Rational Mechanism for Homogeneous Hydrogenation of Carbon Monoxide to Alcohols, Polyols, and Esters

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Abstract: The products derived from synthesis gas conversions by homogeneous catalysis are concluded to be formed via the key intermediate formaldehyde. The intermediacy of formaldehyde is supported by reaction rate studies, comparison reactions of formaldehyde with synthesis gas, and the trapping of formaldehyde and glycolaldehyde intermediates during a reaction as their ethylene glycol acetals. Although the formation of formaldehyde from synthesis gas is thermodynamically unfavorable, it is argued that the concentration of formaldehyde permitted by thermodynamics is more than sufficient for a transient intermediate. The overall mechanism incorporates only steps that are already well established in the science of homogeneous catalysis.

Introduction

A growing interest in the application of homogeneous catalysis to synthesis gas conversions has been triggered by two principal stimuli. First, homogeneous catalysts could potentially offer several advantages over the traditionally used heterogeneous catalysts: namely, higher selectivities to more desirable products, improved reproducibility and controllability of the catalyst, a greater tolerance to sulfur- and nitrogen-containing poisons, and a resistance to carburization. Second, homogeneous catalytic phenomena are more easily studied and interpreted, thus allowing a better fundamental understanding of the reaction chemistry. This knowledge could be useful in designing improved catalytic systems (including heterogeneous processes) for chemicals and fuels production from synthesis gas.

The most thoroughly studied homogeneous synthesis gas conversions are those catalyzed by carbonyl complexes of cobalt,[1-6] ruthenium,[7] and rhodium[4,8,9] under high-pressure conditions. Reports of homogeneous catalysis by manganese,[2] iron,[5] nickel,[5] palladium,[5] osmium,[5,10] iridium,[5,10,11] and platinum[5] complexes have also appeared, but the activities are generally lower. We found that at 225 °C and ~2585 atm in a clean reactor, $V(CO)_6$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Mo(CO)_6$, $Re_2(CO)_{10}$, and $Ir_4(CO)_{12}$ each converted only a very small amount of synthesis gas to methanol, while $Os_3(CO)_{12}$ was inactive.[12] Reliable, reproducible results were obtained only when the autoclave reactor and stirrer were *rigorously* cleaned between experiments (see Experimental Section for details).

Unlike conventional heterogeneous Fischer–Tropsch catalysts, which yield complex mixtures of hydrocarbon and oxygenated hydrocarbon products, the three homogeneous catalysts cited above display an extraordinary preference for producing oxygenated products. For cobalt and rhodium, methanol and ethylene glycol are usually the major primary products, while ruthenium produces only methanol. Depending upon the conditions, methanol homologation to higher alcohols can sometimes be an important secondary reaction. Formate esters of the products are also observed. Since the three soluble catalysts yield primarily the same products, it is reasonable to expect that a common mechanism operates. Three recent review articles[13-15] have addressed the mechanism of Fischer–Tropsch synthesis from the viewpoint of organometallic step processes well established in homogeneous catalysis. Yet no consensus mechanism has emerged for alcohols synthesis.

Herein is proposed a unified mechanism which explains the entire spectrum of products and uses only conventional organometallic mechanistic concepts. A basic and controversial component of the mechanism is the participation of formaldehyde as the key intermediate from which all products derive. Experimental support for this proposal is drawn from rate data, comparison reactions of formaldehyde with synthesis gas, and chemical trapping experiments.

Results and Discussion

Rate Studies. Due to experimental difficulties in obtaining reliable rate data at high pressures, rate measurements were approached from several directions to ensure confidence in the results. When a tetraglyme solution charged with $Co_2(CO)_8$ was held at 200 °C under an equimolar mixture of carbon monoxide and hydrogen, a smooth first-order uptake of gas occurred, causing the pressure to drop from 136 to 116 atm over 6 h (Figure 1). Figure 1 also displays the results of a similar experiment at higher pressure where the pressure fell from 2041 to 1361 atm, also in a first-order fashion. In both experiments, the catalyst's activity has obviously remained constant with respect to time. This aspect was further demonstrated in an experiment where the pressure was maintained at 313 atm and the reaction mixture was sampled at regular intervals. The product composition during the reaction is shown in Figure 2. When these data are replotted in terms of products or product fragments derived from ethylene glycol (the ethylene glycol acetal of acetaldehyde) and from methanol (all the products except the ethylene glycol fragment), Figure 3 is obtained. The plot clearly illustrates how the selectivity and activity of the catalyst remain constant for the duration of the reaction.[16] The plot further shows that ethylene glycol is a primary reaction product and is not formed from methanol. A series of additional experiments was performed at constant pressures, and the final product compositions were determined. Since the catalyst's activity was previously shown to be constant with time, the product yields are directly related to reaction rates. This allows the dependence of reaction rate on pressure to be deduced, and it is shown in Figure 4. In agreement with the data

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(1) Gresham, W. F. U.S. Patent 2636046 (to E. I. duPont), 1953.

(2) Rathke, J. W.; Feder, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 3223.

(3) Feder, H. M. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 45. Feder's article had not yet appeared when the manuscript to the present paper was completed. **Note Added In Proof.** Feder's article, coauthored by J. W. Rathke, has now been published, and it is in general agreement with the present work.

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(16) The selectivity and activity of the rhodium catalyst are also constant during reactions: Kaplan, L. Presented at the 179th National Meeting of the American Chemical Society, Houston, Texas, March 1980; PETR No. 16.

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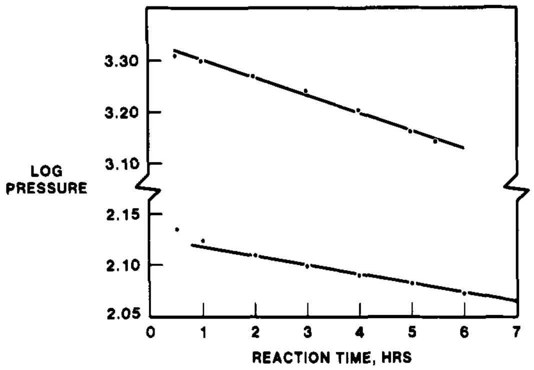

Figure 1. Synthesis gas pressure as a function of time for cobalt-catalyzed reactions.

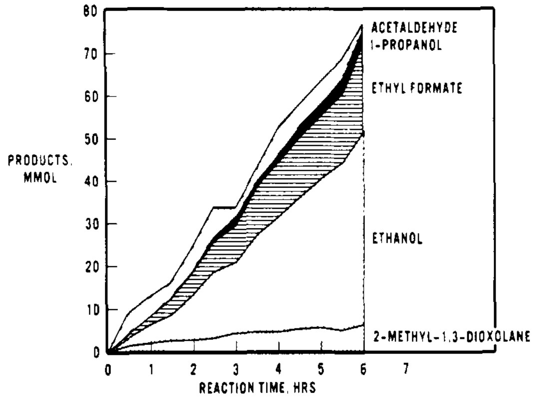

Figure 2. Product formation as a function of time for a cobalt-catalyzed reaction at 313 atm.

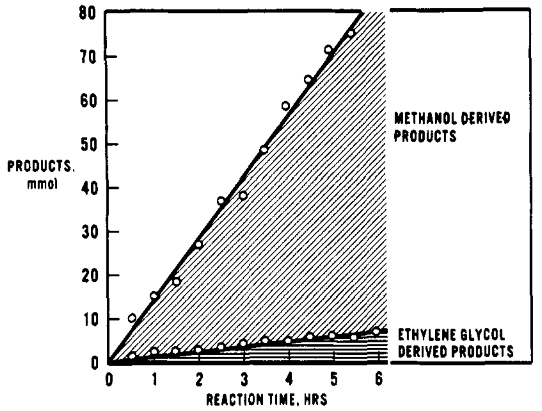

Figure 3. Data from Figure 2 replotted to illustrate the constant formation rates of methanol and ethylene glycol.

in Figure 1, a first-order dependence on pressure is observed. Feder has made similar studies within a narrower pressure range and has reached the same conclusion.[17] By using varying CO/H_2 ratios, he also was able to define more precisely the pressure dependence, namely, that the reaction is first order in hydrogen and zero order in carbon monoxide. As the rate of total products formation increases with increasing pressure, so does the ethylene glycol/methanol molar ratio. This ratio is 0.10, 0.19, and 0.60 at 313, 1361, and 1973 atm, respectively. This conclusion assumes the selectivity remained constant during each high-pressure reaction as it did in the 313-atm experiment. Sampling during high-pressure experiments was precluded by safety regulations. Since the two product formation rates increase nonuniformly with pressure while the total products formation rate increases linearly with pressure, *ethylene glycol and methanol must derive from a common intermediate whose rate of formation is linearly related to the pressure.* To have the two product formation rates independently vary with pressure, both in a complex way, and yet still have the total products formation rate accidently show a first-order dependence on pressure over such a broad pressure range is highly unlikely.

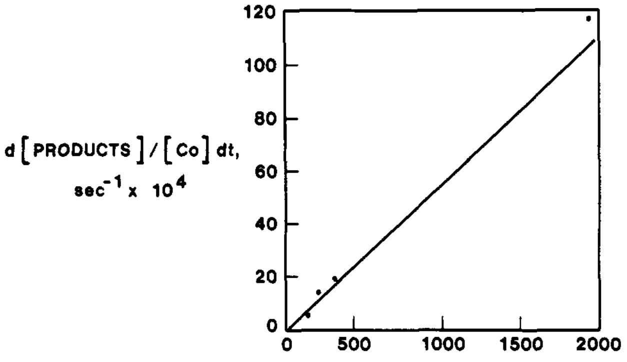

Figure 4. Rate of cobalt-catalyzed total products formation as a function of pressure.

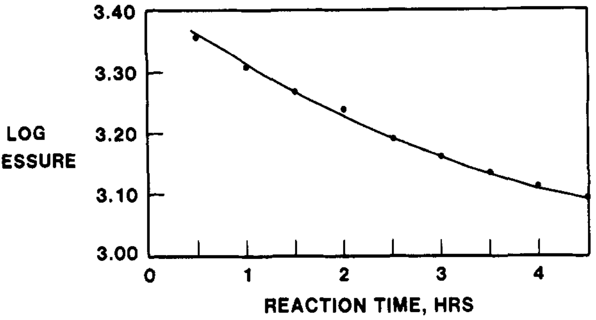

Figure 5. Synthesis gas pressure as a function of time for a rhodium-catalyzed reaction.

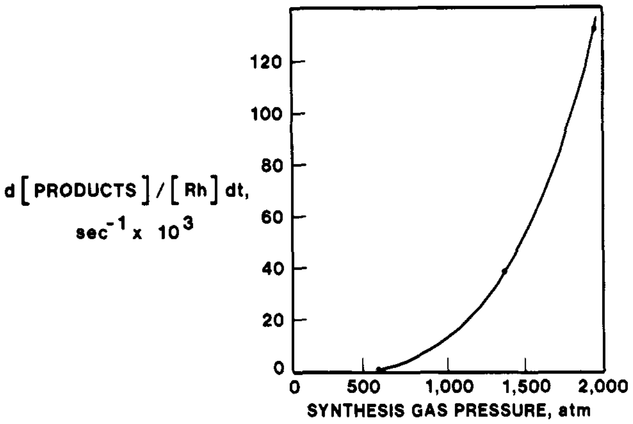

Figure 6. Rate of rhodium-catalyzed total products formation as a function of pressure.

The uptake of synthesis gas by a tetraglyme solution containing a rhodium catalyst, initially introduced as $Rh(CO)_2acac$, and 2-hydroxypyridine promoter is shown in Figure 5 on a log pressure plot. The pronounced curvature of the data is indicative of a reaction that is higher than first order in pressure. As was done for the cobalt system, experiments at several pressures (each maintained constant) were performed and product compositions were determined upon termination of each experiment. Since the selectivity and activity of this catalyst remain constant throughout a reaction,[16] the product yields are directly related to reaction rates. A plot of total products formation rate vs. pressure is illustrated in Figure 6. The rate is proportional to the pressure taken to the 3.3 power (calculated by a statistical fit to a power curve with an estimated uncertainty of ±0.5). This unusual relationship likely is attributable to the pressure-dependent equilibria between

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[17] This dependency was revealed by a referee of an earlier manuscript, who cited unpublished ref 3.

Table I. Cobalt-Catalyzed Reactions of Paraformaldehyde with Synthesis Gas[a]

	expt 1	expt 2
paraformaldehyde (CH_2O mequiv)	667	333
products, mmol		
methanol	219	94
methyl formate	3	1
ethanol	11	22
1-propanol	<1	<1
2-methoxyethanol	5	5

[a] Both experiments were performed with 1.0 mmol of $Co_2(CO)_8$ and 2.0 mmol of PEt_3 in 40 mL of tetraglyme and an initial pressure of 170 atm at 25 °C. Experiment 1 was held at 150-170 °C for 2.5 h and then at 220-225 °C for 2 h. Experiment 2 was held at 205 °C for 5 h.

Table II. Products from a Rhodium-Catalyzed Synthesis Gas Reaction at 1973 atm[a]

product	yield, mmol
methanol	284
methyl formate	52
ethanol	191
ethyl formate	20
1-propanol	121
1-propyl formate	29
1-butanol	<31
ethylene glycol	1000
ethylene glycol monoformate	118
propylene glycol	118
glycerol	120
1,3-dioxolane	2
2-(hydroxymethyl)-1,3-dioxolane	20

[a] The experiment was performed with 1.0 mmol of $Rh(CO)_2acac$ and 5 mmol of 2-hydroxypyridine in 100 mL of tetraglyme at 230 °C for 4.5 h. Several other minor products (most of them unidentified) were also present.

Table III. Thermodynamic Parameters for Formaldehyde Formation from Synthesis Gas[a]

conditions	ΔH, kcal/mol	ΔG, kcal/mol	K
25 °C, 1 atm	−1.3	8.27	8.69×10^{-7} atm^{-1}
227 °C, 1 atm		13.83	9.02×10^{-7} atm^{-1}
200 °C, 1361 atm			9×10^{-5} L mol^{-1}

[a] The first two lines of data assume ideal-gas behavior. The third K value was determined from enthalpy and entropy changes calculated with the SRK equation of state. These calculations were kindly performed by Dr. George H. Thomson (Phillips Petroleum Co.), to whom I am deeply appreciative.

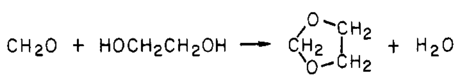
rhodium carbonyl clusters in solution[8,9,18] so that the set of cluster complexes present at each pressure will differ. As a result the rate dependence on pressure cannot be rigorously interpreted, and, at a molecular level, the rate dependence on pressure for each catalytically active species remains uncertain. The simple rate dependence on pressure shown by the cobalt-catalyzed reaction over a broad pressure regime suggests that a pressure-dependent clustering process is unimportant for this system.

Metal-Promoted Reactions of Formaldehyde with Synthesis Gas. When paraformaldehyde (as the source of formaldehyde) was allowed to react with synthesis gas at 200 °C in a tetraglyme solution containing a cobalt catalyst, methanol was produced as the major product while methyl formate, ethanol, 1-propanol, and 2-methoxyethanol were minor products. These same products were observed in the experiments with synthesis gas only, but the relative yields are now different. In addition, the presence of paraformaldehyde increased the product formation rate by a factor of 5. In contrast to the reactions with synthesis gas only, methanol formation now is more rapid than its homologation. When the paraformaldehyde concentration was halved in Table I, so was the yield of products. Several recent patents have described the cobalt- and rhodium-catalyzed reactions of paraformaldehyde with synthesis gas at lower temperatures. With cobalt, ethylene glycol was produced at 160 °C[19] and glycolaldehyde at 110 °C.[20] Both of these products are also formed with rhodium catalysts where methanol is also mentioned as a coproduct.[21,22] Especially revealing is a report on stoichiometric reactions of $HCo(CO)_4$ with monomeric formaldehyde at 0 °C and 1 atm of CO.[23] After hydrolysis, 60–90% yields of glycolaldehyde were obtained (eq 1). Neither methanol nor its formate ester was observed.

$$CH_2O + HCo(CO)_4 \xrightarrow[0\ ^\circ C,\ CH_2Cl_2]{1\ atm\ of\ CO} \xrightarrow{H^+} HOCH_2CHO \quad (1)$$

The above experiments demonstrate that formaldehyde can serve as a precursor to both methanol and ethylene glycol and, further, that either cobalt or rhodium complexes can catalyze the process. It also appears that ethylene glycol (or glycolaldehyde) makes up a higher percentage of the reaction products at lower temperatures.

Chemical Trapping of Reaction Intermediates. In some reactions where both ethanol and ethylene glycol were produced, 2-methyl-1,3-dioxolane was found among the products. This product is the ethylene glycol acetal of acetaldehyde (the ethanol precursor), and its formation is sufficiently favorable that, in at least one of the cobalt-catalyzed reactions, the total ethylene glycol product was tied up as the acetal of acetaldehyde. The tendency for acetal formation during the reaction suggested that, if formaldehyde was formed in the presence of ethylene glycol, it might also be intercepted as an acetal. To test this idea, a reaction was performed at a very high pressure (1973 atm), where the steady-state concentration of formaldehyde would be maximized, and with a rhodium catalyst that produces high yields of ethylene glycol. The product mixture for this reaction is given in Table II. 1,3-Dioxolane, the ethylene glycol acetal of formaldehyde (eq 2), was identified as one of the minor products. In addition,



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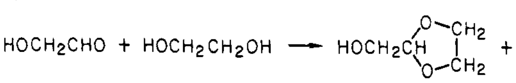
and perhaps just as significant, 2-(hydroxymethyl)-1,3-dioxolane was also found, showing that glycolaldehyde had also been present (eq 3). Neither of these acetals nor the parent aldehydes had



(3)

previously been described as products in catalytic synthesis gas conversions. The detection of the glycolaldehyde acetal strengthens the case for a formaldehyde intermediate in light of the results discussed in the preceding section.

Thermodynamic Considerations. The conversion of synthesis gas to formaldehyde is a thermodynamically unfavorable process. Because of this, formaldehyde has not been regarded as a credible intermediate in synthesis gas conversions (a formaldehyde complex has been proposed as a viable intermediate).[13] While this thermodynamic limitation precludes formaldehyde from being a significant reaction product, it does not forbid its production in kinetically significant amounts and its participation as a reaction intermediate. Table III presents thermodynamic data for formaldehyde formation at several temperature/pressure combinations. The equilibrium constant, K, for eq 4 is both temperature and

$$CO(g) + H_2(g) \overset{K}{\rightleftharpoons} CH_2O(g) \quad (4)$$

pressure dependent. On the basis of the value of K at 1361 atm and 200 °C, the maximum amount of formaldehyde that can be

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(21) Goetz, R. W. German Offen. 2741589, 1978; *Chem. Abstr.* **1978**, *88*, 190089.

(22) Wall, R. G. U.S. Patent 4144401 (to Chevron Research), 1979.

(23) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *172*, C27.

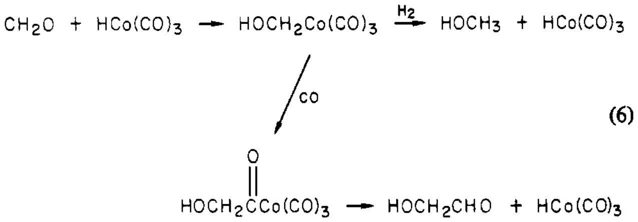
present in our 300-mL autoclave (the amount of CO and H_2 has been experimentally determined under these conditions) is 4 mmol. The actual product formation rate under these conditions is 25 (mmol/mmol of Co)/h. The rhodium-catalyzed rate is about sixfold faster. With the knowledge that formaldehyde readily reacts with synthesis gas in the presence of cobalt or rhodium catalysts, these product formation rates are well within the realm of possibility for even a much lower steady-state concentration of formaldehyde. The intermediacy of formaldehyde is, therefore, compatible with the thermodynamics of the system. The proposal that formaldehyde only exists complexed to the catalyst is rendered unnecessary. The production of a formaldehyde acetal (vide supra) argues that the formaldehyde is uncomplexed.

Overall Mechanism. (A) Rate-Determining Step. If the equilibrium in eq 4 is established and the rate-determining step occurs in a subsequent event, the reaction rate would most likely display a complex dependence on pressure. Since the reaction is first order in pressure (first order in hydrogen and zero order in carbon monoxide), equilibrium 4 is not satisfied, and the rate-determining step occurs earlier. A proposal consistent with the pressure dependence is shown in eq 5, where the rate-determining step is hydrogenolysis of the formyl complex.

$$HCo(CO)_4 \rightleftharpoons OHCCo(CO)_3 \xrightarrow[\text{rds}]{H_2} CH_2O + HCo(CO)_3 \qquad (5)$$

This implies that the steady-state concentration of formaldehyde will be less than that permitted by the equilibrium constant and that formaldehyde reacts further as rapidly as it is formed. Since all the products are believed to be derived from formaldehyde, the rate of total products formation is actually equivalent to the rate of formaldehyde formation.

(B) Formaldehyde Reaction Paths. Once formaldehyde is formed, readdition of the metal hydride can occur in either of two directions to yield either a hydroxymethyl- (eq 6) or a methoxy–cobalt (eq 7) intermediate. The direction of addition is presumably temperature dependent, since the ethylene glycol/methanol product ratio is temperature dependent. The products from eq 6 and 7 are methanol, methyl formate, and glycolaldehyde. Glycolaldehyde was never observed as a product in our reactions, but its ethylene glycol acetal was.



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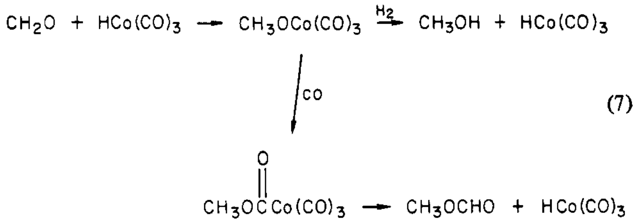

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Knowledge of the precise details of how the metal hydride adds to formaldehyde would be useful in predicting the preferred direction of the addition. If the addition is nonradical, then the polarity of the metal hydride bond could determine the direction with the acidic $HCo(CO)_4$ complex preferentially yielding $HOCH_2Co(CO)_4$. If the process involves radicals, hydrogen atom transfer to formaldehyde would preferentially yield $\cdot CH_2OH$ since this radical is estimated to be 9 kcal/mol more stable than $\cdot OCH_3$.[24] Collapse of $\cdot CH_2OH$ with its $\cdot Co(CO)_4$ partner will lead to the same $HOCH_2Co(CO)_4$ intermediate. The radical mechanism seems unlikely since the estimated activation enthalpy for such a process, ca. 26 kcal/mol,[25] suggests a very slow reaction for $HCo(CO)_4$ at 0 °C[26]—in contrast to the actual findings of Roth and Orchin.[23] Irrespective of how the intermediate is formed, it will then undergo hydrogenolysis or carbonylation/hydrogenolysis to yield either methanol or glycolaldehyde, respectively (eq 6). The competition between these two routes should be influenced by the carbon monoxide pressure, with carbonylation becoming more favored as the pressure is increased. This is consistent with experiment since the ethylene glycol fraction of the total products is greater at higher pressures. Dombeck[27] recently reported some model compound studies with **1**, **2**, and **3** that bear directly on this discussion.

$$\underset{\mathbf{1}}{(CH_3)_3CCOCH_2Mn(CO)_5} \qquad \underset{\mathbf{2}}{CH_3CH_2OCH_2Mn(CO)_5}$$
$$\underset{\mathbf{3}}{CH_3Mn(CO)_5}$$

These compounds were subjected to elevated temperatures at varying hydrogen pressures, and a carbonylation/hydrogenolysis process prevailed, except at very low pressures, where only hydrogenolysis occurred.

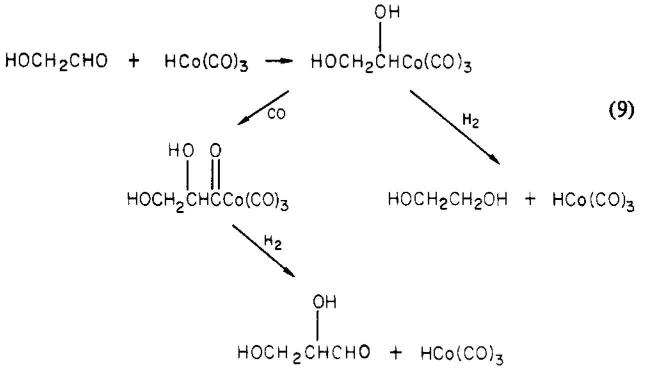
The methoxy intermediate in eq 7 will also undergo either hydrogenolysis or carbonylation/hydrogenolysis. The carbonylation process again should be more favored as the carbon monoxide pressure is increased, and the methyl formate to methanol ratio did increase with increasing pressure (see also ref 7). The competition between eq 6 and 7 and the pathways within them will most probably also be affected by additional factors not considered here.

The formation of methyl formate (and other formate esters) could conceptually also arise via interaction of the alcohol with a metal formyl (eq 8).[28]

$$ROH + OHCCo(CO)_3 \rightarrow ROCHO + HCo(CO)_3 \qquad (8)$$

However, the rate of formation of methyl formate is constant with time (see also ref 2 and 7) as the methanol concentration is increasing, so this process does not seem to be of much importance. When the alcohol concentration becomes significant, this process might play some role.

(C) Glycolaldehyde Reaction Paths. Once glycolaldehyde is formed, it will reinteract with the catalyst in a fashion similar to formaldehyde. This is shown in eq 9 and 10. The dominant direction of metal hydride addition to the aldehyde function will be dictated by the factors previously discussed plus an additional steric effect favoring eq 10. Once the addition occurs, the in-



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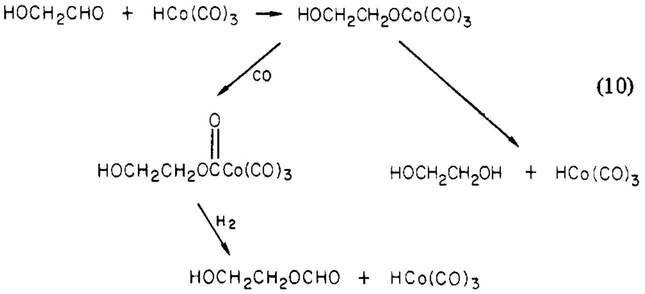

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(25) This value was estimated by the method outlined in ref 26.

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Table IV. Synthesis Gas Conversion Experiments

	run						
	1	2	3[a]	4	5	6	7
catalyst, mmol	$Co(OAc)_2$, 5	$Co(OAc)_2$, 5	$Co_2(CO)_8$, 1	$Co_2(CO)_8$, 1	$Co_2(CO)_8$, 1	$Rh(CO)_2acac$, 1	$Rh(CO)_2acac$, 1
promoter, mmol	$Ni(OAc)_2$, 6	$Ni(OAc)_2$, 5				2-PyOH,[b] 5	2-PyOH, 5
av press, atm	126	213	313	1361	1973	544	1361
temp, °C	200	190	200	230	230	230	230
time, h	6.0	4.0	6.0	4.0	4.0	4.0	4.0
products, mmol							
methanol	tr[c]	tr	tr	66	97	9	166
methyl formate	tr		tr	27	38		25
ethanol	52	94	45	39	39		11
ethyl formate	tr	4	20	14	9		1
1-propanol	9	8	3	4	10		2
1-propyl formate			tr		4		1
ethylene glycol				<29	103	5	323
ethylene glycol monoformate					23		11
propylene glycol					14		
glycerol							12

[a] Also analyzed in this reaction were acetaldehyde (3 mmol), 2-methyl-1,3-dioxolane (7 mmol), and methane (8 mmol). [b] 2-Hydroxypyridine. [c] Trace.

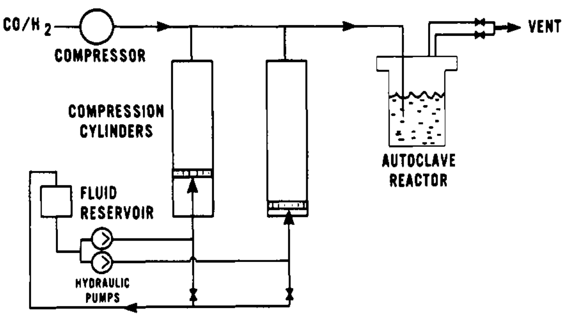
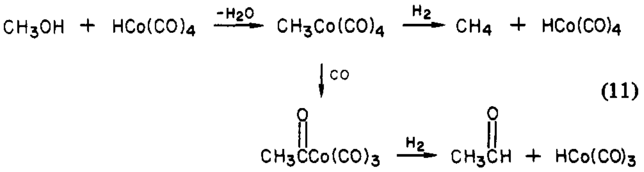


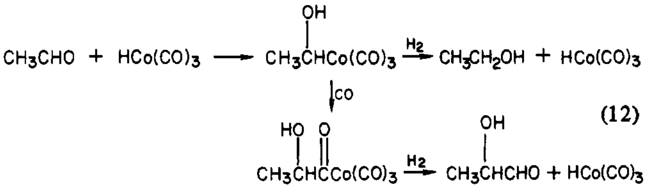
Figure 7. Schematic drawing of gas compression system.

termediates will undergo either hydrogenolysis or carbonylation/hydrogenolysis. These events produce ethylene glycol, ethylene glycol monoformate, and glyceraldehyde. Only the monoformate ester of ethylene glycol is predicted, exactly what was observed. The glyceraldehyde serves as a precursor to glycerol and, after further carbonylation, to erythritol. These latter two products have been observed in several instances.[4,9] The complex polyols are, therefore, formed via aldehyde intermediates by a sequence of conventional organometallic step processes and not via a continuously growing chain (as in coordination-catalyzed olefin polymerization).

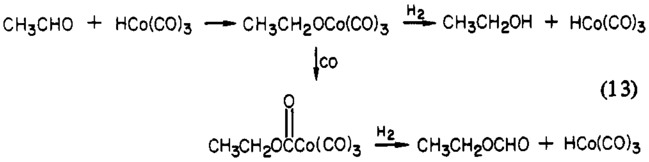
(D) Alcohol Homologation. The principal products described in the preceding mechanistic discussion, methanol and ethylene glycol, may be regarded as the primary products of the reaction. Nearly all of the other products found in the reaction, but not yet discussed, are derived from methanol. The cobalt-catalyzed homologation of alcohols with synthesis gas has been known for 30 years,[29,30] and at least 21 products have been identified from the homologation of methanol.[31] Acetaldehyde has been concluded to be a primary intermediate in the methanol reaction[30,32] which suggests the process shown in eq 11. The methane predicted by eq 11 was found among the products in a 4 mol % yield in the experiment conducted at 313 atm. The acetaldehyde, which was frequently observed in very small amounts, will react further with the catalyst via eq 12 and 13 in a fashion similar to the glycolaldehyde reactions. Again, hydrogenolysis or carbonylation/hydrogenolysis of the initial adduct leads to the products ethanol, ethyl formate, and 2-hydroxypropionaldehyde. The ethanol/ethyl formate mole ratio remains fairly constant with time, consistent with the mechanism. The 2-hydroxypropionaldehyde will react further to yield propylene glycol and presumably also its monoformate ester and 2,3-dihydroxybutyraldehyde.



$$\begin{array}{l} CH_3OH + HCo(CO)_4 \xrightarrow{-H_2O} CH_3Co(CO)_4 \xrightarrow{H_2} CH_4 + HCo(CO)_4 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow CO \\ \qquad\qquad\qquad\qquad\qquad CH_3\overset{O}{\overset{\|}{C}}Co(CO)_3 \xrightarrow{H_2} CH_3\overset{O}{\overset{\|}{C}}H + HCo(CO)_3 \end{array} \tag{11}$$



$$\begin{array}{l} CH_3CHO + HCo(CO)_3 \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCo(CO)_3 \xrightarrow{H_2} CH_3CH_2OH + HCo(CO)_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow CO \\ \qquad\qquad\qquad\qquad CH_3\overset{HO}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}Co(CO)_3 \xrightarrow{H_2} CH_3\overset{OH}{\overset{|}{C}}HCHO + HCo(CO)_3 \end{array} \tag{12}$$



$$\begin{array}{l} CH_3CHO + HCo(CO)_3 \longrightarrow CH_3CH_2OCo(CO)_3 \xrightarrow{H_2} CH_3CH_2OH + HCo(CO)_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow CO \\ \qquad\qquad\qquad\qquad CH_3CH_2O\overset{O}{\overset{\|}{C}}Co(CO)_3 \xrightarrow{H_2} CH_3CH_2OCHO + HCo(CO)_3 \end{array} \tag{13}$$

Homologation of ethanol gives predominantly 1-propanol, which in turn is homologated to predominantly 1-butanol.[30] A small amount of 2-methoxyethanol was often found as a product, and it may have resulted from a reaction of the tetraglyme solvent. An alternative explanation for its appearance is a catalyzed homologation of methoxymethanol (the hemiacetal of formaldehyde with methanol). The homologation of ethylene glycol to 1,3-propanediol was not noticed in the present study but has been observed elsewhere.[5] In cases where acetate esters are observed, alcoholysis of the acyl intermediate in eq 11 must become an important reaction.

The preceding discussion promulgates all the intermediates believed to be of significance in homogeneous synthesis gas conversions. A strength of the overall scheme is that it incorporates only mechanistic steps already well established in the science of homogeneous catalysis. A more detailed definition of how individual steps occur and a determination of relative rates of competitive reactions would seem to be interesting prospects for future investigations.

Experimental Section

Synthesis gas was purchased from Matheson Gas Co. as an equimolar mixture of carbon monoxide and hydrogen. All metal complexes were purchased from Strem Chem. Co. Immediately before use, tetraglyme was percolated through activated alumina. Reactions at less than 340 atm were performed in standard 300- and 1000-mL Autoclave-Engineers

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J. Am. Chem. Soc. **1981**, *103*, 141–148

stirred autoclaves. Higher pressure experiments were run in the equipment described below.

High-Pressure Reactor and Compression System. All operations at high pressures were conducted in a steel-reinforced-concrete cell equipped with remote controls. Reactions were performed in a magnetically stirred 300-mL Autoclave-Engineers special heavy-duty autoclave rated for 3400 atm at 343 °C. The autoclave was heated by a large electric heating mantle. Cooling could be accomplished by passing a fluid through a groove between the inner lining and outer wall of the autoclave. Reaction temperatures were sensed by thermocouples that extended into a thermowell. Pressures in the system were measured by strain-gage pressure transducers.

A simplified diagram of the compression system appears in Figure 7. Rupture disk assemblies, most valves, and other accessories are not shown. A small compressor was used to feed the synthesis gas into two piston-driven compression cylinders and the autoclave. Typical pressures at this stage were 272–408 atm. The gas in the first cylinder was then forced into the second cylinder and the autoclave by advancing the piston with hydraulic fluid. The piston was advanced until the desired pressure was reached or until the piston had traveled the full length of the cylinder. When necessary, this procedure was repeated with the second compression cylinder.

Reactions. In each experiment, the autoclave was charged with catalyst components, promoters (if any), and 75.0 g of tetraglyme. The autoclave was closed and flushed with synthesis gas, and synthesis gas was added until the pressure was about 60% of the desired reaction pressure. Heating was then begun. Because of the very large mass of the autoclave, heatup required about 4 h. As the reaction temperature was reached, additional synthesis gas was added until the desired reaction pressure was reached. This point was considered as time zero. A proportional controller maintained the solution temperature within ±5 °C of the set point. During constant-pressure experiments, each time the pressure fell 13.6 atm below the desired pressure, it was increased by 27.2 atm by adding more synthesis gas. At a specified time, heating and stirring were stopped, and cooling fluid was passed through the autoclave. When the autoclave had cooled, unreacted synthesis gas was cautiously vented, and the product solution was recovered.

Products were analyzed by GLC on a Perkin-Elmer 3920B chromatograph using a thermal conductivity detector. Separations were achieved with a 6 ft × 0.25-in. column packed with 60/80 Chromosorb 101 that was held at 50 °C for 2 min, programmed at 16 °C/min to 260 °C, and maintained at 260 °C for 30 min. Product identities were determined by GLC/mass spectral analysis and were confirmed by retention time comparisons with authentic samples. Product yields were measured by comparing GLC peak areas to that of an added internal standard and were corrected for differences in detector responses. The ethylene glycol yield obtained by distillation of a product mixture was in very good agreement with that determined by GLC. The experimental results upon which Figures 2–4 and 6 are based are listed in Table IV.

Reactor Cleaning. During reactions, many of the metals (especially rhodium) deposited onto the walls, stirring impeller, stirring shaft, and thermowell of the autoclave. These deposits significantly influenced ensuing experiments. This problem was eliminated only by vigorous reaming of the autoclave body with steel wool spun by an electric drill and by using a small motor-powered brush to scour the other parts. This was done routinely after each experiment.

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Kinetics and Mechanism of the Conjugate Addition of Lithium Dimethylcuprate to α,β-Unsaturated Ketones

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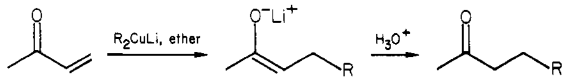
Abstract: The kinetics of the reaction of several α,β-unsaturated ketones with excess lithium dimethylcuprate in the presence and absence of lithium iodide was studied by stopped-flow ultraviolet spectroscopy in diethyl ether solution at 25.0 °C, by measuring the rate of disappearence of a spectroscopically observable intermediate. Under these conditions, the conjugate additions are first order in ketone but exhibit a more complex dependence upon cuprate concentration. The rates of reaction of aryl-substituted 1-phenyl-3-methyl-2-buten-1-ones and β-aryl-substituted chalcones with $(CH_3)_2CuLi$ were also measured, and the rate and equilibrium constants for these reactions were correlated separately with Hammett σ constants. The rates of reaction of mesityl oxide and isophorone were also studied by stopped-flow infrared spectroscopy. Rapid scanning experiments in which reacting solutions of several enones were scanned over the carbonyl double-bond region of the infrared spectrum revealed the presence of an intermediate. These results are consistent with a mechanism in which the reactants are in equilibrium with an intermediate complex, which may unimolecularly rearrange to form a trialkylcopper(III) species with copper bonded to the β-carbon of the lithium enolate, followed by a reductive elimination process involving the copper ligands to form the β-methyllithium enolate product and methylcopper.

Introduction

Although the conjugate addition of lithium diorganocuprates to α,β-unsaturated ketones (eq 1) is widely used in organic synthesis,[1,2] the formulation of a detailed mechanism for this reaction has been impeded by the lack of kinetic data and by the scarcity of information regarding the structure and composition of these reagents in solution. Lithium dimethylcuprate has not been isolated,[2a] but two lithium diarylcuprates with intramolecular amine ligands were isolated and shown to exist in diethyl ether solutions as dimers, with each aryl group bridging a lithium and a copper atom.[3] Variable-temperature ^{13}C NMR studies of ethereal solutions of halide-free lithium dimethylcuprate showed only a single line for the methyl signals down to −80 °C,[4] and both proton[5-7] and carbon[6] NMR experiments on several cuprate



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