

SUPERCRITICAL CATALYTIC CO HYDROGENATION

J. W. Rathke,* M. J. Chen, and R. J. Klingler

Abstract

Cobalt carbonyl hydride catalyzed hydrogenation of carbon monoxide in a homogeneous supercritical carbon monoxide medium is reported for the first time. The reaction rate and products and the cobalt containing species associated with the catalytic reaction were measured in situ at 180 and 200 °C and at total pressures of hydrogen and carbon monoxide near 260 atm using a high-pressure nuclear magnetic resonance (NMR) probe. The second order rate constant at 200 °C, $12 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$, measured in supercritical carbon monoxide is close to the reported value for the nonpolar solvent, benzene ($15 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$) and considerably smaller than that reported in the more polar solvent, 2,2,2-trifluoroethanol ($84 \times 10^{-8} \text{ s}^{-1} \text{ atm}^{-1}$). The products of the reaction including methanol and methyl formate were quantified by in situ ^1H NMR, while in situ ^{59}Co NMR revealed cobalt carbonyl hydride and dicobalt octacarbonyl as the only detectable cobalt species. Separate experiments established that the homologation of methanol, the pathway for production of higher alcohols under CO hydrogenation conditions in polar solvents, did not occur to a measurable extent in the nonpolar supercritical CO medium used here.

Introduction

Considerable research on homogeneous catalysts for the hydrogenation of CO was undertaken in several laboratories in the late 1970's and early 1980's. Work on these systems has been reviewed (1,2). The most studied of homogeneous CO hydrogenation catalysis systems is the cobalt carbonyl catalyzed reaction (3), which has been shown to follow a rate law that is first order in both $\text{HCo}(\text{CO})_4$ and H_2 pressure (4). The reaction is believed to proceed through an early coordinated formaldehyde intermediate which produces, dependent upon the reaction conditions and solvent, variable amounts of methanol, methyl formate, and ethylene glycol as initial reaction products. In the proposed mechanism, higher alcohols and higher formate esters are produced by secondary homologation and transesterification reactions associated mainly with the initially produced methanol and methyl formate (4, 5).

Since most of the early kinetic studies on these systems were accomplished using high-pressure autoclaves, it seems possible that recent advances in high-pressure spectroscopic techniques that would allow in situ scrutiny of these systems might provide more information on them, today. Here we test the use of a high-pressure toroid NMR probe on the cobalt carbonyl catalyzed CO hydrogenation in supercritical carbon monoxide medium for the first time. Use of a single-phase homogeneous supercritical system containing catalyst and

reactant gases was utilized to avoid gas-liquid mixing problems that might otherwise interfere with kinetic studies in an unstirred NMR pressure vessel using conventional liquid media.

Experimental Section

^1H and ^{59}Co NMR spectra were recorded using a General Electric GN 300 spectrometer equipped with an 89-mm Oxford magnet at 300.5 and 71.1 MHz, respectively. The measurements employed a variable temperature multinuclear high-pressure Be-Cu NMR probe containing an internal toroid detector that was designed in-house and has been described previously (6). Kinetic studies were initiated by loading fresh samples of $\text{Co}_2(\text{CO})_8$ (purchased from Alfa and stored under refrigeration) into the pressure probe in a helium atmosphere glove box. The probe was then pressurized with the requisite gases and heated to the desired temperature. Pressures were measured to within ± 0.07 atm using a strain gauge pressure transducer (Omega Model PX302-5KGV). Temperature control utilized a copper-constantan thermocouple built into the probe and was constant to within ± 0.1 . Measured temperatures agreed to within ± 1.0 °C with independent chromel-alumel thermocouple measurements covering the range 25-175 °C. Concentrations of $\text{HCo}(\text{CO})_4$, CH_3OH , and $\text{CH}_3\text{O}_2\text{CH}$ were measured by integration of their ^1H NMR signals at $\delta = -11.8$, 3.36, and 3.60 PPM, respectively, relative to the ^1H signal for H_2 at 4.45 PPM (TMS = 0.0 PPM). Absolute concentrations of each species were determined on the basis of the known concentration of H_2 , which was calculated from its pressure using the ideal gas law. First-order rate constants were determined in accord with earlier work (4, 5) from the slope of linear plots of the sum of the molar concentrations of the organic reaction products vs. time. Note that this rate differs from the overall rate of CO consumption, but instead is a measure of the rate of conversion of a putative formaldehyde complex, which is believed to be at or near the transition state of the catalytic process (5). Second-order rate constants were obtained by dividing the slopes of the first-order rate plots by the hydrogen pressure, $P(\text{H}_2)$, and the measured concentration of $\text{HCo}(\text{CO})_4$, which varied due to sampling methods used in the earlier work (5), but which was constant during the in situ experiments described here. Cobalt containing species were also monitored using ^{59}Co NMR spectra recorded between the ^1H NMR measurements. Signals for $\text{Co}_2(\text{CO})_8$ at -2200 PPM and $\text{HCo}(\text{CO})_4$ at -3000 PPM (external $\text{K}_3\text{Co}(\text{CN})_6 = 0.0$ PPM) were the only ones observed during the CO hydrogenation experiments.

Higher alcohols and ethylene glycol were not produced in detectable quantities in the supercritical CO medium. Separate experiments established that $\text{HCo}(\text{CO})_4$ catalyzed homologation of methanol, responsible for higher alcohol production in more polar media under CO hydrogenation conditions, does not occur to a significant extent in supercritical CO. Thus, methanol (430mg) and $\text{Co}_2(\text{CO})_8$ (50 mg) were heated to 180 C with $P(\text{H}_2) = 108$ atm, $P(\text{CO}) = 152$ atm, for 70 hours in the NMR probe without detectable production of ethanol.

Results and Discussion

The $\text{HCo}(\text{CO})_4$ catalyzed hydrogenation of carbon monoxide is an extremely sluggish reaction that requires long reaction times even at high-pressures and temperatures. At 180 °C, the small ^1H NMR signals from the organic products were difficult to resolve from the baseline of the large signal due to H_2 at the high pressure required for reaction. However, ^{59}Co NMR spectra showed substantial and well separated signals for $\text{HCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$, even at concentrations used here of ≤ 0.01 M. Typical in situ ^1H and ^{59}Co NMR spectra measured during CO hydrogenation at 180 °C are shown in Fig. 1. Although 180 °C is probably near the lowest temperature useful for rate measurements by this method, the resultant rate plots in Fig. 2 are quite linear, and yield a second-order rate constant, $k(2) = 4.8 \times 10^{-8} \text{ atm}^{-1} \text{ s}^{-1}$, as shown in Table 1. The reaction has a substantial temperature coefficient, and at 200 °C the reaction is significantly faster and more easily measurable, with $k(2) = 12 \times 10^{-8} \text{ atm}^{-1} \text{ s}^{-1}$. As expected, this latter value agrees well with the rate constant for another non-polar medium, benzene, for which $k(2)$ was measured at $15 \times 10^{-8} \text{ atm}^{-1} \text{ s}^{-1}$ at 200 °C, albeit using high- pressure autoclave methods (4).

Conclusions

The results reported here show that the rate of CO hydrogenation in supercritical carbon monoxide medium is comparable to that measured earlier in nonpolar benzene medium (4). Methanol homologation to produce higher alcohols and the production of ethylene glycol are reactions favored by highly polar media (4,5) and did not proceed to any measurable extent in the nonpolar supercritical CO medium. The results also establish that kinetic studies of the homogeneous hydrogenation of carbon monoxide are feasible in a supercritical medium in a high-pressure NMR probe. This is the case, even though CO hydrogenation with the $\text{HCo}(\text{CO})_4$ catalyst normally requires long reaction times under severe pressure and temperature conditions.

In future work on this system, accurate determinations of such parameters as activation barriers and kinetic isotope effects, afforded by high-pressure NMR in a gas-like medium that is highly amenable to theoretical calculations will allow scrutiny of the early steps in this important reaction. The earlier work with autoclaves had established a strong temperature coefficient and a significant isotope effect on this system, but the uncertainties and complexities associated with sampling from autoclaves discouraged attempts to accurately determine these parameters with the high-pressure techniques available at that time. Evaporation of the volatile $\text{HCo}(\text{CO})_4$ into the autoclave headspace increased by removal of liquid samples, and uncertain quenching of samples containing this unstable species are problems associated with autoclave sampling methods that are alleviated by the high-pressure NMR technique used here.

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Table 1
Second-order rate constants, $k(2)$, for CO hydrogenation in various solvents.

Solvent	Temp., °C	P (H ₂), atm	P (CO), atm	[HCo(CO) ₄], M	$k(2)$, atm ⁻¹ s ⁻¹
benzene	200	145	145	See Ref. 4	15 x 10 ⁻⁸
1,4-dioxane	196	148	148	See Ref. 4	25 x 10 ⁻⁸
CF ₃ CH ₂ OH	200	153	153	See Ref. 4	84 x 10 ⁻⁸
scCO	200	103	156	10 x 10 ⁻³	12 x 10 ⁻⁸
scCO	180	103	156	6.0 x 10 ⁻³	4.8 x 10 ⁻⁸

Figure 1
In situ ⁵⁹Co NMR spectrum (upper trace) and ¹H NMR spectrum (lower trace) during CO hydrogenation in supercritical CO at 180 °C.

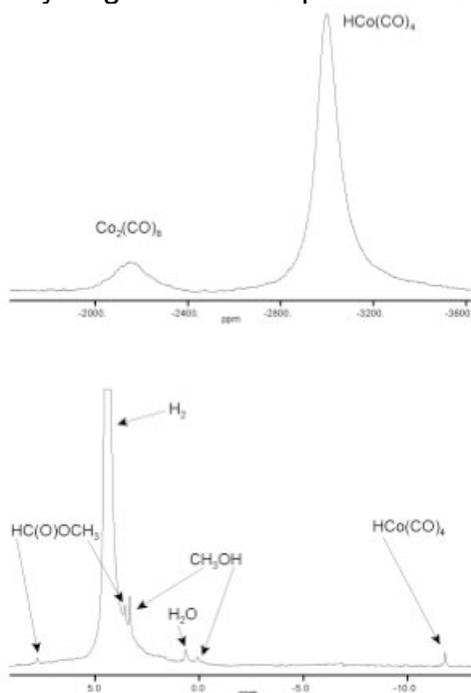


Figure 2

Rate plot showing the production of methanol, \blacktriangle , methyl formate, \blacksquare , and their sum, \bullet , from CO hydrogenation in supercritical CO at 180 °C.

