that the position of the I_3^- anion caused a dramatic influence on the rates of electron transfer in **2** and **4**.

Recently, the influence of solvate molecule motion on the properties of mixed-valence iron acetate complexes has been recognized.[35] A phase transition involving the onset of solvate dynamics was found in these iron acetate complexes. Furthermore, the phase transitions were established with heat capacity measurements. It would be very instructive if one could employ thermal analysis on mixed-valence complexes **1**–**5** to determine whether the I_3^- anions are or are not rapidly oscillating between two vibronic states.

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Registry No. **1**, 135568-59-1; **2**, 138208-46-5; **3**, 125840-44-0; **4**, 135568-52-4; **5**, 135568-55-7; **11**, 135568-53-5; 1′,1‴-bis(*p*-chlorobenzyl)biferrocene, 138208-47-6; 1′,1‴-bis(*p*-iodobenzyl)biferrocene, 138208-48-7; 1′,1‴-bis(*o*-bromobenzyl)biferrocene, 138208-49-8; 1′,1‴-bis(*o*-iodobenzyl)biferrocene, 138208-50-1; 1′,1‴-bis(*p*-bromobenzoyl)biferrocene, 138208-51-2; 1′,1‴-bis(*p*-iodobenzoyl)biferrocene, 138208-52-3; 1′,1‴-bis(*o*-bromobenzoyl)biferrocene, 138208-53-4; 1′,1‴-bis(*o*-iodobenzoyl)biferrocene, 138208-54-5.

Supplementary Material Available: Tables of thermal parameters for 1′,1‴-bis(*p*-bromobenzyl)biferrocene, **2**, and **4** (4 pages); tables of structure factors for the same three compounds (52 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Outer-Sphere Oxidation of Metal Carbonyl Anions with Coordination Complexes Containing Chloride

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Reactions of metal carbonyl anions, $CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_5^-$, $CpMo(CO)_3^-$, $CpCr(CO)_3^-$, and $Co(CO)_4^-$, with $CrCl_3{\cdot}3S$ (S = THF, CH_3CN) and reactions of $Mn(CO)_5^-$ and $Re(CO)_5^-$ with $[Co(o\text{-}phen)_2Cl_2]ClO_4$ are reported. Net oxidation/reduction chemistry is observed with formation of metal carbonyl dimers and $CrCl_2{\cdot}4S$ or $Co(o\text{-}phen)_2Cl_2$. Metal carbonyl halides are also observed and shown to arise from a secondary reaction of the metal carbonyl dimer with the oxidant. The products and rates are most consistent with outer-sphere electron-transfer reactions. Reactions of $CpFe(CO)_2^-$ with $CpFe(CO)_2X$ (X = Cl, Br, I) are also reported. The rate dependence on X is very small and in the order expected for nucleophilic substitution.

The close relationship between S_N2 and SET (single-electron-transfer) mechanisms in reactions of organic anions with halide-containing compounds continues to be explored.[1] The inorganic analogues of inner-sphere and outer-sphere electron transfer have remained distinct due to the requirement of a coordination site for an inner-sphere process.[2] However, reactions of the metal carbonyl anions are not as easy to classify into mechanisms. Reactions with MeI have been used to define the nucleophilicity for the metal carbonyl anions.[3] Evaluation of the oxidation potentials and reactions with outer-sphere electron acceptors has been used to establish the outer-sphere reactivity of the metal carbonyl anions.[4] Unfortunately, as might be expected, the order of the metal carbonyl anions in nucleophilic reactions[3]

$$CpFe(CO)_2^- > Re(CO)_5^- > Mn(CO)_5^- > CpMo(CO)_3^- > Co(CO)_4^-$$

is the same as for outer-sphere reactions.[4c] From the data collected thus far the change in rate with nucleophilicity is larger (10^8 for the anions listed)[3] in comparison to reaction with outer-sphere acceptors (10^4 for the anions listed).[4c] The similarity in order makes it very difficult to distinguish between an outer-sphere (or SET) mechanism and an inner-sphere electron-transfer mechanism that is initiated by nucleophilic attack by the anion.

$$2M^- + 2\text{oxidant} \rightarrow [2M^\bullet + 2\text{oxidant}^-] \rightarrow M_2 + 2\text{oxidant}^- \quad (1)$$

$$2M^- + 2\text{oxidant} \rightarrow 2[M\text{–oxidant}] \rightarrow [2M^\bullet + 2\text{oxidant}^-] \rightarrow M_2 + 2\text{oxidant}^- \quad (2)$$

The two mechanisms differ only in the presence of the nucleophile–electrophile adduct in the inner-sphere mechanism. The difficulty in distinguishing between these two is more related to the SET and S_N2 mechanisms in organic reactions than differentiation between inorganic electron-transfer mechanisms.[1]

Reactions of metal carbonyl anions with metal carbonyl halides have been used to form metal–metal bonds, es-

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pecially between different metal centers.[5] These reactions involve displacement of halide by the metal carbonyl anion.

$$\mathrm{M^- + M'\text{-}X \rightarrow M\text{-}M' + X^-} \qquad (3)$$

$$\mathrm{M, M' = metal\ carbonyl\ fragments}$$

In reaction of $Re(CO)_5^-$ with $Re(CO)_5I$, a CO ligand was eliminated instead of the I^-, resulting in $Re_2(CO)_9I^-$.[6]

$$\mathrm{Re(CO)_5^- + Re(CO)_5I \rightarrow Re_2(CO)_9I^- + CO} \qquad (4)$$

The mechanism was tentatively assigned as an outer-sphere electron transfer.[6]

To extend our knowledge of the reactions of metal carbonyl anions, we now report kinetic studies of reactions with three types of halide complexes: (1) $Co(o\text{-phen})_2Cl_2^+$, (2) $CrCl_3{\cdot}3THF$, and (3) metal carbonyl halides.

Experimental Section

Materials. All synthetic procedures were carried out under an inert atmosphere using glovebox or Schlenk techniques unless otherwise noted. Solvents were dried by standard procedures. Elemental analyses were performed by Oneida Research Services Inc. and are reported in Table S1 (supplementary material). Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer or on a Mattson Polaris FTIR and are reported in Table S2 (supplementary material). All chemicals were used as received. The following compounds were prepared by procedures in the literature: $[PPN][(C_5Me_5)Fe(CO)_2]$,[7] $[PPN][CpFe(CO)_2]$,[7] $[PPN][Re(CO)_5]$,[7] $[PPN][Mn(CO)_5]$,[7] $[PPN][Co(CO)_4]$,[7] $[PPN][CpM(CO)_3]$[7] (M = Cr, Mo, W), $Re(CO)_5Br$,[8] $Mn(CO)_5Br$,[9] $CpFe(CO)_2X$ (X = Cl,[10] Br,[11,12] I[11,12]), $CpMo(CO)_3X$ (X = Cl,[13] Br,[13] I[14]), $(C_5Me_5)Fe(CO)_2Br$[15] (PPN = bis(triphenylphosphine)nitrogen(1+)). All IR spectra of these compounds were consistent with those reported. The $CrCl_3{\cdot}3THF$ was purchased or prepared as follows: Anhydrous $CrCl_3$ (5.0 g) was mixed with Zn dust (0.15 g) and the mixture refluxed in THF for 8 h. The reaction mixture was filtered while hot, and THF was removed in vacuo. The purple solid was recrystallized twice from hot THF. Dichlorobis(1,10-phenanthroline)cobalt(III) chloride, $[Co(o\text{-phen})_2Cl_2]Cl{\cdot}H_2O$, was prepared according to standard procedure.[16] The cobalt(III) perchlorate salt was obtained by dissolving the freshly prepared chloride in dilute $HClO_4$ solution. The precipitate was collected and recrystallized twice from hot water. The purities for the compounds were confirmed by elemental analyses (Table S1) and UV–vis spectra. To remove the H_2O, $[Co(o\text{-phen})_2Cl_2]ClO_4{\cdot}H_2O$ (0.5 g) was stirred for 2 h in dry CH_3CN (50 mL). The solution was then filtered and the volume of the filtrate reduced to 10 mL. Slow addition of Et_2O resulted in crystallization of the anhydrous salt.

Reactions between Metal Carbonyl Anions and $[Co(o\text{-phen})_2Cl_2]ClO_4$ or $CrCl_3{\cdot}3THF$. For each reaction an excess of Co(III) complex (or $CrCl_3{\cdot}3THF$) and metal carbonyl anion were mixed in 15 mL of CH_3CN. An infrared spectrum was recorded immediately, and the reaction was monitored by infrared until no further reaction was observed. The solvent was removed, and the residue was extracted with hexanes, separated by column chromatography, and characterized by infrared spectroscopy. The remaining solid was dissolved in CH_3CN and also characterized by IR spectroscopy. For characterization of cobalt or chromium complexes, the CH_3CN was removed in vacuo and the residue was dissolved in degassed water and characterized by UV–vis spectroscopy.

Reaction between Metal Carbonyl Anions and Metal Carbonyl Halides. For each reaction, an approximate 1:1 molar ratio of metal carbonyl anion and metal carbonyl halide were mixed in 20 mL of THF. The reaction was monitored by IR spectroscopy immediately and continually until reaction was completed. The reaction mixture was concentrated and extracted with hexane, separated by column chromatography, and characterized by IR spectroscopy. The residue was also dissolved in CH_3CN and characterized by IR spectroscopy.

Reaction between Metal Carbonyl Dimers and $Co(o\text{-phen})_2Cl_2^+$. For each reaction the dimer and an excess of $[Co(phen)_2Cl_2](ClO_4)$ were mixed in CH_3CN. The characterization procedures were similar to those described above.

Kinetic Studies. All the kinetic experiments were performed on our IR stopped-flow spectrophotometer as described previously.[17] All reactions were performed under pseudo-first-order conditions with at least 10-fold excess of oxidant at 25 °C. Typical concentrations of metal carbonyl anion and Co(III) for the kinetic studies were 0.001 and 0.01–0.30 M, respectively, in CH_3CN depending on the reaction rates. The rates were monitored by the observed decrease in intensity of the infrared absorbance in CH_3CN at 1841, 1784, 1860, 1860, 1886, 1762, 1780, and 1770 cm^{-1} for anions $(C_5Me_5)Fe(CO)_2^-$, $CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_5^-$, $Co(CO)_4^-$, $CpCr(CO)_3^-$, $CpMo(CO)_3^-$, and $CpW(CO)_3^-$, respectively. The observed rate constants, the standard deviation, and the error at the chosen confidence limit were calculated using the OLIS stopped-flow operating system. The second-order rate constants k were obtained as the slope of plots of k_{obs} versus [oxidant]. Some of the reaction rates were too rapid to measure from the normal plot of k_{obs} versus concentration of excess oxidant. For reactions with a rate constant $>1000\ s^{-1}\ M^{-1}$ the rate constant was obtained as follows: The concentrations of all reactants were measured precisely, generally 0.001 M for the metal carbonyl anion and 0.005 M for the cobalt(III) complexes, $CrCl_3{\cdot}3THF$, or metal carbonyl halides in CH_3CN, and the rate constants were calculated by dividing the obtained k_{obs} value by concentration of cobalt(III), $CrCl_3{\cdot}3THF$, or halide complex.

Results and Discussion

Products. Reaction of the metal carbonyl anions with an excess of $Co(o\text{-phen})_2Cl_2^+$ or $CrCl_3{\cdot}3S$[18] leads to the metal carbonyl dimer, the metal carbonyl chloride, and $Co(o\text{-phen})_2Cl_2$ or $CrCl_2{\cdot}4S$, respectively. The ratios of metal carbonyl chloride to metal carbonyl dimer depended on M and the time of the reaction with the dimer M_2 formed first and the metal carbonyl chloride formed slowly (over several hours). The chloride complex is formed by reaction of dimer with $Co(o\text{-phen})_2Cl_2^+$.[19]

$$\mathrm{M_2 + 2[Co(\mathit{o}\text{-}phen)_2Cl_2^+]Cl \rightarrow 2M\text{-}Cl + 2Co(\mathit{o}\text{-}phen)_2Cl_2} \qquad (5)$$

On the basis of the increase in metal carbonyl chloride with reaction time and the relative rates (see later section), it seems likely that the metal carbonyl dimer, M_2, is the primary product and that the metal carbonyl chloride is formed in a subsequent reaction. Thus, the reactions re-

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[18] $CrCl_3{\cdot}3THF$ gives an instant color change when dissolved in CH_3CN. Although we have made no effort to fully identify this species, we presume that it is $CrCl_3{\cdot}3CH_3CN$. We have chosen to indicate our uncertainty by designating $CrCl_3{\cdot}3THF$ dissolved in CH_3CN as $CrCl_3{\cdot}3S$.

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Table I. Rate Constants of Reactions between Metal Carbonyl Anions and $CrCl_3 \cdot 3THF$ (Excess) in CH_3CN at 25 °C

anion	k (s^{-1} M^{-1})	anion	k (s^{-1} M^{-1})
$CpFe(CO)_2^-$	$2500^a \pm 100$	$CpMo(CO)_3^-$	7 ± 2
$(C_5Me_5)Fe(CO)_2^-$	$1500^a \pm 30$	$CpCr(CO)_3^-$	6 ± 0.5
$Re(CO)_5^-$	280 ± 20	$Co(CO)_4^-$	NR
$Mn(CO)_5^-$	19 ± 1		

[a] The rate was too rapid to measure accurately by IR stopped-flow, which instead was obtained by dividing the k_{obs} value for the reaction between 0.001 M anion and 0.005 M $CrCl_3 \cdot 3THF$ by the concentration of $CrCl_3 \cdot 3THF$ used.

Table II. Rate Constants for Reaction between a Metal Carbonyl Anion and Its Metal Carbonyl Halide in THF at 25 °C

anion	halide	k (s^{-1} M^{-1})
$CpFe(CO)_2^-$	$CpFe(CO)_2Br$	400 ± 60
$CpMo(CO)_3^-$	$CpMo(CO)_3Br$	63.7 ± 0.7
$Re(CO)_5^-$	$Re(CO)_5Br$	0.43 ± 0.04
$Mn(CO)_5^-$	$Mn(CO)_5Br$	0.36 ± 0.04

Table III. Rate Constants for Reactions of $[Co(o\text{-}phen)_2Cl_2](ClO_4)$ with Metal Carbonyl Anions in CH_3CN at 25 °C

anion	k (s^{-1} M^{-1})	anion	k (s^{-1} M^{-1})
$Re(CO)_5^-$	2800 ± 100	$Co(CO)_4^-$	NR
$Mn(CO)_5^-$	1900 ± 100	$Re(CO)_5^{-\,a}$	7900 ± 100

[a] Complexed with Na.

sponsible for product formation appear to be (represented for reaction with $CrCl_3 \cdot 3S$):

$$2M^- + 2CrCl_3 \cdot 3S \rightarrow M_2 + 2CrCl_2 \cdot 4S \quad (6)$$

$$M_2 + 2CrCl_3 \cdot 3S \rightarrow 2MCl + 2CrCl_2 \cdot 4S \quad (7)$$

$$M = \text{a metal carbonyl}$$

Kinetics. All of the reactions reported were well behaved kinetically with the rate law

$$\text{rate} = k[M^-][\text{oxidant}] \quad (8)$$

The second-order rate constants were evaluated as the slope of plots of the pseudo-first-order rate constant k_{obs} versus [oxidant].

The rate constants for reaction of the metal carbonyl anions with $CrCl_3 \cdot 3S$ in CH_3CN are shown in Table I. The rate constants vary with the nature of the metal carbonyl anion in a manner consistent with the trend in nucleophilicity of the metal carbonyl anion[3] or with the electromotive driving force[20] in an outer-sphere reaction. The correlation of ln k versus potential (Figure 1) is quite satisfactory. The rates of the electron-transfer reactions are all more rapid than the rate of reaction of the metal carbonyl anion with the metal carbonyl halides (Table II). Thus, the metal carbonyl halide cannot be important in formation of the metal carbonyl dimer. The 17-electron complex $M^\bullet$ is thus implicated.

Reaction of the metal carbonyl anions with $Co(o\text{-}phen)_2Cl_2^+$ provided clean reactions for kinetic analysis only for the $M(CO)_5^-$ (M = Mn, Re) complexes. Those rate constants are provided in Table III. Reaction of $Mn(CO)_5^-$ or $Re(CO)_5^-$ with $Co(o\text{-}phen)_2Cl_2^+$ is faster than the analogous reaction with $CrCl_3 \cdot 3S$. Since ligand dissociation from $Co(o\text{-}phen)_2Cl_2^+$ does not occur on this time scale, a possible role for ligand dissociation is unlikely in these electron-transfer reactions.

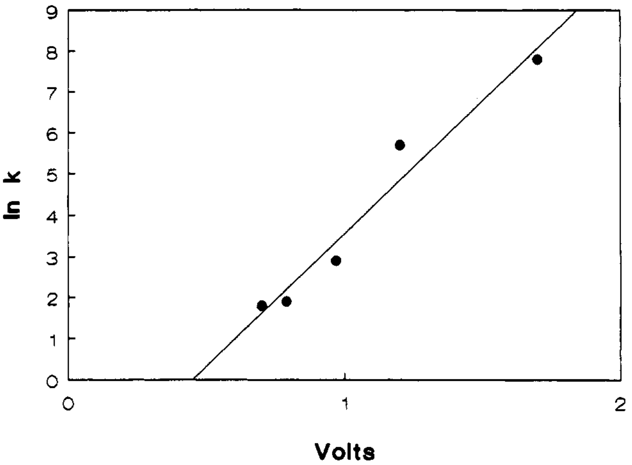

Figure 1. Plot of the natural logarithm of the rate constant versus the potential for reaction of the metal carbonyl anions $CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_5^-$, $CpMo(CO)_3^-$, and $CpCr(CO)_3^-$ with $CrCl_3 \cdot 3S$. The rate constants are given in Table I, and the potentials are for $2M^- \rightarrow M_2$.[4b]

Table IV. Rate Constants for Reaction between $[PPN][CpFe(CO)_2]$ and Different Halides in THF at 25 °C

halide	k (s^{-1} M^{-1})
$CpFe(CO)_2Cl$	1000 ± 40
$CpFe(CO)_2Br$	1390 ± 60
$CpFe(CO)_2I$	1530 ± 60

Using Na^+ as the counter ion for reaction of $Re(CO)_5^-$ with $Co(o\text{-}phen)_2Cl_2^+$ leads to an increase in the rate of the reaction. As discussed previously,[4c] the effect of sodium ion is relatively small (within a factor of 5 faster or slower) but unpredictable.

The reactions of the metal carbonyl anions with metal carbonyl halides are clean and lead to the dimers and free halide.

$$M^- + M\text{–}X \rightarrow M_2 + X^- \quad (9)$$

We have examined the kinetics of these reactions to aid in interpreting the product distribution in reactions of $Co(o\text{-}phen)_2Cl_2^+$ and $CrCl_3 \cdot 3S$ with M^-. The rate constants are given in Table II. These rate data show that the species containing cyclopentadienyl groups react more rapidly. We previously observed such a phenomenon in reactions of anions with dimers[4b] and attributed it to nucleophilic attack involving ring slippage. We examined the dependence on halide for reaction of $CpFe(CO)_2^-$ with $CpFe(CO)_2X$. The rate constants (Table IV) show a fairly small dependence on the X group, with the rate increasing in the order typical for the leaving group in an S_N2 reaction: $Cl^- < Br^- < I^-$.

Mechanistic Discussion. Two mechanisms would be consistent with the kinetic and product data for reaction of the metal carbonyl anions with $CrCl_3 \cdot 3S$ or $Co(o\text{-}phen)_2Cl_2^+$: nucleophilic attack or outer-sphere electron transfer. Since the reactions of $CrCl_3 \cdot 3S$ and $Co(o\text{-}phen)_2Cl_2^+$ are similar in rates and products, it is likely that a similar mechanism pertains. We exclude a mechanism involving dissociation of a ligand since ligand dissociation occurs on a slower time scale. A nucleophilic attack mechanism, while possible, seems unlikely since the coordination complexes offer no likely sites for attack. In reaction of Co(III) centers with a variety of nucleophiles, there is no evidence for a seven-coordinate complex.[2]

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[20] The driving force is evaluated assuming M_2 is the product.

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Cr(III) centers show more tendency toward associative reactions, but no definitive evidence for a seven-coordinate intermediate exists.[2] Nucleophilic attack at the chloride seems unlikely and would probably lead to the chloro carbonyl complex as the initial product. Nucleophilic attack on the coordinated *o*-phenanthroline was not observed in reactions of the metal carbonyl anions with $Co(o\text{-phen})_3^{3+}$.[4c] Thus, an outer-sphere mechanism is most likely for reaction of metal carbonyl anions with $Co(o\text{-phen})_2Cl_2^+$ and $CrCl_3{\cdot}3S$.

$$M^- + Co(o\text{-phen})_2Cl_2^+ \rightarrow [M^\bullet, Co(o\text{-phen})_2Cl_2] \qquad (10)$$

$$2M^\bullet \rightarrow M_2$$

The good (0.98 correlation coefficient) correlation of the ln *k* versus driving force is consistent with an outer-sphere process.

Reactions of $Co(o\text{-phen})_2Cl_2^+$ with $Mn(CO)_5^-$ and $Re(CO)_5^-$ occur more readily than reactions of $Co(o\text{-phen})_3^{3+}$. Although the reduction of $Co(o\text{-phen})_2Cl_2^+$ is not reversible, the peak potential for reduction is ~0.3 V more positive than that for $Co(o\text{-phen})_3^{3+}$.[21] The greater potential for reactions of the metal carbonyl anions with $Co(o\text{-phen})_2Cl_2^+$ in comparison to $Co(o\text{-phen})_3^{3+}$ leading to more rapid reactions are consistent with an outer-sphere process for both reaction types. Thus, all data currently available are consistent with an outer-sphere electron-transfer process for reaction of metal carbonyl anions with $Co(o\text{-phen})_2Cl_2^+$ and with $CrCl_3{\cdot}3S$.

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Supplementary Material Available: Tables of microanalytical data and IR spectral data of the complexes and figures showing rate–concentration plots (6 pages). Ordering information is given on any current masthead page.

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[21] Cyclic voltammetry was performed on CH_3CN solutions (~1×10^{-3} M) at a Pt working electrode and referenced to Ag/Ag^+. Peak potentials $E_{p,a}$ were determined at a scan rate of 100 mV/s.[3a]

Thermodynamics for the Hydrogenation of Dicobalt Octacarbonyl in Supercritical Carbon Dioxide[†]

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Some thermodynamic parameters relevant to hydroformylation catalysis in supercritical media are reported. Equilibrium constants for the hydrogenation of $Co_2(CO)_8$ to produce $HCo(CO)_4$ in supercritical CO_2 at a gas density of 0.5 g/mL were determined using in situ high-pressure ^1H and ^{59}Co NMR spectral measurements. van't Hoff plots for temperatures between 60 and 180 °C yielded the enthalpy and entropy changes for the reaction, 4.7 ± 0.2 kcal/mol and 4.4 ± 0.5 cal/(mol·K), respectively. The results for the CO_2 medium are close to reported values for liquid *n*-heptane solutions. The enthalpy and entropy of dissolution of $Co_2(CO)_8$ in CO_2, 4.9 ± 0.4 kcal/mol and 8 ± 1 cal/(mol·K), respectively, are also reported. Solubility measurements were facilitated with use of a novel toroid NMR detector, which differs from conventional detectors in its internally confined magnetic flux. This feature allowed selective measurement of gaseous or dissolved species within the detector coil while minimizing interference from undissolved solids or liquids exterior to it.

I. Introduction

Because of their gaslike transport properties, complete miscibilities with gases, and sharp changes in dissolving power with fluid density, supercritical fluids[1] offer the possibilities both of accelerating diffusion-controlled reactions of gases with liquid or solid substrates and of separating catalysts or products by energy-efficient pressure (and thereby, fluid density) alterations. These features would seem to be particularly beneficial in homogenous catalysis, where diffusion across the gas–liquid interface and catalyst separation are typical problems.

As part of a study of the oxo reaction in supercritical CO_2,[2] we report here the enthalpy and entropy changes for dissolution of $Co_2(CO)_8$ in CO_2 at a gas density of 0.5 g/mL and for the reaction of $Co_2(CO)_8$ with hydrogen (eq 1) in this medium.

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \qquad (1)$$

II. Experimental Section

Solubility and equilibrium constant measurements were conducted in the in situ mode using a General Electric GN 300/89 NMR spectrometer equipped with a home-built pressure probe (Be-Cu, Brush-Wellman alloy 25 pressure vessel). The design and several variations of it are more fully described elsewhere.[2,3] The probe uses a novel toroid detector (elongated in the *z* direction of the magnetic field) which differs from the usual Helmholtz or solenoid detectors in its internally confined magnetic flux. The toroid detector (inner radius, 1.2 mm; outer radius, 7.1 mm; height, 16 mm) consisted of 4 turns of 20-gauge Teflon-coated (0.004 in.) copper magnet wire (Phoenix Wire, Inc.) and was double-tuned

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