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Oxo Chemistry in Supercritical Carbon Dioxide

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INTRODUCTION

Because of their unique physical properties, supercritical fluids are a potentially ideal media for conducting homogeneous catalytic processes that involve the reaction of gases with soluble liquids or solid substrates. The absence of a gas-liquid interface eliminates interfacial diffusion and the gas-like viscosities minimize diffusional times through the fluid phase. Quite often these diffusional processes are the rate limiting step in liquid solvent systems. Reactive gas concentrations in supercritical media are typically much higher than in normal liquids. For example, the concentration of H_2 in supercritical CO_2 at 25°C and a partial pressure of 300 atm is 12 M (completely miscible), whereas, in water and in *n*-heptane it is 0.23(1) and 1.8 M(2), respectively, under these conditions. In addition, the liquid-like densities which are achievable with supercritical fluids, greatly facilitate the dissolution of many liquids and solids. Since the solubility of dissolved species in a supercritical fluid is density-dependent,(3) separation of the various reaction components may be achieved by pressure, and hence density, alteration.

We have begun an investigation of the cobalt carbonyl-catalyzed oxo process in supercritical CO_2 using *in situ* high pressure NMR spectroscopy. The use of supercritical CO_2 as the solvent media eliminates gas-liquid mixing problems which have complicated some of the earlier research.(4) The effect of supercritical CO_2 on the oxo reaction was determined by comparing the linear to branched aldehyde yield and rate and other equilibrium processes involved in the catalytic cycle with measured values in conventional liquid solvents.

In situ high-pressure NMR spectroscopy allows us to not only identify reaction intermediates and measure their concentration under actual reaction conditions, but also to determine rate constants and relevant thermodynamic quantities for various processes involved in the catalytic cycle. To accomplish this we have developed a home-built pressure probe which uses a toroid detector. Because of its internally confined magnetic flux, the toroid detector in pressure probes has certain advantages over the Helmholtz or solenoid detectors normally used in NMR. One advantage is improved sensitivity by reducing magnetic coupling to the metal pressure vessel. A second advantage is the selective measurement of gaseous or dissolved species within the detector coil while minimizing interference from undissolved solids or liquids exterior to it. In addition, the physical properties of supercritical fluids are of great value in high-pressure NMR. Due to the low viscosity of supercritical fluids, the rotational correlation times and, therefore, line widths of quadrupolar nuclei, such as ^{59}Co, are significantly decreased.(5) This increased sensitivity allows direct observation of the cobalt species present in the oxo reaction, $RC(O)Co(CO)_4$, $HCo(CO)_4$, and $Co_2(CO)_8$, without complications stemming from absorption band overlaps which are frequently observed in techniques such as infrared spectroscopy.

RESULTS AND DISCUSSION

A. Hydrogenation of Dicobalt Octacarbonyl

In the presence of H_2, the equilibration of $Co_2(CO)_8$ and $HCo(CO)_4$ occurs according to eq. 1.

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

The equilibrium in CO_2 occurred reproducibly when approached from either the forward or reverse directions of eq. 1. The equilibrium constants ($K_{eq} = 0.025$, $K_p = 8.8 \times 10^{-3}$ M atm^{-1}) were measured at 80°C in supercritical CO_2 ($\rho = 0.5$ g/mL) with 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). The observed K_p compares favorably to the literature K_{eq} values reported by Penninger et al.(6) for *n*-heptane ($K_{eq} = 0.124$) and Mirbach(7) for methylcyclohexane ($K_{eq} = 0.17$) when these values are converted to K_p values, 7.7×10^{-4} and 8.8×10^{-4} M atm^{-1}, respectively. The closer correspondence of the K_p values for liquids and supercritical CO_2 apparently stems from the activity of the 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 $Co_2(CO)_8$ in supercritical CO_2 are comparable to the rate constants measured in conventional hydroformylation solvents. At 80°C in supercritical CO_2 ($\rho = 0.5$ g/mL) at nearly constant hydrogen pressure ($P_{H2} = P_{co} = 41$ atm, $[Co_2(CO)_8] = 0.0168$ M), a second-order rate constant for the forward reaction of $k_1 = 1.6 \times 10^{-6}$ atm^{-1} s^{-1} was observed by measuring the decrease in $Co_2(CO)_8$ concentration with time far from equilibrium. From this rate constant and the equilibrium constant, a second-order rate constant for the reverse reaction of $k_{-1} = 1.8 \times 10^{-3}$ M^{-1} s^{-1}, was obtained. These rate constants are in good agreement with those reported by Mirbach(8) 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}).

Equilibrium constants for the hydrogenation of dicobalt octacarbonyl were measured at two different initial concentrations of $Co_2(CO)_8$ (0.0171 and 0.0481 M) at 20°C intervals for the temperature range of 60-180°C. The equilibrium constants measured at the two concentrations agreed closely, with the largest discrepancy being 11% at 160°C. The enthalpy and entropy changes for the reaction, 4.7 ± 0.2 kcal/mol and 4.4 ± 0.5 cal/mol·K, respectively, were determined from a van't Hoff plot. Since the activities of the gases are more closely related to their pressures than their concentrations, defining the standard state of hydrogen as 1 atm pressure provides more meaningful enthalpy and entropy changes. Using the hydrogen pressure as the standard state, the enthalpy and entropy changes become 4.0 kcal/mol and -4.2 cal/mol·K, respectively, which agree closely with Ungvary's results(2), $\Delta H° = 4.3$ kcal/mol and $\Delta S° = -2.6$ cal/mol·K.

B. Hydroformylation of Propylene

At 80°C in supercritical CO_2 ($\rho = 0.5$ g/ml) and the initial reactant loadings, $[Co_2(CO)_8] = 0.017$ M, $P_{H2} = P_{CO} = 42$ atm, $[C_3H_6] = 0.14$ M, the hdyroformylation of propylene proceeds cleanly, yielding only the expected *n*- and iso-butyraldehyde products. The ratio of the normal to iso butyraldehyde yield is 7.3 which is an improvement over the ratio of 4.9 measured in benzene(8) at slightly higher initial pressures, $P_{H2} = P_{CO} = 80$ atm, and Co loading, $[Co_2(CO)_8] = 0.026$ M. The yield of each isomer was determined by integration of their characteristic proton signals near δ = 9.6 ppm and 9.8 ppm for *n*- and iso-butyraldehyde, respectively. At the relatively low temperatures employed, hydrogenation of the propylene to produce propane or of the aldehyde isomers to produce the corresponding alcohols is insignificant, and *in situ* ^1H and $^{13}C\{^1H\}$ spectra did not detect any other products.

The cobalt species present during the course of the reaction were monitored by means of ^{59}Co spectra for $Co_2(CO)_8$ and $HCo(CO)_4$ at -2200 and -3030 ppm, respectively (saturated aqueous $K_3Co(CN)_6$ = 0.0 ppm).(9) A small, assymmetrical peak near -2030 ppm corresponds closely with the chemical shift value obtained for n-$C_3H_7C(O)Co(CO)_4$ in tetrahydrofuran. The assymmetry of this peak might stem from both normal and iso derivatives. No other cobalt species, including $Co_4(CO)_{12}$, were detected. The cobalt complexes reached a near steady-state condition early in the hydroformylation reaction which persisted until nearly all of the propylene was consumed, which required approximately 15 hours. During this period the $HCo(CO)_4$ concentration is maintained below its equilibrium value.

A rate of d[aldehyde]/dt = 0.77×10^{-5} M s^{-1} was measured for propylene hydroformylation in supercritical CO_2 system (initial conditions: $[C_3H_6]$ = 0.53 M, $[Co_2(co)_8]$ = 10.5 mM, $P_{H2} = P_{CO}$ = 56.1 atm) which compares favorably with the rate observed by Mirbach(7), 1.2×10^{-5} M s^{-1} for 1-

octene hdyroformylation in methylcyclohexane (initial conditions: $[C_8H_{16}]$ = 0.83 M, $[Co_2(co)_8]$ = 6.6 mM, $P_{H2} = P_{CO}$ = 47.5 atm).

Because it is known that the hydroformylation reaction is not very sensitive to solvent effects(10), the similar rate and selectivity observed between the supercritical CO_2 and the conventional nonpolar liquid media is not unexpected, especially since the rate and equilibrium constants for the hydrogenation of $Co_2(CO)_8$, in supercritical CO_2 and liquids, such as methylcyclohexane and *n*-heptane, are nearly equal.

CONCLUSIONS

The cobalt-catalyzed hydroformylation of propylene in supercritical CO_2 proceeds well with rate and equilibrium values in good agreement with values measured in conventional hydrocarbon liquid media. One interesting observation is that the olefin hydroformylation reaction is faster than the rate of $HCo(CO)_4$ formation from $Co_2(CO)_8$.(7,11) The Heck and Breslow mechanism accounts for this by proposing an additional hydrogen activation occurs via the intermediate acyl complex.(7,12,13) However, other possibilities exist including other olefin complexes, odd-electron species, or clusters in the hydrogen activation mechanism. The observed coalescence of the ^{59}Co signals for $HCo(CO)_4$ and $Co_2(CO)_8$ near 200°C indicates a dynamic process that may involve the tetracarbonyl radical.

The supercritical fluid/toroid probe technique is advantageous for the measurement of thermodynamic parameters such as enthalpy changes. Since only one phase is present, corrections for liquid expansion/compression or determination of gas/liquid partitioning, often necessary for measurements in liquid media, are obviated in supercritical systems.

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