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MECHANISM OF THE HOMOGENEOUS HYDROGENATION OF CARBON MONOXIDE

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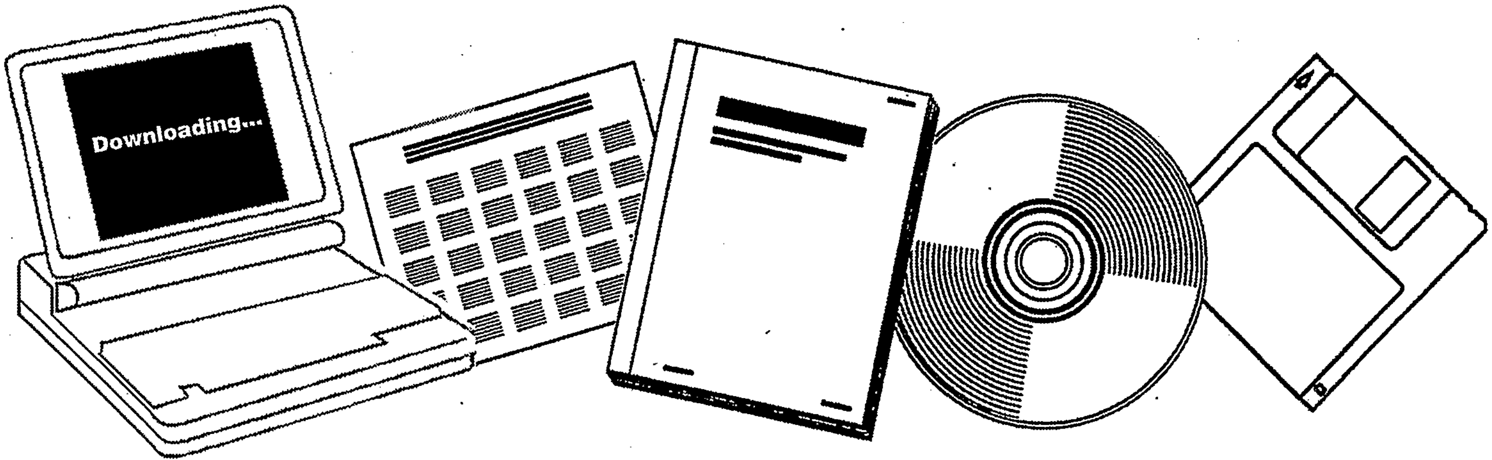

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Jerome W. Rathke and Harold M. Feder

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MECHANISM OF THE HOMOGENEOUS HYDROGENATION OF CARBON MONOXIDE*

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A study delineating the major mechanistic features of the $HCo(CO)_4$ catalyzed carbon monoxide hydrogenation is reported. A reaction path involving hydrogen migration to a coordinated carbonyl to give a formyl complex, followed by additional hydrogen migrations to yield a coordinated formaldehyde complex, appears to fit the data best. The primary reaction products - methanol, methyl formate, and ethylene glycol - are formed as a result of hydrogen migration to oxygen or carbon in $(^2h\text{-}H_2CO)CoH(CO)_3$ to form hydroxymethyl or methoxy groups.

I. INTRODUCTION

Homogeneous catalytic hydrogenation of carbon monoxide by mononuclear transition metal complexes[1,2,3,4] to form oxygenated products is now well established. Products which we have observed in the cobalt carbonyl hydride catalyzed reaction[1,2] at pressures below 375 atm. and temperatures below 230°C are methanol and higher alcohols up to C_5, their formate esters, acetaldehyde, propionaldehyde, ethylene glycol, and its mono- and di-formate esters, water and carbon dioxide. We have also observed trace amounts (negligible in our calculations) of methane and acetate esters. Larger fractions of acetate esters have been reported[4] for the cobaltcarbonyl-catalyzed system under conditions[5] which lead to higher conversions than in the work reported here, in which 1M total products is seldom exceeded. Still other products which have been reported[4,6] are glycerol and other polyhydroxylic alcohols and 1,2- and 1,3-propylene glycols. We suspect there arise because of the more severe reaction conditions described in those reports. Despite the variety of soluble metal complexes (based on the metals Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt)[7] reported (1-4) to lead to carbon monoxide hydrogenation, in each case which we regard as primary reaction products in the $HCo(CO)_4$ system-methanol, methyl formate, and ethylene glycol- have been obtained. The presence or absence of additional products may be rationalized on the basis of whether the complex in question can catalyze secondary reactions such as the alcohol homologation reaction. The primary formation of the same three compounds may be true even where the active catalyst is strongly suspected to be a metal cluster complex.[8] For these reasons, we believe that the thorough observations we have made on the $HCo(CO)_4$ catalyzed carbon monoxide hydrogenation are relevant to these other catalyst systems. (Less clear is the relationship between these systems and the hydrocarbon forming cluster catalysts[9] reported by Muetterties.)

We have proposed a mechanism[2] for the cobalt carbonyl hydride catalyzed hydrogenation summarized as follows:

$$HCo(CO)_4 \rightleftharpoons (CO)_3Co\ CHO \qquad (1)$$

$$(CO)_3Co\ CHO + H_2 \rightarrow (CO)_3\ H\ Co(^2h\text{-}CH_2O) \qquad (2)$$

$$(CO)_3HCo(^2h\text{-}CH_2O) \overset{fast}{\rightarrow} (CO)_{3,4}Co\ CH_2OH \overset{fast}{\rightarrow} CH_3OH + C_2H_4(OH)_2 \qquad (3)$$

$$(CO)_3HCo(^2h\text{-}CH_2O) \overset{fast}{\rightarrow} (CO)_{3,4}Co\ OCH_3 \overset{fast}{\rightarrow} CH_3O_2H \qquad (4)$$

The secondary products form *via* the route:

$$CH_3OH \xrightarrow{HCo(CO)} 4 \text{ higher alcohols, ROH} \qquad (5)$$
$$CH_3O_2OH + ROH \rightarrow RO_2CH + CH_3OH \qquad (6)$$

This mechanism was shown to be consistent[2] with the following observations: (a) the products are the same as those we obtained by $HCo(CO)_4$ catalyzed hydrogenation of the formaldehyde precursors, paraformaldehyde and s-trioxane, which likely react *via* the complex (II). (b) The rate law is $d(\Sigma$ Products$)/dt = k^{(2)}[HCo(CO)_4]P_{H_2}$. (c) The activation parameters in benzene solution are $\Delta H^* \sim 40$ kcal mol, $\Delta S^* \sim 0$ Gibbs mol^{-1}. (d) The rates are increased (*via* changes in ΔS^*) only by a factor of ~ 20 in the solvent series heptane < benzene < p-dioxane < 84% p-dioxane + 16% water < 2,2,2-trifluoroethanol at 200°C. (e) Synthetic studies, partifularly those of Roper,[10] demonstrate the rearrangement of $Os(^2h\text{-}CH_2O)(CO)_2(P\phi_3)_2$ at 75° to $Os\ (CHO)H(CO)_2(P\phi_3)_2$, thus establishing a reaction pathway connecting formyl and formaldehyde complexes.

Our earliest suggestion[1] that formyl radical may be produced *via* a hydrogen atom transfer radical pair mechanism was excluded[2] on the basis that it did not fit the observed kinetic orders. This report describes additional experiments which further characterize the $HCo(CO)_4$ catalyzed CO hydrogenation reaction, elaborates further on the produce-determining steps, and makes comparisons of our results with those of others which have appeared since our last report.

II. EXPERIMENTAL

Pressure reactions were conducted in an Autoclave Engineers 300 ml stainless steel Magnedrive autoclave from which liquid samples could be taken without interruption of a reaction. In each case the catalyst was added as $Co_2(CO)_8$. Because sampling and conversion of carbon monoxide and hydrogen to liquid products perturbed the initial gas phase pressure and composition, makeup gases were added to restore the nominal composition and pressure after each sampling. Removal of liquid samples also cause decreases in catalyst concentration owing to vaporization of $HCo(CO)_4$ into the increased head space in the reactor. Cobaltcarbonyl hydride concentrations were measured titrimetrically[11] in each sample and the variable, $Y \equiv \int_0^t [HCo(CO)_4]dt$, was used as the abscissa in rate plots to allow for decreases. Rate constants were determined by plotting the sums of the molar concentrations of products, excluding H_2O and CO_2, (ΣP)[12] *vs.* Y. These plots are linear; division of their slopes by the prevailing values of P_H gave second-order rate constants.[13] Concentration measurements were made at room temperature and are not corrected for liquid expansion at reaction conditions. Additional experimental techniques were given in previous reports.[1,2]

III. RESULTS

Primary and Secondary Reaction Products

Figure 1 shows a typical product distribution plot for cobalt carbonyl hydride catalyzed hydrogen reduction of carbon monoxide in dioxane solution. As was stated earlier, we believe that methanol, methyl formate and ethylene glycol are primary reaction products formed from a common early intermediate, $(CO)_3HCo(^2h\text{-}CH_2O)$. As such, these materials should be *formed* in constant relative amounts. This is not evident from Fig. 1 because secondary reactions occur. Methanol is further converted to higher alcohols *via* the well known homologation reaction[14] and reaches a steady state concentration where its rate of homologation equals its production rate (Fig. 1). The observation of strong upward curvature of the plots for the formation of the higher alcohols suggests that their rates of production are dependent on the accumulation of the next lower alcohol. That this is the case in CH_3OH homologation is shown in Fig. 2. This figure shows that the homologation of methanol dissolved in dioxane is first-order in CH_3OH concentration under CO hydrogenation conditions. The major reaction products were ethanol and higher alcohols, with small amounts of intermediate aldehydes also observed. A second observation that can be from Fig. 1 is the ratio of the concentration of each formate ester to its corresponding alcohol remains relatively constant with time. One possibility considered was that the alcohols and formate esters are in equilibrium with carbon monoxide:

$$ROH + CO \rightleftharpoons RO_2CH \qquad (7)$$

This equilibrium is known to be catalyzed by bases.[15] However, no evidence for the reaction was observed when a dioxane solution of CH_3O_2CH was subjected to cobalt carbonyl hydride under CO hydrogenation conditions. Rapid methanol formation, as expected from reversal of eqn. (7), was not observed; rather, it was formed at its normal rate *via* CO hydrogenation. Ethanol formation *via* homologation was also normal. Ethyl formate, however, was formed at much higher than normal ratio to ethanol. This result suggested that the observations regarding higher alcohols and their formates could be accounted for by transesterification reactions, *e.g.*,

$$CH_3O_2CH + ROH \overset{K}{\rightleftharpoons} RO_2CH + CH_3OH \qquad (8)$$

The existence of the equilibrium was confirmed. The measured value of the equilibrium constant, K, for R = Et at 200°C was ∿ 0.8. Keim *et al.*[4] have suggested that $C_2H_5O_2CH$ is formed by reaction of C_2H_5OH with a formyl intermediate, $(CO)_nCo\ HCO$. We cannot rule out the possibility that this pathway is operative to some minor extent, but we conclude that transesterification does occur rapidly under our reaction conditions and adequately accounts for the results.

Variation of Primary Reaction Products with Reaction Conditions

If the only secondary reactions of importance are homologation and transesterification, the amounts of the primary reaction products CH_3OH, CH_3O_2CH, and $C_2H_4(OH)_2$ should be calculable based on the stoichiometries of these reactions. Such a calculation might allow observation of the behavior of the primary reaction products without the complications created by these secondary reactions. The estimated amounts of these primary materials, $[CH_3OH]_p$, $[CH_3O_2CH]_p$, and $[C_2H_4(OH)_2]_p$ which would be observed in the absence of secondary reactions were calculated as follows:

$$[CH_3OH]_p, = [CH_3OH] + [\text{higher alcohols}] + [\text{aldehydes}] - [HOC_2H_4O_2CH] - 2[C_2H_4(O_2CH)_2] - [CF_3CH_2O_2CH]^{16} \qquad (9)$$

$$[CH_3O_2CH]_p = [CH_3O_2CH] + [\text{higher formate esters}] + [HOC_2H_4O_2CH] + 2[C_2H_4(O_2CH)_2] + [CF_3CH_2O_2CH]^{16} \qquad (10)$$

$$[C_2H_4(OH)_2]_p = [C_2H_4(OH)_2] + [HOC_2H_4O_2CH] + [C_2H_4(O_2CH)_2] \qquad (11)$$

A plot of these quantities in Fig. 3 shows their linear variation with ΣP, their sum, which is also linear in Y. This linear variation should in fact be observed only if the products in question are primary and their rates of formation do not depend on the concentration of an intermediate reaction product which builds up in the course of reaction. The slopes of such plots represent the fraction of primary products; they are tabulated as $f(CH_3OH$, $f(CH_3O_2CH)$, and $f(C_2H_4(OH)_2)$ for a variety of reaction conditions in Table I. Their relative ratios should reflect inherent tendencies toward branching in the reaction scheme and should be influenced only by reaction conditions, consistent with our mechanistic scheme (eqns. 1-6). Further confirmation of these considerations was obtained when the reaction was conducted under conditions which suppressed homologation. The concentrations of the observed primary products themselves (as distinguished from the values calculated with eqns. 9-11) then varied linearly with Y. Such a situation is shown in Fig. 4, where added PBu_3 inhibited the homologation reaction. We must emphasize that eqns. 9-11 use the approximation that all of the formate esters arise by transesterification of the initially formed CH_3O_2CH with higher alcohols. We have observed minor amounts of formate esters when CH_3OH is homologated in dioxane solution. We suspect that these formate esters are produced when acetaldehyde and other intermediate aldehydes are hydrogenated.[17] However, the amounts of formate esters produced were small relative to amounts produced by carbon monoxide hydrogenation and would lead (if significant) to upward curvature of the $f(CH_3O_2CH)$ plot in Fig. 3. These equations also neglect any additional amounts of formate esters which may arise through hydrogenation of glycolaldehyde (a species which we have implicated[2] in ethylene glycol formation).

A secondary reaction which has also been neglected in developing eqn. 9-11 is hydrolysis of formate esters by the water which is produced in the homologation of alcohols. Apparently any formic acid which is produced in this reaction is further catalytically converted to H_2 and CO_2.[2] Hydrolysis is not usually significant. This is demonstrated by the good material balance between water observed in the reaction and the stoichiometric amounts of water calculated from production of higher alcohols, their esters and methane with only water as the by-product. This calculated amount is denoted as the oxygen deficit. The equality is presented in Fig. 5. However, hydrolysis does become a significant factor when large amounts of water (>10 times that normally produced in the reaction) are added to the solvent. As observed in Table I, expt. 8, no formate esters were then obtained and eqn. 10 cannot, of course, give any estimate of the amount of CH_3O_2CH actually produced in the reaction. With these limitations in mind we regard the F values shown in Table I as reasonable estimates of the fractions of primary products formed in the reaction. It is essential to emphasize the distinction between these quantities and the amounts of these materials which are observed in the reaction. For example, Keim *et.al.*,[4] have measured the variation of the observed amounts of CH_3OH, CH_3O_2CH, and $C_2H_4(OH)_2$ in the cobalt carbonyl hydride catalyzed system under a variety of reaction condition. In cases where extensive secondary reactions occur, observed quantities would be only indirectly related to the amounts of primary products formed in the reaction.

IV. DISCUSSION

One significant observation that can be made from Table I is that $f(CH_3O_2CH)$ does not vary appreciably when the hydrogen pressure is varied at constant CO pressure . This observation is based on the paired experiments 1 and 2, 3 and 4, 9 and 10 in both 1,4-dioxane and 2,2,2-trifluoroethanol solution. In each pair increase of the hydrogen pressure, at relatively constant CO pressure, causes $f(CH_3O_2CH)$ to remain nearly constant, $f(CH_3OH)$ to decrease sharply, and $f(C_2H_4(OH)_2)$ to show a corresponding increase. We take this as reasonable evidence that CH_3OH and $C_2H_4(OH)_2$ are formed from one intermediate and CH_3O_2CH from a different intermediate. In our reaction scheme, eqns. 3 and 4, the ethylene glycol and methanol forming intermediate is a hydroxymethyl complex, $(CO)_{3,4}CoCH_2OH$(I) and the CH_3O_2CH forming intermediate is a methoxy complex, $(CO)_{3,4}CoOCH_3$(II).[18] For this reason, we take $f(CH_3OH)$ + $f(CH_2H_4(OH)_2$ as a measure of the relative fraction of I and $f(CH_3O_2CH)$ as a measure of the relative fraction of II which have been converted to products. For measurements in 2,2,2-trifluoroethanol (expts. 9,10,11) the ratio $f(CH_3O_2CH)/f(CH_3OH) + f(C_2H_4(OH)_4)$ is nearly proportional to P^2_{CO} at various $HCo(CO)_4$ concentrations and hydrogen pressures. A somewhat lower CO pressure dependence is observed for measurements in 1,4-dioxane. This CO dependence may arise by CO addition and "insertion" steps necessary to convert $(CO)_3CoH(^2h\text{-}CH_2O)$ to methyl formate:

$$(CO)_3CoH(^2h\text{-}CH_2O) \overset{CO}{\rightleftharpoons} \overset{\substack{(CO)_3CoC(O)OCH_3 \\ \text{or}}}{(CO)_4CoOCH_3} \overset{CO}{\rightleftharpoons} (CO)_4CoC(O)OCH_3 \rightarrow CH_3OC(O)H.$$

Dombek[19] has shown that a hydroxymethyl ester complex analogous to I, $(CO)_5MnCH_2OR$ ($R = COC(CH_3)_3$), is converted to the corresponding methanol and glycol esters, CH_3OR and HOC_2H_4OR[20] when treated with H_2 and CO at 75-100°C. He has found that for this complex, higher hydrogen pressures favor the formation of glycol ester relative to methyl ester. This behavior is in agreement with our observation, mentioned previously, that increasing the hydrogen pressure (at constant CO pressure) results in an increase in

$f(C_2H_4(OH)_2)$ and a corresponding decrease in $f(CH_3OH)$. Because this hydrogen dependence does not effect the branch leading to methyl formate, we suspect that the path (eqn. 3) leading to I from $(CO)_3CoH(^2h\text{-}CH_2O)$ is not reversible. Dombek[19] did not measure the effect of CO on the branching ratios of the methyl and glycol esters, but did observe that addition of a decarbonylation reagent, $(CH_3)_3NO$, favored formation of the methyl ester. This is in agreement with our observation (see Table I, expts. 3 and 5) that decreasing CO pressure increases $f(CH_3OH)/f(C_2H_4(OH)_2)$. Roth and Orchin[21] have shown that $HCo(CO)_4$ converts formaldehyde stoichiometrically to glycolaldehyde (a precursor to ethylene glycol) at 0° and 1 atm. CO pressure. They did not observe methanol or methyl formate as products. The formation of only ethylene glycol is in agreement with our observation (see Table I, expt. 12) and that of others[4] that ethylene glycol formation is favored at lower temperatures. In Roth and Orchin's work[21] the absence of methyl formate formation - also favored by low temperature - is not surprising in view of the previously mentioned strong CO pressure dependence. Roth and Orchin[21] have also proposed I as an intermediate in this reaction.

Keim, Berger, and Schlupp[4] have suggested that $(CO)_nCoCH_2OCo(CO)_n$ may be the ethanol and ethylene glycol forming intermediate in the cobalt hydride catalyzed CO hydrogenation reaction. We believe that we have adequately demonstrated that ethanol is formed mainly *via* CH_3OH homologation and in view of the preceeding discussion are satisfied with I as at least the major intermediate in ethylene glycol formation. We have found no need to invoke dicobalt intermediate species.

Our view of the steps which determine the branching ratio of the primary is summarized as follows:

$$\begin{tikzcd}
\mathrm{(CO)_3CoH(^2h\text{-}H_2CO)} \arrow[r, shift left, "\mathrm{CO}"] \arrow[d] & \mathrm{II} \arrow[l, shift left] \arrow[r, shift left, "\mathrm{CO}"] & \mathrm{(CO)_4CoC(O)OCH_3} \arrow[l, shift left] \arrow[r] & \mathrm{CH_3O_2CH} \\
\mathrm{I} \arrow[r, shift left, "\mathrm{CO}"] \arrow[d] & \mathrm{(CO)_3CoC(O)CH_2OH} \arrow[l, shift left] \arrow[r, "\mathrm{H_2}"] & \mathrm{\{HOC(O)CH_2OH \rightarrow C_2H_4(OH)_2\}} & \\
\mathrm{CH_3OH} & & &
\end{tikzcd}$$

Rate constants, $k^{(2)}$, for the CO hydrogenation reaction are also tabulated in Table I. Those measured in 1,4-dioxane solution at 182°C are in good agreement with the rate law $d\Sigma P/dt = k^{(2)}[HCo(CO)_4]P_{H_2}$, however, those measured in 2,2,2-trifluoroethanol solution at 182° do show a trend toward higher $k^{(2)}$ values with increasing $HCo(CO)_4$ concentration. We suspect that the cause of this may be increasing ionic dissociation of $HCo(CO)_4$ as an acid in the more dilute solutions in the polar solvent. The room temperature dielectric constant of 2,2,2-trifluoroethanol is 26.7; that of 1,4-dioxane is 2.2.

Experiment 6, Table I shows that the $HCo(CO)_4$ catalyzed CO hydrogenation reaction has an inverse kinetic deuterium isotope effect, $k_H^{(2)}/k_D^{(2)}$ $\sim$0.7 at 182°C in 1,4-dioxane solution. This kinetic isotope effect shows that *net* transfer of one hydrogen atom from a bond with low force constant (Co-H) to a bond with a much higher force constant (*e.g.*, C-H) must take place in whatever sequence of steps which precedes and includes the transition state as in eqns. 1 and 2. Interestingly, a deuterium isotope effect of 0.76 ± .05 at 183° has been reported for Fischer-Tropsch synthesis of hydrocarbons over a cobalt-thoria catalyst.[22] However, the relationship, if any, between the homogeneous reaction and the Fischer-Tropsch reaction is far from clear. We are currently investigating the cobalt metal catalyzed Fischer-Tropsch reaction to determine if any relationship can be found.

ACKNOWLEDGEMENTS

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TABLE I. REACTION PARAMETERS FOR THE COBALT CARBONYL HYDRIDE CATALYZED HYDROGENATION OF CARBON MONOXIDE AT 182°C.

Experiment No.	Conditions	Average $[HCo(CO)_4]$ $\underline{M}$	P_{H_2}(atm.)	P_{CO}(atm.)	$10^7k^{(2)}$(atm.$^{-1}$sec^{-1})	Percent FCH_3OH	 FCH_3O_2CH	 $FC_2H_4(OH)_2$
1	a	.12	96.5	115	2.0	50	25	24
2	a	.10	192	121	1.7	44	25	33
3	a	.078	30.2	113	1.8	75	23	2.4
4	a	.089	100	123	2.0	48	19	33
5	a	.051	26.5	340	1.9	65	28	7.8
6	b	.11	102	111	2.7	43	20	35
7	c	.03	149	149	.69	72	7.0	22
8	d	.084	115	115	2.4	52	0	43
9	e	.081	154	179	2.7	45	26	29
10	e	.034	97.1	170	2.0	54	24	22
11	e	.052	161	108	2.0	68	12	20
12	f	.0025	161	108	46	90	10	0

[a] in 1,4-dioxane solution

[b] in 1,4-dioxane solution with deuterium used in place of hydrogen.

[c] in 1,4-dioxane solution with 3 PBu_3/Co. The major hydridic species is believed to be $HCo(CO)_3PBu_3$.

[d] in 1,4-dioxane solution containing 8.5$\underline{M}$ H_2O.

[e] in 2,2,2-trifluoroethanol solution.

[f] at 214°C in 2,2,2-trifluoroethanol solution.

REFERENCES

1. Rathke, J. W. and H. M. Feder, J. Am. Chem. Soc., 100, 3623 (1978).
2. Feder, H. M. and J. W. Rathke, Ann. N.Y. Acad. Sci., 333, 45 (1980).
3. Bradley, J. S., J. Am. Chem. Soc., 101, 7419 (1979).
4. Keim, W., M. Berger, and J. Schlupp, J. Catal., 61, 359 (1980).
5. When high concentrations of alcohols are allowed to build up, alcoholysis of acetylcobalt intermediates may occur, *e.g.*, $CH_3C(O)Co(CO)_n + CH_3OH \rightarrow CH_3O\ C(O)CH_3$. This reaction was proposed in ref. 4, and is also evident in the cobaltcarbonyl-catalyzed homologation of methanol. We further suspect that hydrophobic solvents, such as aliphatic or aromatic hydrocarbons, which permit an insoluble polar second phase (enriched in water, alcohols, and glycols) to form in the course of reaction, may also contribute to acetate ester formation.
6. Gresham, W. F., British Patent 655237 (to E. I. DuPont)(1951)
7. Evidence that the catalyst is mononuclear is reported only in the cases of Mn,[1] Co,[2,4] and Ru.[3]
8. Pruett, R. L., Ann. N.Y. Acad. Sci., 295, 239 (1977).

9a. Demitras, G. C. and E. L. Muetterties, J. Am. Chem. Soc., 992796 (1977).

9b. Thomas, M. G., B. F. Beier, and E. J. Muetterties, J. Am. Chem. Soc., 98, 1296.

10. Brown, K. L., G. R. Clark, C. E. L. Headford, K. Marsden, and W. R. Roper, J. Am. Chem. Soc., 101, 503 (1979)
11. Iwanaga, R., Bull. Chem. Soc. Jpn., 35, 247 (1962).
12. It should be noted that ΣP is not simply related to the amount of carbon monoxide consumed in the reaction but instead (at least in our mechanistic scheme) to the amount of $(CO)_3HCo(h^2\text{-}CH_2O)$ which is converted to organic products.

REFERENCES (Continued)

13. For the sake of accurate thermochemical kinetic parameters it would be more suitable to use the molar concentrations of hydrogen for the calculation of the second order rate constants. Unfortunately, Henry's law constants connecting the pressure and concentrations at elevated temperatures are not available for the solvents used.

14. Piacenti, F. and M. Branchi, In Organic Syntheses *via* Metal Carbonyls, I. Wender & P. Pino, Eds. 2:1, John Wiley & SONS, Inc., New York, N.Y. (1977).

15. Hine, J., Divalent Carbon, p. 79, Ronald Press Co., New York, N.Y., (1964).

16. Applies in cases where CF_3CH_2OH was used as the solvent.

17. Aldridge, C. L. and H. B. Jonassen, J. Am. Chem. Soc., 85, 886 (1963).

18. Based on these observations our earlier suspicion[2] that some CH_3OH may be formed from II was discarded as at best probably a minor pathway.

19. Dombek, B. Duane, J. Am. Chem. Soc., 101, 6466 (1979).

20. He also observes that the glycolaldehyde ester, $HC(O)CH_2OR$, is an intermediate in the formation of the glycol ester.

21. Roth, Jerome A. and Milton Orchin, J. Organomet. Chem., 172, 27 (1979).

22. Sakharov, M. and E. Dokukina, Kinetika i Kataliz. 2, 710, (1961).

FIGURE CAPTIONS

Fig. 1. Product distribution in the cobalt carbonyl hydride catalyzed carbon monoxide hydrogenation in 1,4-dioxane solution at 182°. For reaction conditions see Table I, experiment 5.

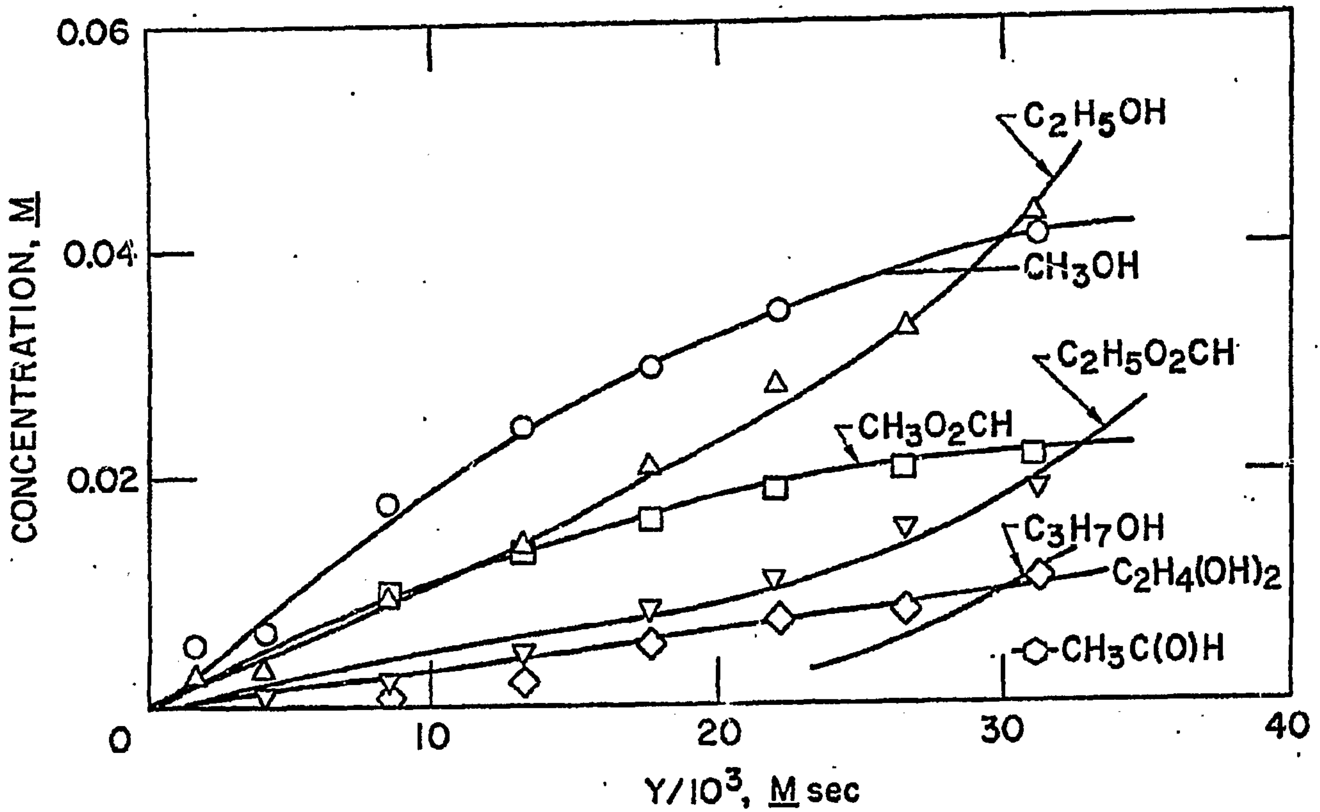
Fig. 2. First-order rate plot for methanol homologation in 1,4-dioxane solution at 182°C; P_{H_2}, 113 atm.; P_{co}, 109 atm.; $HCo(CO)_4$, .042M.

Fig. 3. Calculated quantities of primary reaction products as a function of total products for carbon monoxide hydrogenation in 1,4-dioxane solution at 182°. For reaction conditions are Table I, experiment 5.

Fig. 4. Product distribution in the tri-n-butyl phosphine substituted cobalt carbonyl hydride catalyzed carbon monoxide hydrogenation. For reaction conditions see Table I, experiment 7.

Fig. 5. Material balance on water production and water producing reactions for data in 1,4-dioxane solution at 182°C.

FIG. 1


0.06
0.04
0.02
CONCENTRATION, M
0
10
20
30
40
Y/10^3, M sec
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CH_3OH
$C_2H_5O_2CH$
CH_3O_2CH
C_3H_7OH
$C_2H_4(OH)_2$
$CH_3C(O)H$

FIG. 2

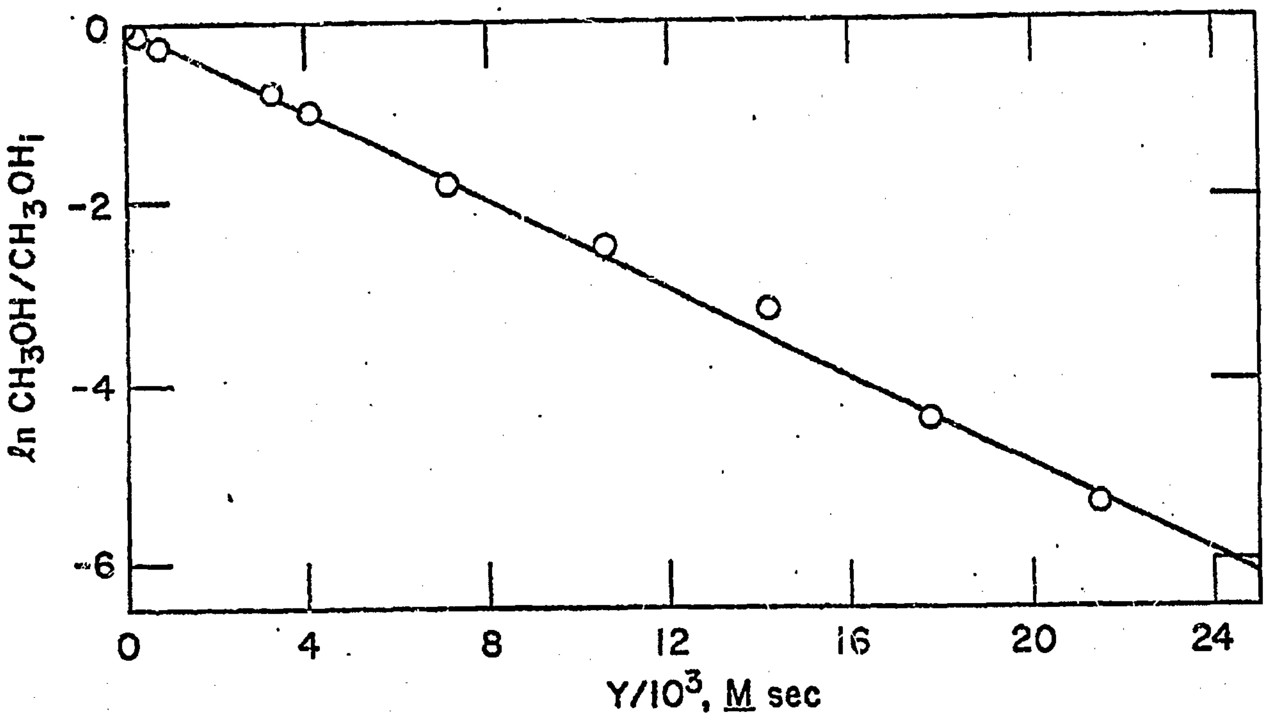


FIG. 3

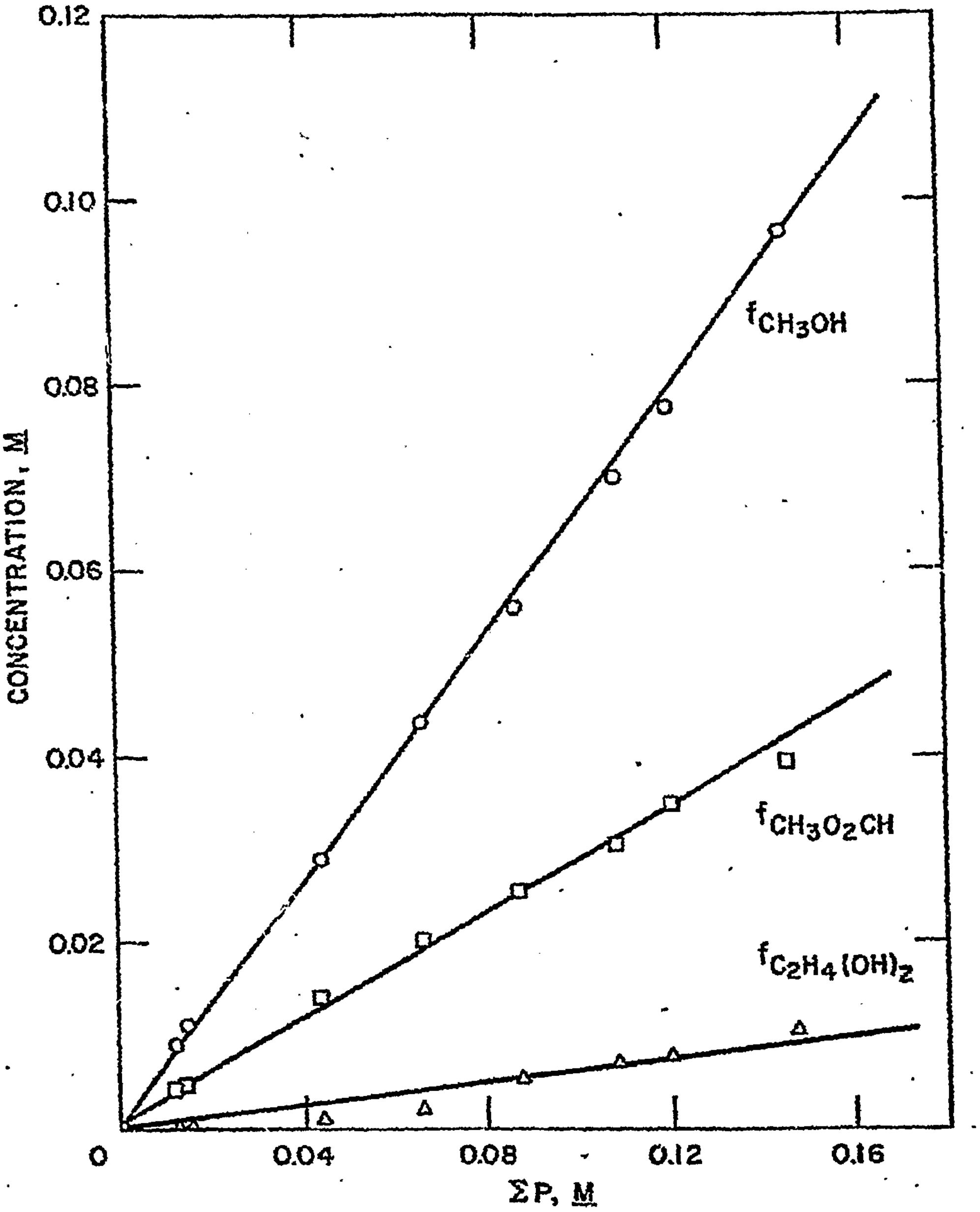
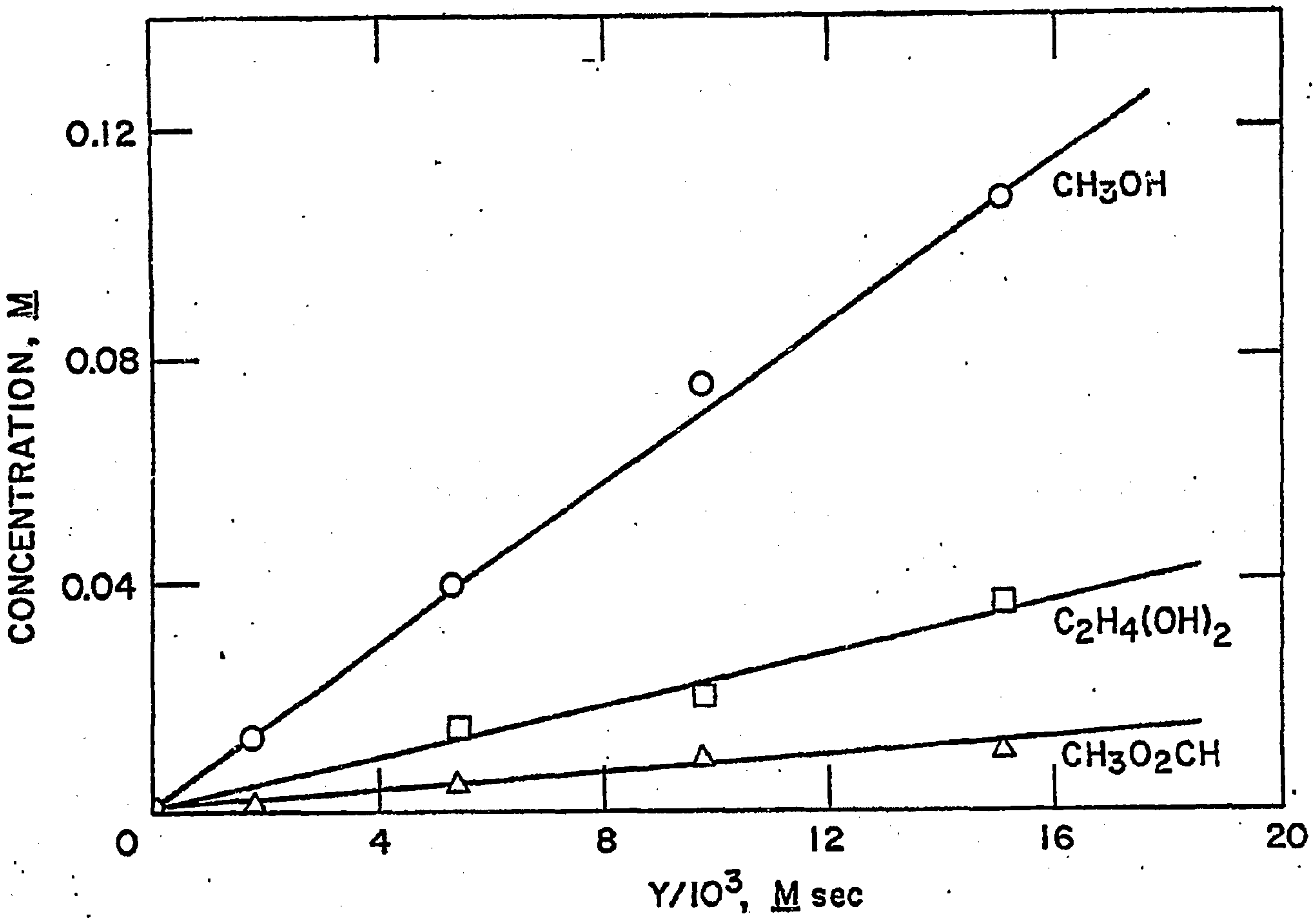

0.12
0.10
0.08
0.06
0.04
0.02
0
CONCENTRATION, M
0.04
0.08
0.12
0.16
ΣP, M
f_{CH_3OH}
$f_{CH_3O_2CH}$
$f_{C_2H_4(OH)_2}$

FIG. 4



0.12
0.08
0.04
CONCENTRATION, M
0
4
8
12
16
20
Y/10^3, M sec
CH$_3$OH
C$_2$H$_4$(OH)$_2$
CH$_3$O$_2$CH

FIG. 5