from ref 32. Atomic coordinates are given in Table IV.

Molecular Orbital Calculations. Calculations were performed by using average, experimental bond lengths and bond angles in an idealized geometry. Idealizations included (1) maintaining a mirror plane containing the two metal atoms and the bridging ligands, (2) assuming equal C–C bond lengths of 1.41 Å, C–H bond lengths of 1.1 Å, and a regular pentagonal geometry for the Cp rings, and (3) assuming Co–C bond lengths for the apical carbonyls of 1.905 Å. For the hypothetical compound with hydride closer to Co, the Mo–Co–H bond angle was maintained at the experimental value as the Co–H distance was shortened. Parameters for the extended Hückel calculations with weighted H_{ij}'s[7] are taken from the literature[33] and are reported in Table V.

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Supplementary Material Available: Tables of anisotropic thermal parameters and complete interatomic distances and angles (3 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Propylene Hydroformylation in Supercritical Carbon Dioxide†

J. W. Rathke,* R. J. Klingler,* and T. R. Krause

Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

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The cobalt carbonyl catalyzed hydroformylation of propylene and related equilibrium and dynamic processes were investigated by means of high-pressure NMR spectroscopy with supercritical carbon dioxide (d = 0.5 g/mL) used as the reaction medium to avoid gas/liquid mixing problems associated with conventional solvents. At 80 °C, the hydroformylation proceeds cleanly in CO_2, giving a somewhat improved yield of linear to branched butyraldehyde products, 88%, without use of stirring. The rate of propylene hydroformylation and in situ measurements of the steady-state concentrations of catalytic intermediates [$RC(O)Co(CO)_4$, $HCo(CO)_4$, and $Co_2(CO)_8$] were found to be comparable to values for other linear–terminal olefins in nonpolar liquid media. For the hydrogenation of $Co_2(CO)_8$ (to form $HCo(CO)_4$) at 80 °C in CO_2, the equilibrium constant, $K_p = 8.8 \times 10^{-4}$ M atm^{-1}, and the rate constants for the forward and reverse reactions (1.6×10^{-6} atm^{-1} s^{-1} and 1.8×10^{-3} M^{-1} s^{-1}, respectively) compared closely with values for liquid methylcyclohexane solutions. Potential dynamic processes involving $Co_2(CO)_8$, $Co_4(CO)_{12}$, or $HCo(CO)_4$ were explored at temperatures up to 205 °C at 338 atm by means of ^{59}Co, ^{13}C, and ^{1}H NMR spectroscopy. Due to the low viscosity of the supercritical medium, linewidths for the ^{59}Co nucleus were decreased by a factor of about 6 compared to values in normal liquids. An NMR pressure–probe design that uses an efficient toroid detector is also described.

I. Introduction

Although supercritical fluids have seldom been explored for this purpose, they have properties that could make them nearly ideal media for conducting homogeneous catalytic processes that involve the reactions of gases with soluble liquid or solid substrates. Since only one phase is present, gas–liquid mixing, which is often rate limiting in liquid solvents, is not problematic for supercritical fluids. In addition, reactive gas concentrations in supercritical media are typically much higher than achievable in normal liquids. For example, the concentration of H_2 at 25 °C and a partial pressure of 300 atm in supercritical CO_2 is 12 M, while in water and in *n*-heptane the hydrogen concentrations under these conditions are only 0.23[1] and 1.8 M,[2] respectively. Perhaps of greatest significance, catalyst and product separations that normally would be accomplished by energy intensive distillations might be more efficiently achieved in supercritical fluids. Due to the sharp changes in solubilities of dissolved species with density of the supercritical medium,[3] separations might be accomplished by facile pressure alterations to control fluid density, and, in turn, catalyst or product solubility. A variety of processes for separating problematic mixtures such as ethanol/water and others using supercritical fluids have been proposed.[4-7]

In this report we describe in situ high-pressure NMR experiments relevant to the oxo process, which judged from the gas–liquid mixing problems complicating some of the earlier research,[8] might be expected to benefit from the use of supercritical media. The experiments were designed to determine the effect of supercritical CO_2 on the linear to branched aldehyde product ratio (which is of considerable industrial significance and is known to be concen-

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† This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

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tration and stirring rate dependent in liquid media) and to compare other rate and equilibrium processes involved in the catalytic cycle with measured values in conventional solvents.

From the beginning of our own efforts, it became apparent that the properties of supercritical fluids are also of great value in high-pressure NMR experiments. The need for a separate stirring mechanism in the pressure probe and the normally requisite measurements of gas–liquid partition coefficients are obviated. Furthermore, due to the low viscosity of the medium, rotational correlation times and, therefore, linewidths of quadrupolar nuclei, such as ^{59}Co relevant here, are significantly decreased.[9] This latter effect greatly enhances the utility for NMR of many of the metal nuclides present in organometallic catalysts. For the hydroformylation reaction, the increased resolution allows direct observation of the relevant cobalt species: $RC(O)Co(CO)_4$, $HCo(CO)_4$, $Co_2(CO)_8$, and $Co_4(CO)_{12}$ (had it been present) without complications stemming from the frequent overlaps that occur with use of infrared spectroscopic techniques.

A compact pressure probe design that uses a toroid detector is also reported. Toroids are intrinsically more efficient than other detector types, i.e., those based on solenoid and Heimholtz coils,[10-14] and are especially useful in metal pressure probes since sensitivity losses due to magnetic coupling with the pressure vessel are minimized by confinement of the magnetic flux within the torus.[10]

II. Experimental Section

Kinetic and equilibrium constant measurements were conducted in the in situ mode by using a General Electric GN 300/89 NMR spectrometer equipped with a home-built pressure probe (Be-Cu, Brush-Wellman alloy 25 pressure vessel) of the type shown in Figure 1. The configuration used here differed from the one in the figure in that the gas connections at the top of the reactor body were not used, instead, one of the radio-frequency feedthrough ports in the bottom plug was employed to admit a single gas line ($^1/_{16}$ in. o.d. × 0.017 in. i.d., Be–Cu tubing obtained from Uniform Tube Corporation) that extended through the bottom plug and detector coil to the height of the glass liner. In this configuration, best linewidths for narrow proton signals are about 5.0 Hz. 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., dielectric rating, 3200 V) copper magnet wire (Phoenix Wire, Inc.) and was double tuned to observe ^1H (f_H = 300.5 MHz) and ^{59}Co or ^{13}C (f_X = 71.1 or 75.6 MHz, respectively). The tuned transmission line consisted of RG-223 cable of sufficient length, 18 in. ($^3/_4\lambda$ at 300.5 MHz) to allow location of the capacitor box housing C_4 and C_5 external to the magnet. Capacitors C_1–C_3 were located within the magnet, 1.5 in. from the bottom of the pressure vessel, and were tuned remotely by using plastic extension rods. All capacitors were glass dielectric, 2-120 pF, nonmagnetic types obtained from Voltronics Corporation. Pressure fittings used in the gas connection and rf feedthroughs were machined from Be–Cu screws (10–32) obtained from Unicorn Manufacturing, Inc. The Vespel (DuPont, SP-1) clamp, bolted to the Be–Cu screw used in the rf feedthrough, prevented expulsion of the electrical conductor from the vessel at high pressures (to 1700 atm at 25 °C) while achieving electrical isolation from ground. Heating was supplied by a water-jacketed electrical furnace that fit snugly around the pressure vessel. The heating element consisted of 50 turns of bifilar wound constantan wire powered from the spectrometer's temperature controller, with capacitance filtering used to remove voltage spikes from the controller's output. Temperature control was constant to within ±0.1 °C by using a copper–constantan thermocouple built into the furnace. Measured temperatures agreed within ±0.1 °C with independent determinations inside the pressure vessel covering the range, 25–175 °C.

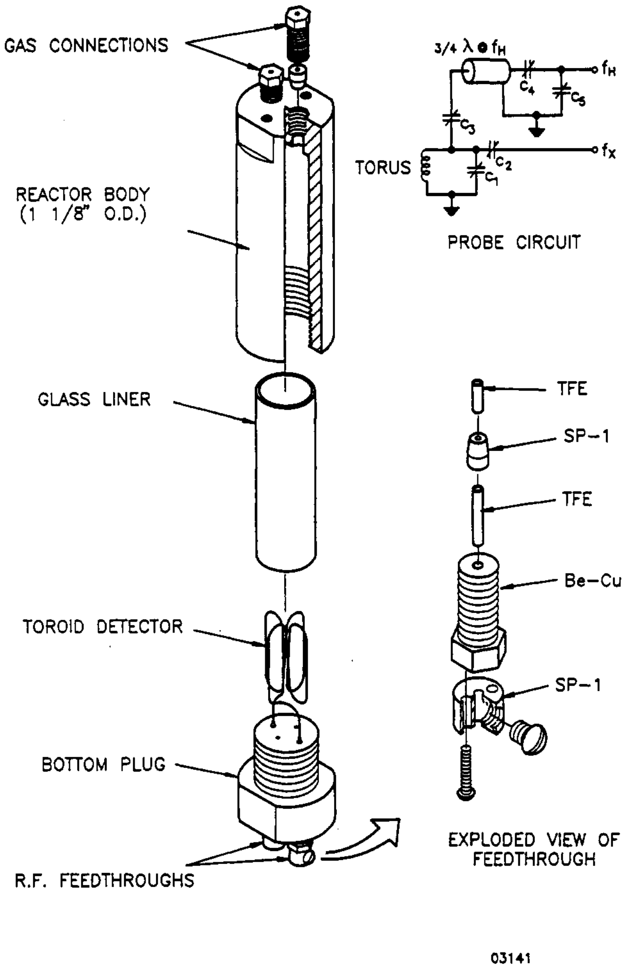

Figure 1. Compact pressure probe design using a toroid NMR detector.

The probe was used to record spectra of $HCo(CO)_4$ in supercritical CO_2 at a total pressure of 338 atm at 205 °C with no apparent ill effects. However, to avoid contamination problems, which might occur dur to noticeable cobalt carbonyl dissolution in the Teflon components, the detector coil and Teflon insulators in the feedthrough were replaced after each experiment. The use of toroid detectors in pressure probes and representative spectra obtained for a variety of nuclei are reported elsewhere.[10,15]

Experiments with supercritical CO_2 were initiated by admitting the required pressures of reactive gases, measured to within ±0.07 atm by using a strain-gauge pressure transducer (Omega, Model PX302-5KGV), into the pressure vessel containing a weighed amount of $Co_2(CO)_8$. The vessel was then heated to 34 °C and liquid CO_2 was added by means of a high-pressure syringe pump until the measured pressure increase was 82 atm, thereby achieving a fluid density of approximately 0.5 g/mL.[3] A temperature slightly above its critical value of 31.2 °C was used for the addition to ensure complete vaporization of CO_2 to avoid a potentially hazardous pressure surge which could be generated by the syringe pump were the vessel to inadvertently fill with liquid-which is, of course, far less compressible than the vapor. Complete dissolution of $Co_2(CO)_8$ in CO_2 at this density required 2.5 h at 34 °C, as determined by monitoring its ^{59}Co signal at $\delta = -2200$ ppm (saturated aqueous $K_3Co(CN)_6$ = 0.0 ppm).[16] Concentrations

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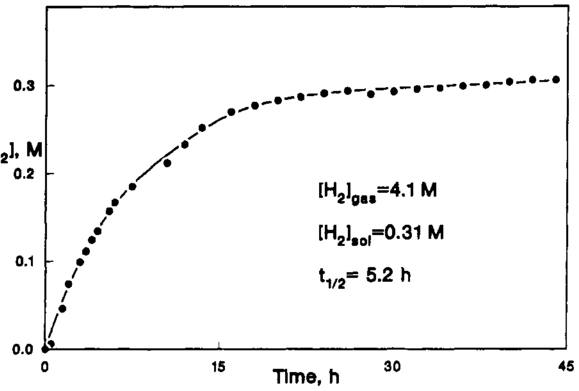

Figure 2. Dissolution of H_2, 100 atm, in benzene-d_6, 7.0 mL, in the NMR probe without stirring at 22 °C.

greater than 0.1 M, well above those used here, were easily obtained. Automated magnet shimming and spectral observations were commenced 15 min (the interval required for complete thermal equilibration) after heating the closed system to the desired reaction temperature.

III. Results and Discussion

A. Comparison of Liquid and Supercritical Media. The diffusivities of small molecules in CO_2 at its critical point are 1–2 orders of magnitude higher than typical values for solutes in organic liquids which average[3] 10^{-5} cm^2/s. Due to the small size of the pressure vessel (8.73 mL, Figure 1) and to the agitation of the gases (H_2, CO, CO_2, etc.) that must occur upon their addition, it can be assumed that even without stirring, an equilibrium distribution of gases in the vapor or supercritical fluid phase prevails shortly after pressurization. Indeed, the observed CO_2 does not change significantly after completion of gas addition. That this is not the case for a gas (H_2, 100 atm) and a liquid (C_6D_6, 7.0 mL) when the former is admitted above the liquid/gas interface and additional provisions for mixing are not present is demonstrated in Figure 2. The data for the figure was obtained by integrating the ^1H NMR signal of dissolved H_2 (δ = 4.45 ppm) versus the calibrated ^1H signal of the residual protons in C_6D_6 (δ = 7.15 ppm). It is readily apparent that the hydrogen dissolution rate ($t_{1/2}$ = 5.2 h at 22 °C) is far too slow for all but the most sluggish of hydrogen consuming reactions. In addition, the hydrogen concentration in the vapor phase (4.1 M, calculated from the ideal gas law) is more than 1 order of magnitude higher than the value measured in liquid C_6D_6 at saturation (0.31 M). The comparisons just cited make supercritical fluids attractive media for fast reactions that involve gases and, in rate measurements, obviate the need for special stirring mechanisms, which otherwise would be required and are particularly cumbersome in NMR applications.[17]

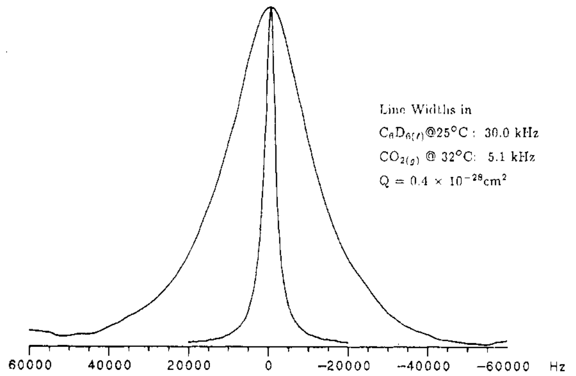

Figure 3. ^{59}Co NMR spectra of $Co_2(CO)_8$, 0.04 M, comparing widths at half height for supercritical CO_2 (d = 0.5 g/mL) and liquid benzene solutions.

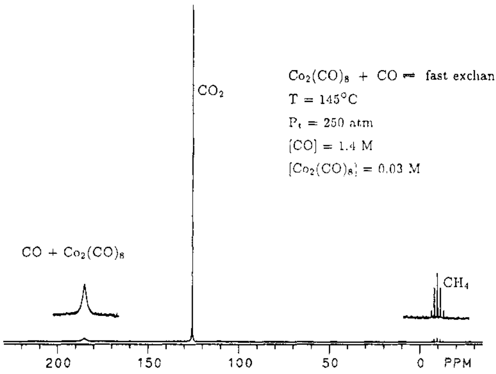

Figure 4. ^{13}C NMR spectrum in CO_2 at fast exchange conditions for CO and $Co_2(CO)_8$. Methane, 6.8 atm, was added to allow magnet shimming on its ^1H signal. The ^{13}C signal due to the Teflon coating on the detector coil near 110 ppm is barely perceptible.

Supercritical fluids, even when compressed to achieve liquid-like densities, have gas-like viscosities that are frequently 1 order of magnitude lower than those of typical liquids. At its critical point CO_2 has a viscosity of only 0.025 cP while benzene at 25 °C has a viscosity of 0.61 cP.[3] As exemplified in Figure 3, the lower viscosities have a beneficial line-narrowing effect on quadrupolar nuclei stemming from the increased transverse relaxation times, T_2, that accompany decreased viscosity.[18] For ^{59}Co, with an electric quadrupole moment of 0.4 × 10^{-28} cm^2, the lines are sufficiently broad in normal liquids to cause partial overlap even for peaks having substantially different chemical shift values, and digitization problems for peaks having widths comparable to the largest available spectral window.[16] As shown in Figure 3, the width at half height for $Co_2(CO)_8$ in C_6D_6 at 25 °C is 30.0 kHz while in supercritical CO_2 at 32 °C and a density of 0.5 g/mL, the line is only 5.1-kHz wide. Similar narrowing effects for ^{55}Mn and ^{187}Re in supercritical CO_2 have also been observed.[15]

B. Equilibrium and Dynamic Processes in Supercritical CO_2. Carbon dioxide does not interact strongly with cobalt carbonyls, and at least at the high pressures of carbon monoxide used here, CO_2 participation in the type of equilibria and exchange processes that occur with the carbonyls and H_2 and CO appears to be negligible. Thus the normally separate ^{13}C resonances measured at 34 °C for free CO (δ = 185 ppm, C = 1.4 M, P_{CO} = 35 atm) and coordinated CO in $Co_2(CO)_8$ (δ = 201 ppm, [$Co_2(CO)_8$] = 0.03 M), coalesce at 145 °C to form a broad singlet near 186 ppm as shown in Figure 4. Under these conditions where CO exchange is rapid, the CO_2 resonance (δ = 126 ppm, C = 11 M) remains sharp, indicating that CO_2 exchange is comparatively slower or, at least, less extensive.

In the presence of H_2, equilibration of $Co_2(CO)_8$ to form $HCo(CO)_4$ (eq 1) appears normal in supercritical CO_2. The

$$Co_2(CO)_8 + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2HCo(CO)_4 \qquad (1)$$

reaction was monitored by integration of the ^{59}Co resonances for $Co_2(CO)_8$ and $HCo(CO)_4$ at −2200 and −3030 ppm, respectively. In order to minimize transmitter offset effects due to the large chemical shift difference, it was necessary to use quadrature phase detection, with placement of the transmitter frequency precisely between the

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(17) Vander Velde, D. G., Jonas, J. *J. Magn. Reson.* **1987**, *71*, 480–484.
(18) Robert, J. M.; Evilia, R. F. *J. Am. Chem. Soc.* **1985**, *107*, 3733.

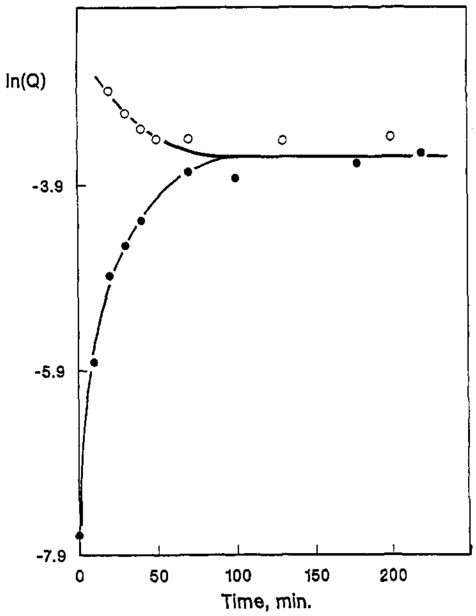

Figure 5. Plot of ln Q, Q = $[HCo(CO)_4]^2/[Co_2(CO)_8][H_2]$, vs time for the reaction of H_2 with $Co_2(CO)_8$, showing approach to equilibrium from the forward and reverse directions at 80 °C in supercritical carbon dioxide.

two peaks. As shown in Figure 5, equilibration in CO_2 occurred reproducibly when approached from either the forward or reverse directions of eq 1. The equilibrium constants ($K_{eq} = 0.025$, $K_p = 8.8 \times 10^{-4}$ M atm^{-1}) were measured at 80 °C in CO_2 ($d = 0.5$ g/mL) with use of an initial $Co_2(CO)_8$ concentration of 0.042 M, and H_2 and CO partial pressures of 40 atm ($[H_2] = [CO] = 1.4$ M). It is noteworthy that the seemingly differing equilibrium constant measured by Penninger et al.[19] for *n*-heptane solutions at 80 °C, $K_{eq} = 0.124$, becomes virtually the same as that for supercritical CO_2 when converted to a K_p value, 7.7×10^{-4} M atm^{-1}, by using Ungvary's H_2 solubility data for *n*-heptane.[2] Similar comparisons hold for equilibrium constants for methylcyclohexane solution at 80 °C ($K_{eq} = 0.17$, $K_p = 8.8 \times 10^{-4}$ M atm^{-1}) when values calculated from Mirbach's data are used.[20] The closer correspondence of the K_p values for liquid and supercritical media apparently stems from the activity of gaseous H_2 being more closely related to its pressure than to its concentration.

The forward and reverse rate constants (k_1, k_{-1} in eq 1) for the hydrogenation of cobalt octacarbonyl in supercritical CO_2 are also comparable to those measured in typical hydroformylation solvents. Thus, Ungvary[2] has shown that at CO pressures above 25 atm, the hydrogenation rate in *n*-heptane solution is independent of P_{CO} and first order in both P_{H_2} and $[Co_2(CO)_8]$. At 80 °C in supercritical CO_2 solution ($d = 0.5$ g/mL), at nearly constant hydrogen pressure ($P_{H_2} = P_{CO} = 41$ atm, $[Co_2(CO)_8]_i = 0.0168$ M) and for data far from equilibrium, a plot of ln $[Co_2(CO)_8]$ vs time was linear. Division of the first-order rate constant obtained from this plot by P_{H_2} yielded the second-order rate constant for the forward reaction, $k_1 = 1.6 \times 10^{-6}$ atm^{-1} s^{-1}. From this rate constant and the equilibrium constant, the second-order rate constant for the back reaction, $k_{-1} = 1.8 \times 10^{-3}$ M^{-1} s^{-1}, was obtained. These rate constants are in close agreement with those measured by Mirbach[20] for methylcyclohexane solutions at 80 °C ($k_1 = 1.5 \times 10^{-6}$ atm^{-1} s^{-1}, $k_{-1} = 1.7 \times 10^{-3}$ M^{-1} s^{-1}).

We have also tested for the presence of other equilibrium or dynamic processes involving $Co_2(CO)_8$ or $HCo(CO)_4$ that might be evident under more forcing conditions. The ^{59}Co and ^{1}H spectra of a supercritical CO_2 solution containing $Co_2(CO)_8$, H_2, and CO (4.4×10^{-3} M, 0.28 M, and 2.8 M, respectively) were recorded at intervals of 10–25 °C for temperatures between 34 and 205 °C. Conversion of $Co_2(CO)_8$ to $HCo(CO)_4$ became appreciable at 100 °C and was complete at 170 °C. ^{59}Co and ^{1}H resonances due to $HCo(CO)_4$ (at −3030 and −11.7 ppm, respectively) showed no significant change in width or in relative chemical shift values up to the highest temperature used in the determination, 205 °C. Apparently, reversible processes that would lead to chemical shift changes or line broadening such as formation of $HC(O)Co(CO)_4$,[21-23] $HCO_2Co(CO)_4$, or $H_3Co(CO)_3$,[24] are not rapid and extensive enough to observe by this means under the conditions tested. However, at temperatures in excess of 200 °C a new dynamic process which interconverts $Co_2(CO)_8$ and $HCo(CO)_4$ has been noted. The nature of this process is under investigation and will be reported elsewhere. In addition, at a higher $Co_2(CO)_8$ concentration (0.017 M) and a different H_2/CO ratio ($[H_2] = [CO] = 1.4$ M) a small, as yet unidentified, peak was observed in the ^{59}Co spectrum ($\delta = -1370$ ppm, HHW = 660 Hz) at temperatures between 100 and 140 °C. Although this resonance might be due to one of the alforementioned species, the small size (approximately 1% of the area of the $HCo(CO)_4$ resonance) would prevent observation of related signals in the ^{1}H spectra, even if they were present. Due to dynamic range problems associated with the strong proton signal of H_2 and use of a 12 bit A/D converter, a compound containing only one hydrogen atom per cobalt moiety would not be observable at this low concentration. Due to the potential importance of the unknown species, we are currently attempting to find conditions more conducive to its formation and characterization.

Since $Co_4(CO)_{12}$ is a product of the stoichiometric hydroformylation of olefins with $HCo(CO)_4$ at low pressures,[25] its fate under the conditions of our experiments was also explored. At 34 °C in supercritical CO_2 solution ($P_{H_2} = P_{CO} = 35$ atm, $[Co_4(CO)_{12}] = 8.42 \times 10^{-3}$ M) separate ^{59}Co resonances are observed for the one apical and three basal cobalt moieties (at −652 and −2000 ppm, respectively). As the temperature is increased the two resonances move closer together and finally merge at 70 °C to form a broad resonance near −1660 ppm. In addition to the dynamic process that equilibrates apical and basal cobalt in $Co_4(CO)_{12}$, there is an additional reaction at 80 °C to form $Co_2(CO)_8$ which is fairly rapid, $t_{1/2} \approx 30$ min. It is noteworthy that $HCo(CO)_4$ begins to form only after the $Co_2(CO)_8$ concentration becomes substantial. This latter observation indicates that $HCo(CO)_4$ is probably formed from the $Co_2(CO)_8$ and apparently not by a more direct pathway involving H_2 and $Co_4(CO)_{12}$. Although not measured in this experiment, the equilibrium concentration of $Co_4(CO)_{12}$ at 80 °C must be very small since its formation from $Co_2(CO)_8$ at these pressures begins to become measurable only at about 165 °C.

C. Propylene Hydroformylation. In a recent high-pressure IR–UV study using methylcyclohexane solutions of 1-octene in a flow apparatus, Mirbach[20] has provided

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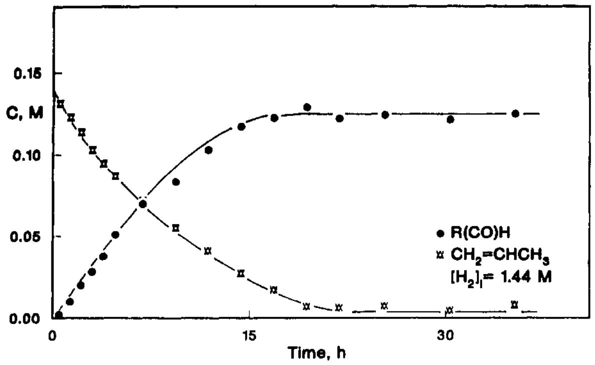

Figure 6. Plot showing the formation of butyraldehydes, RC(O)H = [*n*-butyraldehyde] + [isobutyraldehyde], for the catalytic hydroformylation of propylene in supercritical CO_2 at 80 °C.

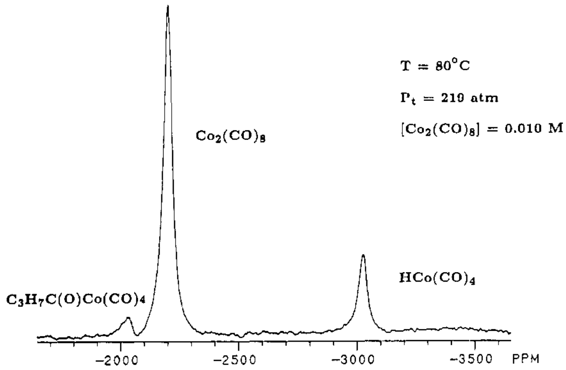

Figure 7. ^{59}Co NMR spectrum of catalytic intermediates, near the steady state, during the hydroformylation of propylene at 80 °C in supercritical CO_2.

quantitative rate estimates for each of the steps proposed to occur in the original Heck and Breslow mechanism.[26,27] Although she used a different olefin in her study, we have chosen to compare our results for propylene with the Mirbach data, mainly because of its completeness. In any case, the hydroformylation rates for a wide range of straight-chain terminal olefins vary only slightly with chain length, as shown by Wender et al.[28]

At 80 °C in supercritical CO_2 (d = 0.5 g/mL) using the conditions, $[Co_2(CO)_8]_i$ = 0.017 M, $P_{H_2} = P_{CO}$ = 42 atm, $[C_3H_6]$ = 0.14 M, propylene hydroformylation proceeds cleanly, Figure 6, yielding only the expected *n*- and isobutyraldehyde products which were measured by integration of their characteristic proton signals near δ = 9.6 and 9.8 ppm, respectively. At the relatively low temperature used, reduction of the olefin to produce alkane, or further reduction of the aldehydes to produce alcohols, even after prolonged reaction (~6 half-lives), is insignificant, and in situ ^{1}H and ^{13}C{^{1}H} spectra did not detect other products.

The cobalt containing intermediates were easily monitored by means of ^{59}Co spectra collected alternately with the ^{1}H data. A typical ^{59}Co spectrum is shown in Figure 7. The small peak near −2030 ppm corresponded closely with the chemical shift value obtained for a tetrahydrofuran solution of an authentic sample of *n*-$C_3H_7C(O)Co(CO)_4$, prepared by reaction of *n*-$C_3H_7C(O)Cl$ with $NaCo(CO)_4$.[29] As judged from the asymmetry of the peak in Figure 7, the resonance might stem from both the normal and iso derivatives. Measurable quantities of $Co_4(CO)_{12}$ were not detected, and as is consistent with Mirbach's IR data,[20] $RC(O)Co(CO)_4$, $Co_2(CO)_8$, and $HCo(CO)_4$ were the only species observed.

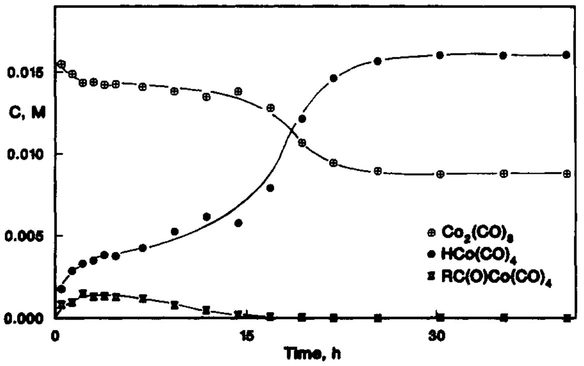

Figure 8. Concentrations of the catalytic intermediates during propylene hydroformylation in supercritical CO_2 at 80 °C.

Table I. Observable Parameters during Hydroformylation at 80 °C

conditions	$[Co_2(CO)_8]_{ss}$, mM	$[HCo(CO)_4]_{ss}$, mM	$[acyl]_{ss}$, mM	d[aldehyde]/dt, M s^{-1}
a	4.6	1.3	2.7	1.2×10^{-5}
b	8.4	3.5	0.8	0.77×10^{-5}

[a] For reaction of 1-octene, 0.83 M, in methylcyclohexane, $[Co_2(CO)_8]_i$ = 6.6 mM, $P_{H_2} = P_{CO}$ = 47.5 atm. [b] For reaction of propylene, 0.53 M, in CO_2 (d = 0.5 g/mL), $[Co_2(CO)_8]_i$ = 10.5 mM, $P_{H_2} = P_{CO}$ = 56.1 atm.

As shown in Figure 8, the cobalt complexes reach a nearly steady-state condition early in the hydroformylation, which persists during the 15-h period, Figure 7, that significant olefin is still present. During this period, $HCo(CO)_4$ is held below its equilibrium value (for eq 1), which is only achieved after the olefin is fully consumed.

Our results for propylene hydroformylation in supercritical CO_2 are compared with those of Mirbach for the reactions of 1-octene in methylcyclohexane solution in Table I. Under otherwise comparable conditions, steady-state concentrations of the intermediates for the two cases do not differ greatly (i.e., by much more than a factor of 3) while the overall hydroformylation rates are quite similar, d[aldehyde]/dt = 1.2 and 0.77×10^{-5}, for the methylcyclohexane and CO_2 systems, respectively.

For the propylene hydroformylation conditions given in Table I, the relative yield of *n*-butyraldehyde, determined by integration of the aforementioned proton signals for the linear and branched isomers, is 88%. The result compares favorably with the value, 83%, measured[30] in benzene solution at 80 °C at slightly higher pressures ($P_{CO} = P_{H_2}$ = 80 atm, $[Co_2(CO)_8]_i$ = 26 mM).

Because it is known that the hydroformylation reaction is not very sensitive to solvent effects,[31] the similar rate and selectivity (albeit the latter is somewhat improved) are probably not unexpected when comparing supercritical CO_2 with nonpolar liquid media. The expectation of comparable results is also reinforced by the near equivalences measured for the rates and equilibrium constant for the hydrogenation of $Co_2(CO)_8$, eq 1, in supercritical CO_2 when compared with results using methylcyclohexane and *n*-heptane solutions. What is most noteworthy is that all

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of the measurements in supercritical CO$_2$ were made entirely without stirring, this for a system that is notorious for spurious results due to gas-depletion effects in normal liquids.[31]

IV. Conclusions

The cobalt-catalyzed hydroformylation of propylene works well in supercritical carbon dioxide, is unencumbered with the normal liquid/gas mixing problems that can occur in conventional solvents, while the several reaction variables tested seem to behave normally.

One of the most intriguing aspects of the olefin hydroformylation reaction stems from the observation that the rate of hydroformylation is often faster than the rate of HCo(CO)$_4$ formation from Co$_2$(CO)$_8$.[20,25] The Heck and Breslow mechanism accounts for this behavior by proposing that the additional hydrogen activation occurs via the intermediate acyl complex.[20,26,27] However, other possibilities exist that might involve olefin complexes, odd-electron species,[32] or clusters[25] in the hydrogen activation mechanism. In future studies, we intend to explore the various possibilities with use of the supercritical fluid/NMR techniques described here.

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Delocalized Electronic Interactions in Chiral Cyclopentadienylrhenium Halide Complexes. Valence Photoelectron Spectra of CpRe(NO)(L)X (Cp = η^5-C$_5$H$_5$, η^5-C$_5$(CH$_3$)$_5$; L = CO, P(C$_6$H$_5$)$_3$; X = Cl, Br, I)

Dennis L. Lichtenberger,* Anjana Rai-Chaudhuri, and Matthew J. Seidel

Laboratory for Electron Spectroscopy and Surface Analysis,
Department of Chemistry, University of Arizona, Tucson, Arizona 85721

John A. Gladysz,* Sename K. Agbossou, Alain Igau, and Charles H. Winter

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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The electron energies and distributions of the title complexes are investigated by valence photoelectron spectroscopy. Assignment and characterization of the ionization bands are assisted by the trends in He I and He II cross sections for ionization intensities, as well as by the widths and vibrational progressions of certain ionization bands. The shifts of the ionizations, which are key to revealing the nature of the electronic structure interactions in a system, are caused by halogen substitutions on the metal, methyl substitutions on the cyclopentadienyl rings, and phosphine substitutions for the carbonyls. The first three ionizations, corresponding to the three occupied d orbitals of the d^6 Re(I) metal center, are widely separated. This is because each of the three metal d orbitals have very different π interactions with the three different CO, NO, and halogen ligands. The ionizations indicate extensive metal–halogen mixing and a very delocalized electronic structure throughout the metal–ligand system. The first two ionizations correspond to the metal–halogen π^* interaction, which results from the filled–filled interaction, with the first ionization including back-bonding to the carbonyl and the second ionization including back-bonding to the nitrosyl. The third ionization involves back-bonding to both the carbonyl and the nitrosyl. The first two ionizations of the iodide complexes show short vibrational progressions corresponding to the CO and NO stretches. The difference in stabilization of the metal levels by metal–carbonyl and metal–nitrosyl back-bonding is determined from the splitting between the first two ionization bands. The M–X π^* orbitals have increasing halogen character from the chloride complex to the iodide complex, but unlike for the previously studied Re(CO)$_5$X complexes, where the first ionization shifted from predominantly metal to predominantly halogen in proceeding from X = Cl to X = I, in this case the first three ionizations remain predominantly metal throughout. There is indication in one case of further delocalized interaction of the M–X π electrons with Cp-based electrons. The extent of delocalized and fluid electron density in these systems is in contrast to other systems like (η^5-C$_5$H$_5$)Fe(CO)$_2$X and (CO)$_5$ReX.

Introduction

Chiral rhenium complexes of the type CpRe(NO)(L)X[1–4] provide easily accessed templates in which metal–ligand interactions can be systematically probed. Many of these formally octahedral compounds are readily prepared in optically active form[5,6] and undergo stereospecific or highly stereoselective transformations.[7–9] In particular, the recent discovery of unusual cationic alkyl halide complexes of the formula[10] [CpRe(NO)(PPh$_3$)(XR)]$^+$BF$_4^-$ prompted interest

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* To whom correspondence should be addressed.

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