91 eV (1,3-dicyanobenzene), for $Cr(CO)_5^-$ that range is 1.01 eV (nitrobenzene) to 1.29 eV (1-bromo-4-nitrobenzene), and for $Fe(CO)_4^-$ that range is 1.29–1.44 eV (maleic anhydride). We note that the lowest critical range, that for $Ni(CO)_3^-$, corresponds to the lowest electron affinity (EA) of the metal carbonyl fragment (EA($Ni(CO)_3$) = 1.08 eV[29]).

Although eight possible cases were examined where the organic electrophile had an electron affinity below the critical range, no products were observed in any of those cases. The upper limits obtained on efficiencies of these reactions were typically 10^{-4}. Of the 24 possibilities examined where the reactant has an electron affinity above the critical range, all were observed to react with an efficiency of 0.10 or greater. Reactivity was observed for the four cases where the electrophile has an intermediate electron affinity, but the efficiencies of those reactions were 0.05 or less.

We conclude from this marked dependence of reactivity on electron affinity that these systems react by a charge-transfer
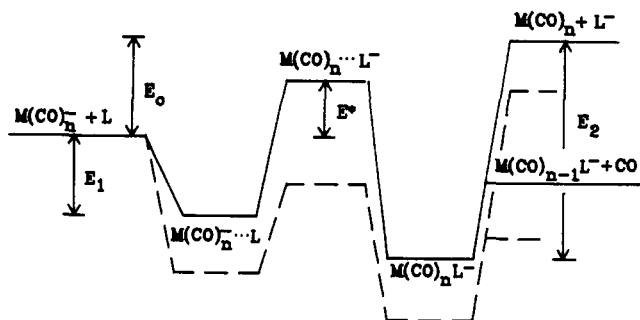
Gas-Phase Reactions of Cr(CO)₅⁻, Fe(CO)₄⁻, and Ni(CO)₃⁻

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Figure 4. Schematic potential surface for the reaction of $M(CO)_nL^-$ with electrophile L. $E_0 = EA(M(CO)_n) - EA(L)$. E_1 is the binding energy between $M(CO)_n^-$ and L. E_2 is the binding energy between $M(CO)_n$ and L^-. E^* is the kinetic barrier between reactants and $M(CO)_nL^-$.

Figure 5. Schematic mechanism for reactions 4 and 5 of $Ni(CO)_3^-$ and 1-bromo-4-nitrobenzene.

mechanism as described in the Introduction. A schematic potential surface for such a mechanism is given in Figure 4. We envision a double well with the initially formed electrostatically bound complex in one well and a datively bound complex of a neutral metal carbonyl fragment and the anion of the organic electrophile in the other well. The barrier between the wells is the barrier for charge transfer. As suggested by the dashed line in Figure 4, as the electron affinity of the ligand increases E_0, the difference between the metal carbonyl and ligand electron affinities, decreases and so should E^*, the height of the central barrier. We also expect that the height of the central barrier should decrease as the binding energy of the initial complex (E_1) or the binding energy of L^- to the metal carbonyl fragment (E_2) increases.

This picture rationalizes the general behavior of the reactivities. As the electron affinity of the electrophile increases, the top of the central barrier drops below the energy of the reactants and the reaction proceeds. Reaction will be relatively inefficient when the top of the barrier is only slightly lower in energy than the reactants, but as the electron affinity of the electrophile increases and the barrier drops the reactions become highly efficient.

Close examination of the reactivities suggests that compounds of different types behave somewhat differently. The variation of reactivity with electron affinity is more nearly monotonic within groups such as substituted nitrobenzenes or carbonyl compounds than for all of the electrophiles as a whole. That may reflect the importance of the specific binding energies E_1 and E_2 in determining the central barrier height.

The value of E_0 necessary to observe reaction is different for $Ni(CO)_3^-$ than it is for $Fe(CO)_4^-$ and $Cr(CO)_5^-$. This is a result of the fact that the "critical range" for $Ni(CO)_3^-$ is only ~0.5 eV less than those for $Cr(CO)_5^-$ and $Fe(CO)_4$ while $EA(Ni(CO)_3)$ is more than 1 eV less than $EA(Fe(CO)_4)$ and $EA(Cr(CO)_5)$. For $Ni(CO)_3^-$ reaction is observed for values of E_0 less than ca. 0.4 eV. For $Fe(CO)_4^-$ and $Cr(CO)_5^-$ the critical value of E_0 is closer to 1 eV. This suggests that charge transfer is particularly facile for $Ni(CO)_3^-$. As discussed below outright charge transfer generally competes with ligand substitution in the reactions of $Ni(CO)_3^-$. Both of these results suggest that $Ni(CO)_3^-$ has some of the $(3d)^{10}(4s)^1$ character that might be expected of Ni in a −1 oxidation state.

Also increasing with electron affinity is the tendency of a ligand to displace more than one CO in either a single step or in sequential steps. These trends are evident from examination of Tables I–VI and suggest that the metal–ligand bond in these systems increases in strength with ligand electron affinity.

Oxidative Addition. Ligands with Halogen Substituents. The ligands with halogen substituents are unusual in several respects. They displace multiple CO ligands to an extent greater than that expected from the general correlation of reactivity with electron affinity. The bromonitrobenzene isomers react predominantly to displace three COs from $Ni(CO)_3^-$ (Table III), and tetra-chlorobenzoquinone displaces four and five COs from $Fe(CO)_4^-$ and $Cr(CO)_5^-$, respectively (Tables I and II). In addition, the halogen-substituted ligands give unusual products. Taken together these results suggest that in some instances, at least, oxidative
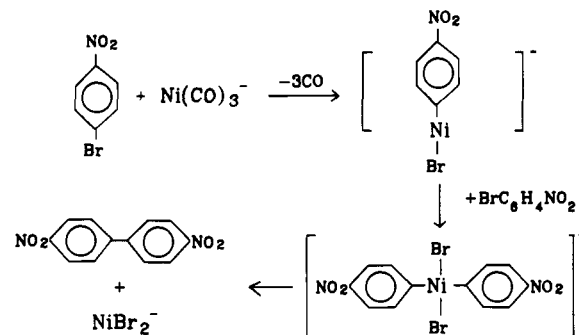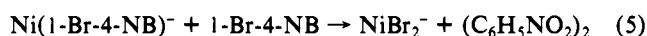
addition of C–X bonds to the metal plays a role in the chemistry of the halogen-substituted ligands.

The most striking set of results suggesting oxidative addition of a C–X bond comes from the reactions of the bromonitro-benzenes with $Ni(CO)_3^-$. The predominant reaction channel in both cases is displacement of three CO ligands. The 1,4-substituted compound reacts sequentially according to[31]

$$Ni(CO)_3^- + 1\text{-Br-4-NB} \rightarrow Ni(1\text{-Br-4-NB})^- + 3CO \quad (4)$$

$$Ni(1\text{-Br-4-NB})^- + 1\text{-Br-4-NB} \rightarrow NiBr_2^- + (C_6H_5NO_2)_2 \quad (5)$$

A proposed reaction mechanism is given in Figure 5. The formation of the 1,7-dinitrobiphenyl molecule is suggested by both mechanistic and energetic considerations. The failure to observe the same reaction in 1-Br-2-NB could be explained by a sterically unfavorable transition state for the coupling reaction. We note that while there are many examples of transition-metal-mediated cleavage of C–C bonds in gas-phase ion-molecule reactions, there are few examples of transition-metal-mediated formation of C–C bonds in ion–molecule reactions.

These oxidative addition products could result from a charge-transfer-mediated process similar to that discussed above in connection with ligand substitution. The C–X bond could add in a concerted way to the 16-electron metal center which results from the charge transfer within the collision complex. This would cleave the C–X bond, but it would produce M–C and M–X bonds releasing enough energy to eject several CO ligands. The major products of reactions of 2,3,5,6-tetrachlorobenzoquinone (Cl_4BQ) with both $Cr(CO)_5^-$ and $Fe(CO)_4^-$ corresponds to displacement of all the CO ligands on the metal (Tables I and II). At long reaction time the initial products add a second ligand (Tables IV and V). These secondary products could be the result of a second oxidative addition giving $MR_2Cl_2^-$, since the +3 oxidation state is readily accessible to Cr and Fe. These Cl_4BQ products are probably formed by a concerted oxidative addition mechanism.

Alternatively, the charge-transfer-mediated mechanism could give R and X^- fragments initially weakly bound to the metal within the collision complex. We have argued previously that such a mechanism accounts for the $Cr(CO)_5Br^-$ product of reaction of $Cr(CO)_5^-$ with *o*- and *p*-bromonitrobenzene.[17] The fact that the Br transfer is more important for the ortho compound supports the proposed mechanism because on reduction at an electrode the ortho compound gives Br^- much more rapidly than does the para compound.[32] If X^- adds to a 16-electron metal center, an 18-electron center results precluding further reaction unless a CO ligand is lost. Our results suggest a tendency of the reaction to stop there. The halogen-transfer products we observe, $Cr(CO)_5Br^-$ and $Ni(CO)_3Br^-$, are coordinatively saturated. Although the process involves making an M–Br, bond it also involves breaking a C–Br bond, and overall the process does not release enough energy to loosen a CO bond.

Our results suggest that the partitioning between halogen transfer and oxidative addition is related to the stability of the

(31) The formulation $Ni(1\text{-Br-4-NB})^-$ is not intended to imply structure.

(32) *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds.; Dekker: New York, 1980; Vol. 14, p 191 ff.
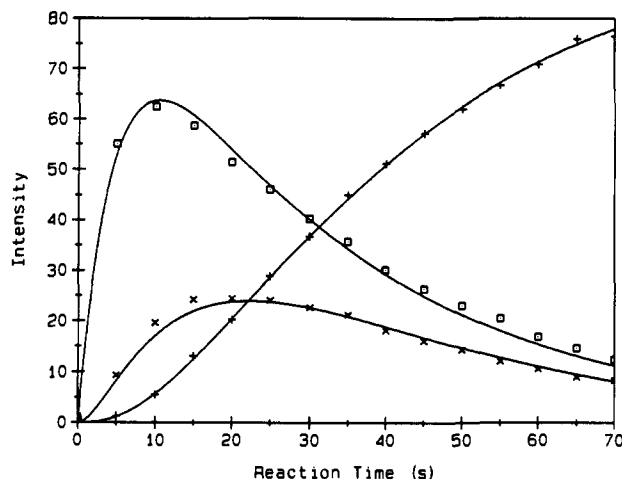
Figure 6. Ion cyclotron resonance signals of Ni(CO)$_3^-$ ($\square$), the product of reaction 6 Ni(CO)$_2$(C$_{12}$H$_{10}$CO)$^-$ ($\times$), and the product of reaction 7 Ni(CO)$_2$(C$_{12}$H$_{10}$)$^-$ ($+$) as a function of the trapping time after an initial 4-eV, 5-ms electron beam pulse. The solid lines are a fit of the data to the kinetic model beginning with formation of Ni(CO)$_3^-$ by electron impact on Ni(CO)$_4$ and continuing with eqs 6 and 7.
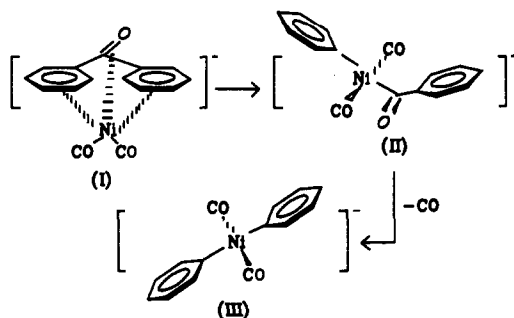

Figure 7. Schematic representation of oxidative addition mechanism by which eq 7 proceeds.

radical anion of the organic halide. For example, as noted above the 1,2-substituted anion is less stable than 1-bromo-4-nitrobenzene anion, and the 1,2-substituted isomer transfers Br to Cr(CO)$_5^-$ to a greater extent than does the 1,4-substituted isomer. Only the 1,2-substituted isomer transfers Br to Ni(CO)$_3^-$ at all.

Oxidative Addition. Ni(CO)$_3^-$ and Benzophenone. The sequential reactions of Ni(CO)$_3^-$ with benzophenone (BPH) suggest a process involving oxidative addition of a C–C bond to the metal:

$$Ni(CO)_3^- + BPH \rightarrow Ni(CO)_2(C_{12}H_{10}CO)^- + CO \quad (6)$$

$$Ni(CO)_2(C_{12}H_{10}CO)^- \xrightarrow{M} NiC_{12}H_{10}(CO)_2^- + CO \quad (7)$$

The time dependence of the three ions involved is shown in Figure 6. Ni(CO)$_3^-$ decays exponentially as a result of reaction 6, and Ni(CO)$_2$(BPH)$^-$ behaves as an intermediate, increasing as a result of reaction 6 and then disappearing as a result of reaction 7. Reaction 7 is simply the loss of an additional CO ligand, but the apparent rate constant, 0.14 s^{-1}, is 4 or 5 orders of magnitude less than the slowest of unimolecular processes. Reaction 7 must therefore be a bimolecular process.

As shown in Figure 7 we suggest that reaction 6 proceeds by oxidative addition to the metal of a bond between a phenyl group and the carbonyl in benzophenone. This produces a 17-electron metal center so that a second phenyl group cannot migrate from the carbonyl to the metal without resulting in a 19-electron configuration. Formation of a collision complex with a neutral, however, releases energy equal to the electrostatic attraction between the ion and the neutral. This energy is available to loosen one ligand, leaving a 15-electron metal center so that the migration of the second phenyl to the metal can proceed. The formation of the metal biphenyl releases sufficient energy so that both the neutral collision partner and a CO ligand can be lost. Isotopic labeling of the carbonyl carbon in benzophenone shows that

consistent with the proposed mechanism the carbonyl carbon is not lost as CO in reaction 7.

Oxidative Addition. Nitrobenzenes. The reactions of the dinitrobenzenes with Fe(CO)$_4^-$ involve the oxidation of CO to CO$_2$ and concomitant reduction of one of the nitro groups to a nitrosyl. Nitrobenzenes with lower electron affinities fail to react with Fe(CO)$_4^-$, indicating that the oxidation process involves a charge-transfer mechanism and requires generation of a vacancy in the coordination shell of the metal. This in turn suggests that the reaction involves oxidative addition of an N–O or a C–NO$_2$ bond to the metal.

Charge Transfer. In some instances outright charge transfer occurs and L$^-$ separates from the collision complex and becomes the observed product:

$$M(CO)_n^- + L \rightarrow L^- + M(CO)_n \quad (8)$$
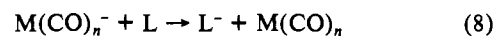
In the case of Ni(CO)$_3^-$ outright charge transfer occurs whenever the process is exothermic. In fact the observed charge transfer from Ni(CO)$_3^-$ to nitrobenzene is slightly endothermic ($E_o = 0.07$ eV), but the efficiency of the charge transfer is modest.[33] Species with electron affinities lower than nitrobenzene do not react by outright charge transfer with Ni(CO)$_3^-$. The charge-transfer results are thus consistent with the reported electron affinity of Ni(CO)$_3$. As noted above the facility with which Ni(CO)$_3^-$ undergoes charge transfer suggests that Ni(CO)$_3^-$ has some of the character of the (3d)^{10}(4s)^1 configuration expected for Ni in the -1 oxidation state.

Only tetracyanoethylene (EA = 3.17 eV) reacts by outright charge transfer with either Cr(CO)$_5^-$ or Fe(CO)$_4^-$. Outright charge transfer between Fe(CO)$_4^-$ and 2,3,7,8-tetrachlorobenzoquinone (Cl$_4$BQ) is exothermic but not observed. This adds to the evidence for a strong interaction between the Cl$_4$BQ anion and Fe(CO)$_4$ so that the two react by oxidative addition rather than separate as products.

Comparison with Related Gas-Phase Results. Weddle and Ridge report that Fe(CO)$_4^-$ reacts with maleic anhydride, methylmaleic anhydride, and dimethylmaleic anhydride but fails to react with malonic anhydride or representative ketones, olefins, and alcohols.[10,11] Since none of the unreactive species has a positive electron affinity, these observations are consistent with the present results.

McDonald, Schell, and McGhee[13] report that Fe(CO)$_4^-$ reacts efficiently by halogen atom transfer and oxidative addition with CF$_3$I (EA = 1.6 ± 0.2 eV) and much less efficiently with CF$_3$Br (EA = 0.9 ± 0.2 eV). This is quite consistent with the pattern observed in the present results. They also report that Fe(CO)$_4^-$ abstracts Br and Cl from BrCCl$_3$ and CCl$_4$ (EA = 2.0 ± 0.2 eV),[34] respectively. These two halomethanes dissociate into halide ion and CCl$_3$ on electron attachment and probably react by a charge-transfer mechanism.

McDonald and Schell[14] report that (CF$_3$)$_2$CO (EA > 1.46 eV) reacts efficiently by ligand substitution with Fe(CO)$_4^-$ and Cr(CO)$_5^-$ which is consistent with the pattern observed in the present study. McDonald and Schell also report that TCNE reacts with Fe(CO)$_4^-$ and Cr(CO)$_5^-$ by both outright charge transfer and ligand substitution. They are unable to obtain rate constants for the TCNE reactions, but the branching ratios obtained in the present study are in satisfactory agreement with theirs. They report a slow (k/k_c = ca. 10^{-4}) ligand substitution reaction between biacetyl (EA = 0.69eV) and Cr(CO)$_5^-$, and they report that a number of substituted ethylenes and ketones do not react at an observable rate with Fe(CO)$_4^-$ or Cr(CO)$_5^-$. Since none of the unreactive species are reported to have positive electron affinities, these results are consistent with the present observations. The McDonald and Schell results were obtained using the flowing afterglow technique where the reactants are included in a flow

(33) From Table III the efficiency of charge transfer to nitrobenzene = (0.53) (0.14) = 0.07 compared with exp($-E_o/kT$) = 0.07 where E_o = EA-(Ni(CO)$_3$) $-$ EA(nitrobenzene) = 0.07eV and T = 300 K.

(34) (a) Page, F. M.; Kay, J.; Gaines, A. F. *Trans. Faraday Soc.* **1966**, *62*, 874. (b) Dispert, H.; Lacmann, K. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *28*, 49. (c) Lacmann, K.; Maneira, M. J. P.; Moutinno, A. M. C.; Weigmann, U. *J. Chem. Phys.* **1983**, *78*, 1767.

of He at about 0.75 Torr so that three body association processes are sometimes observed. These processes do not occur at the much lower pressures of the ICR experiment, so a comparison including these processes is not possible.

McDonald and Schell[14] include in their study several small inorganic ligands that behave somewhat differently from the organic electrophiles. SO_2 (EA = 1.10 eV) reacts efficiently by ligand substitution with both $Fe(CO)_4^-$ and $Cr(CO)_5^-$ (k/k_c = 0.18 and 0.65, respectively) even though its electron affinity is slightly below the range of electron affinities of efficiently reacting organic electrophiles. NO reacts moderately efficiently by ligand substitution with both $Fe(CO)_4^-$ and $Cr(CO)_5^-$ (k/k_c = 0.04 and 0.02, respectively) even though it has a very small electron affinity. NO, however, has an unpaired electron and can therefore react directly with a 17-electron metal complex without violating the 18-electron rule. PF_3 reacts with moderate efficiency with $Fe(CO)_4^-$ but not at all with $Cr(CO)_5^-$ (k/k_c = 0.04 and <10⁻⁴, respectively). It appears that no value has been reported for an electron affinity of PF_3, but it certainly seems to deviate from the pattern observed in the present study. This may reflect unique electronic properties of phosphine ligands.

Jones, McDonald, Schell, and Ali find that rates of halogen atom transfer reactions from alkyl halides, RX, to $Cr(CO)_5^-$, $Fe(CO)_4^-$, and $Ni(CO)_3^-$ tend to decrease as the electron affinity of RX decreases.[16] They also find that $Ni(CO)_3^-$ is more reactive than $Cr(CO)_5^-$ which is more reactive than $Fe(CO)_4^-$. These observations are similar to the pattern we observe for ligand substitution, and Jones et al. suggest an electron-transfer mechanism for halogen atom transfer similar to that suggested above for both halogen transfer and ligand substitution. They also find a correlation between the RX thermal electron attachment rate constants and the rate constants for X transfer from RX to $M(CO)_n^-$. This is intriguingly reminiscent of the correlation described above between the rate of condensed-phase dissociative reduction of bromonitrobenzene isomers and the rates of Br transfer from bromonitrobenzene isomer to $Cr(CO)_5^-$. It would be interesting to pursue further the possibility of correlation between thermal electron attachment rates and ligand substitution rates for the ligands studied here should measurements of thermal electron attachment rate constants for those ligands become available. We note that such an analysis would be complicated by the fact that electron attachment is dissociative only for some ligands and dissociative attachment tends to be much more efficient than nondissociative attachment.

It has also been reported that $Fe(CO)_4^-$ reacts with $Fe(CO)_5$ to give $Fe_2(CO)_8^-$.[35] This reaction proceeds with an efficiency of ca. 0.01. No electron affinity has been reported for $Fe(CO)_5$, but it undergoes dissociative electron attachment with thermal electrons, and the clustering reaction could proceed by a charge-transfer mechanism.

The reactions of more highly unsaturated metal carbonyl anions have been studied more extensively than have the reactions of the 17-electron radical anions.[36] Most closely related to the present results are the studies by McElvany and Allison[37] of reactions of $Cr(CO)_3^-$ and $Fe(CO)_3^-$ with haloalkanes[37] in which the dominant process observed was Cl transfer to the ion. McElvany and Allison also examined reactions of $Fe(CO)_3^-$ and $Cr(CO)_{3,4}^-$ with nitroalkanes.[38] In that case formation of CO_2 as a neutral product was significant in most of the observed reactions. McElvany and Allison suggest that oxidative addition plays a role in these reactions. Movement of charge away from the metal center could also play a role, but it is not requisite for oxidative addition.

Comparison with Related Condensed-Phase Results. Krusic and San Filippo[10] observe by ESR the product of the ligand substitution reaction between $Fe(CO)_4^-$ and maleic anhydride, $Fe(CO)_3$(maleic anhydride)⁻ in room temperature THF solutions of $Na_2Fe(CO)_4$ and maleic anhydride. They conclude that $Fe(CO)_4^{2-}$ is oxidized

by maleic anhydride to $Fe(CO)_4^-$ which then reacts with maleic anhydride

$$Fe(CO)_4^- + \text{maleic anhydride} \rightarrow$$
$$Fe(CO)_3(\text{maleic anhydride})^- + CO \quad (9)$$
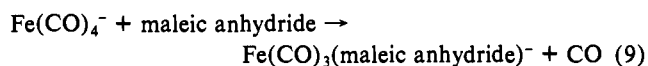
just as it does in the gas phase. The same product is formed by the addition of sodium naphthalide to a THF solution of $Fe(CO)_5$ and maleic anhydride. The ESR indicates that the electron in the product anion resides primarily on the metal and interacts weakly with the vinylic protons and that on the ESR time scale the three CO ligands are equivalent.

Krusic and San Filippo[10] observe analogous ligand substitution processes with other activated olefins dimethyl maleate (*cis*-$CH_3CO_2CH=CHCO_2CH_3$), dimethyl fumarate (*trans*-$CH_3O_2CH=CHCO_2CH_3$), cinnamonitrile ($C_6H_5CH=CHCN$), and acrylonitrile ($CH_2=CHCN$). They were unable to obtain rate constants for these reactions, so it is not possible to determine definitively whether there is the kind of correlation between electron affinity and reactivity in solution that is observed in the gas phase. They do not report, however, any examples of unactivated olefins reacting in the way the activated olefins react, suggesting some correlation between reactivity and electrophilicity. They are able to prepare $Fe(CO)_3$(olefin)⁻ complexes involving unactivated olefins by reducing, for example, $Fe(CO)_3$(1,3-butadiene). The ESR spectra of the resulting radical anions suggested the detachment of one of the diene double bonds to form a 17-electron olefin complex.

The Krusic and San Filippo results[10] suggest that activated olefins that are unreactive in the gas phase are reactive in solution. Of the electrophiles for which they observe ligand substitution product with $Fe(CO)_4^-$, only maleic anhydride has an electron affinity above 1 eV, and only maleic anhydride is observed to react with $Fe(CO)_4^-$ in the gas phase. McDonald and Schell report specifically that acrylonitrile is unreactive with $Fe(CO)_4^-$ in the gas phase (k/k_c < 10⁻⁴). There are several possible explanations for these differences between the gas-phase and condensed-phase results. An activation energy above 5 or 6 kcal/mol is sufficient to render a reaction unobservable by the flowing afterglow or ICR technique. At the much greater density of the condensed phase, however, a reaction with 5 or 6 kcal/mol activation energy could give significant observable product in a few minutes even at relatively low concentrations. The activation energy for the electron-transfer-mediated ligand substitution will probably be different in solution than it is in the gas phase. In fact more striking than the specific differences between the gas-phase and condensed-phase results is the overall similarity noted in the previous paragraph.

Summary and Conclusions

The 17-electron metal carbonyl anions $Cr(CO)_5^-$, $Fe(CO)_4^-$, and $Ni(CO)_3^-$ react with organic electrophiles by a mechanism involving charge transfer to the electrophile within the collision complex followed by interaction between the organic ion and the resulting 16-electron metal center. The products observed correspond to ligand substitution, oxidative addition, and electron transfer. This mechanism reflects itself in the increasing efficiency of the reaction with increasing electron affinity of the electrophile. For each metal carbonyl anion there is a critical range of electrophile electron affinities which divides those electrophiles which react with high efficiency from those which react with low efficiency or not at all. This critical range of electron affinities occurs at lower electron affinity for $Ni(CO)_3^-$ (0.62–0.91 eV), higher electron affinities for $Cr(CO)_5^-$ (1.01–1.29 eV), and still higher electron affinities for $Fe(CO)_4^-$ (1.29–1.44 eV). The tendency to displace more than one CO ligand either in a single step or in sequential steps increases with the electron affinity of the electrophile.

Oxidative addition is particularly characteristic of $Ni(CO)_3^-$. The reaction with 1-bromo-4-nitrobenzene appears to involve two sequential oxidative additions followed by a reductive elimination resulting in $NiBr_2^-$ and 1,6-dinitrobiphenyl. This reaction involves formation of a carbon–carbon bond which is unusual in gas-phase

(35) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67.
(36) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623.
(37) McElvany, S. W.; Allison, J. *Organometallics* **1986**, *5*, 416.
(38) McElvany, S. W.; Allison, J. *Organometallics* **1986**, *5*, 1219.

transition-metal ion chemistry. Also interesting is the reaction of Ni(CO)$_3^-$ with benzophenone which appears to involve formation of Ni(C$_6$H$_5$)$_2$(CO)$_2^-$ as a result of two oxidative additions. The second oxidative addition in this process is activated by the attractive interaction between the reacting ion and a neutral collision partner.

Outright charge transfer when exothermic competes with ligand substitution and oxidative addition in the case of Ni(CO)$_3^-$, but only tetracyanoethylene reacts by outright charge transfer with Cr(CO)$_5^-$ and Fe(CO)$_4^-$. This difference is consistent with the fact that Cr(CO)$_5$ and Fe(CO)$_4$ have significantly higher electron affinities than Ni(CO)$_3$.

The Metal–Alkyl Bond Energy of the Fe(100)–Hydrogen–Ethyl Surface Complex

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Contribution from the Departments of Chemistry and Chemical Engineering, Stanford University, Stanford, California 94305. Received June 27, 1991

Abstract: A thermochemical cycle has been constructed for the reactions of ethylene on H–presaturated Fe(100); this cycle has been used to accurately determine Fe–C$_2$H$_5$ and Fe–H surface bond energies of 38 ± 4 and 59.5 ± 2 kcal/mol, respectively. The Fe–C$_2$H$_5$ bond energy is considerably smaller than that measured in the gas phase. Both values are similar to those expected for mononuclear transition metal complexes, provided that the complex contains a first or second row transition metal and is not sterically crowded.

1. Introduction

With the overall goal of comparing and contrasting transition metal surface reactivity to that of mononuclear complexes and clusters, we have recently undertaken detailed studies of alkene hydrogenation on an Fe(100) surface.[1-3] This particular system was chosen because of the wealth of information available for alkene hydrogenation catalyzed by complexes and by the generally high catalytic activity of iron for all degrees of nuclearity.

As a product of this research we have been able to accurately determine the strength of the Fe–C$_2$H$_5$ (ethyl) bond on the hydrogen-saturated Fe(100) surface; to our knowledge this is the first determination of a metal–alkyl bond energy for a transition metal surface. Considerably more is known about metal–alkyl bond energetics in complexes, however; we thus have compared our results (for Fe–H as well as Fe–C$_2$H$_5$ bonds) to those for complexes to discern similarities and differences between a single metal atom and an extended surface.

The Fe–C$_2$H$_5$ bond energy was calculated by constructing a thermochemical cycle using kinetic data from studies of the forward and reverse reactions of ethylene on hydrogen–saturated Fe(100), whereby an ethyl intermediate is formed. Kinetic studies were performed using the techniques of temperature programmed desorption and temperature programmed reaction spectroscopy (TPD/TPRS).

2. Experimental Section

All experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of 1 x 10^{-10} Torr. TPD/TPRS experiments utilized a quadrupole mass spectrometer (UTI 100C) modified with a collimating orifice approximately 0.8 cm in diameter. A chromel–alumel thermocouple was spotwelded to the Fe(100) sample, and the mass spectrometer and thermocouple signals were interfaced to a computer. The mass spectrometer signal was multiplexed so up to eight masses could be monitored in a single experiment. A liquid nitrogen cooling system allowed sample temperatures as low as 110 K to be reached. Two capillary array dosers were used so that contamination of a given gas sample by other gases being used was minimized. Surface elemental composition was determined by Auger electron spectroscopy (AES), and long range ordering of adsorbates was monitored using low energy electron diffraction (LEED).

Details of the preparation and initial cleaning of the Fe(100) crystal are given elsewhere.[4] Routine cleaning was achieved by Ar ion bombardment with a sample temperature of 700 K. This temperature was high enough to allow diffusion of impurities from the bulk, but low enough to preferentially segregate carbon at the surface rather than in the bulk, so it could be sputtered away more effectively. After each bombardment the crystal was annealed at 1020 K for 30 s. This anneal resulted in a sharp p(1 x 1) LEED pattern and ensured that bulk impurity levels were low enough that impurity segregation to the surface would not occur at the high temperatures reached during a TPRS scan. Surface cleanliness was determined by AES with absolute coverages of carbon, oxygen, and sulfur calibrated in correlation with LEED patterns. Carbided and sulfided Fe(100) each display a c(2 x 2) pattern at the adatom saturation coverages of 0.5 ML, where 1 ML equals the Fe(100) surface atom density of 1.22 x 10^{15} atom/cm^2. A c(2 x 2) pattern is also formed by saturation of the CO dissociative state, resulting in surface coverages of 0.25 ML each for carbon and oxygen.

TPD/TPRS experiments were performed by dosing gases while the Fe sample was held at its base temperature of 110 K, and by desorbing species through the collimator directly into the mass spectrometer. Gases were dosed directly by placing the crystal approximately 0.5 cm in front of the doser.

3. Results

3.1. Formation and Reaction of Ethyl Groups on Fe(100)–H.

Recently we have reported that ethylene has been found to reversibly form ethyl groups (C$_2$H$_5$) on an Fe(100) surface which has been presaturated with 1 ML of hydrogen.[1] (Hereafter the H-saturated Fe(100) surface will be referred to as Fe(100)–H.) Ethylene adsorbs molecularly at 110 K, with a saturation coverage of 0.25 ± 0.05 ML. Upon heating the crystal the desorption of molecular ethylene at ca. 160 K competes with the migratory insertion to form adsorbed ethyl. The maximum yield of ethyl groups in this reaction is 0.12 ± 0.03 ML. Ethyl groups undergo β-H elimination at ca. 220 K to regenerate absorbed ethylene, which rapidly desorbs, and H adatoms. Desorption of hydrogen becomes significant only at temperatures above 250 K; thus the surface remains covered with H adatoms throughout the reactions of ethylene and ethyl.

Our evidence for the formation of C$_2$H$_5$ includes H–D exchange reactions and both primary and secondary kinetic isotope effects in the β-H(D) elimination reaction. Specifically, C$_2$H$_4$ adsorbed on Fe(100)–D incorporates deuterium into the ethylene product

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