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Applications of Homogeneous Water-gas-shift Reaction. I. Further Studies of the Hydroformylation of Propene with CO and H_2O

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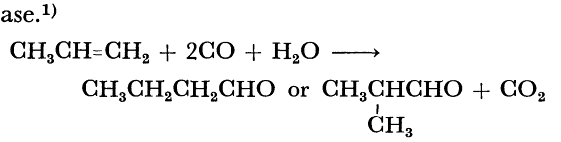
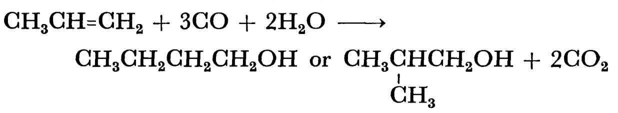
Polar ether solutions prepared *in situ* from $Co_2(CO)_8$ and 1,2-bis(diphenylphosphino)ethane (diphos) are active catalysts for the hydroformylation of propene with CO and H_2O. Under the hydroformylation conditions employed, butyl(C_4) or isobutyl alcohols, butyric(C_4) acids, and dipropyl ketones were found to be formed as by-products. A pronounced formation of C_4 alcohols was observed as the reaction temperature was increased; in fact, the catalyst solutions described above actively reduce butyraldehyde to butyl alcohol. The effects of the CO pressure and of the propene concentration on the formation of C_4 aldehydes are also examined. It turns out that the water molecule as well as $Co_2(CO)_8$ and diphos are essential for the formation of catalytic intermediates, which are themselves responsible for the hydroformylation activity.

Recently, we have reported the homogeneous catalysis of hydroformylation with CO and H_2O, in which the $Co_2(CO)_8$–diphos system was used in such polar ether solvents as THF, dioxane, and diglyme with no base.[1)]



$$CH_3CH{=}CH_2 + 2CO + H_2O \longrightarrow CH_3CH_2CH_2CHO \text{ or } CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO + CO_2 \qquad (1)$$

The use of CO and H_2O in place of hydrogen is not a racent development. It has been well known, for example, that hydrohydroxymethylation(1′) is catalyzed by the $Fe(CO)_5$–organic tertiary amine system.[2)] (Reppe Reaction: The reaction(1′) is more stoichiometric than catalytic.)



$$CH_3CH{=}CH_2 + 3CO + 2H_2O \longrightarrow CH_3CH_2CH_2CH_2OH \text{ or } CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH + 2CO_2 \qquad (1')$$

More recently, special attention has been paid to the possibility of using other transition-metal carbonyl complexes as active catalysts in these reactions, (1) and (1′); a variety of Group 8 metal carbonyl clusters can serve as catalyst precursors in the presence of alkali or amine.[3)]

Our catalyst system is considerably different from other ones in that: a) diphos is an essential component, and b) alkali or organic amines are absent.

Also, $Co_2(CO)_8$ is a more conventional catalyst than other metal carbonyl clusters, such as $Ru_3(CO)_{12}$, $Rh_6(CO)_{16}$. Therefore, there is the possibility of developing a novel industrial process. Thus, further studies of our catalyst system were undertaken under reaction conditions more catalytically active than those reported previously.[1)]

Experimental

Materials. The propene (Research Grade), diphos, and dioxane used as solvent were obtained commercially and were used with no further purification. The $Co_2(CO)_8$ was prepared by the conventional method. The H_2O was distilled under atmospheric pressure prior to use.

Reaction Procedure. The hydroformylation reactions were carried out in a 100-ml stainless-steel autoclave, in which $Co_2(CO)_8$, diphos, H_2O, and dioxane had been placed. After the vessel was sealed, both propene and CO were introduced. The system was then brought to the desired reaction temperature and pressure by the additional charging of CO under heating. Stirring was then begun, and the reaction took place. The CO pressure was kept constant during the reaction by supplying the gas from a 400-ml pressure storage vessel through a pressure regulator. The reaction temperature was controlled within a range of ±1 °C.

The catalytic reductions of butyraldehyde to butyl alcohol were performed in an identical manner, except for the use of butyraldehyde (25 mmol) in place of propene (25 mmol).

Analysis of Products. Gas analysis was performed at 50 °C with a gas chromatograph using a 6-m Carbowax column. The amount of CO_2 was determined by titration methods. The liquid products other than C_4 acids were analyzed at 100 °C by means of a gas chromatograph equipped with FID using a 6-m column packed with polyethylene glycol adipate. C_4 acid analysis was performed at 150 °C using a gas chromatograph equipped with FID and using a 4-m squalane column. The infrared spectra of catalyst solutions were recorded on a Hitachi type 215 spectrometer.

Results and Discussion

Preliminary Studies Involving the Effect of CO Pressure. The $Co_2(CO)_8$-catalyzed hydroformylation of propene with CO and H_2O was carried out in dioxane solvent, since it was greatly effective for this reaction; only a little hydrogen as a co-product was detected in the dioxane. This reaction can proceed catalytically only in the presence of phosphine; of all the phosphines used, diphos was the most effective. A diphos 1: $Co_2(CO)_8$ 1 ratio was used in order to inhibit the partial decomposition of the catalyst.

In a previous report,[1)] the reaction was run at 135 °C for 17 h under an initial pressure of 12 kg/cm²; C_4 aldehydes (9.2 mmol, *ca.* 37% conversion based on propene) were thus produced with 0.04 mmol of C_4 alcohols, (2), (3). In addition, we have recently found that, under the conditions employed, butyric (C_4) acids (1.0 mmol, (4)) and dipropyl ketones (0.8 mmol, (5)) were formed as by-products in detectable amounts.

$$C_3H_7\text{-}CHO + CO + H_2O \longrightarrow C_3H_7\text{-}CH_2OH + CO_2 \qquad (2)$$

$$CH_3CH{=}CH_2 + 3CO + 2H_2O \longrightarrow C_3H_7\text{-}CH_2OH + 2CO_2 \quad (3)$$

$$CH_3CH{=}CH_2 + CO + H_2O \longrightarrow C_3H_7\text{-}COOH \quad (4)$$

$$2CH_3CH{=}CH_2 + 2CO + H_2O \longrightarrow (C_3H_7)_2CO + CO_2 \quad (5)$$

Reaction 4 is a cobalt-catalyzed hydrocarboxylation, which is of little interest to us because it is a well-known example of a Reppe Reaction, which proceeds with no production of CO_2. At 165 °C, CO(50 kg/cm^2), 13.0 mmol of C_4 aldehydes was obtained at a 5 h-reaction and few C_4 acids were formed, though a higher CO pressure favored the formation of the acids (Fig. 1). As is shown in Fig. 1, the total amounts of C_4 aldehydes (abbreviated as [aldehydes]) decreased with the increase in the CO pressure, which is analogous to observations in a normal $Co_2(CO)_8$-catalyzed hydroformylation using CO/H_2.[4)]

Effect of the Temperature. In normal $Co_2(CO)_8$-catalyzed reactions, the C_4 aldehydes which are formed during the hydroformylation are readily reduced to the corresponding C_4 alcohols at a higher reaction temperature.[5)]

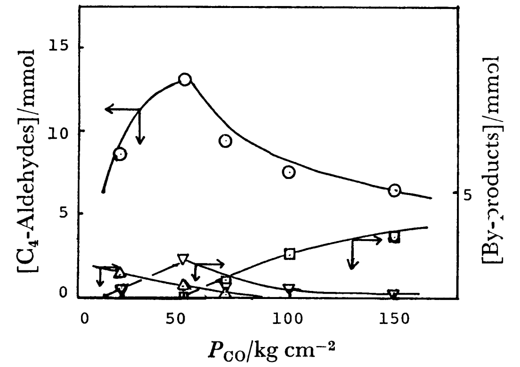


Fig. 1. Effect of CO pressure.
$Co_2(CO)_8$ 2 mmol, diphos 2 mmol, H_2O 60 mmol, dioxane 50 ml, propene 25 mmol, temp 165 °C, time 5 h.
—○—: C_4-aldehydes, —△—: C_4-alcohols, —□—: C_4-acids, —▽—: dipropyl ketones.

The temperature-dependence on the product yields is illustrated in Fig. 2; the reactions were performed using the $Co_2(CO)_8$–diphos system for 5 h under CO (50 kg/cm^2, const). As one would expect, [aldehydes] rather decreased with the increase in the reaction temperature and there was a pronounced formation of C_4 alcohols. It is not obvious from the data whether the C_4 alcohols are formed step-by-step *via* hydroformylation (1) and then reduction (2), or directly from propene (3). Thus, the possibility of the reduction of butyraldehyde to butyl alcohol with CO and H_2O was tested under the same conditions as those employed in Fig. 2, except that butyraldehyde (25 mmol) was used in place of propene. The reduction (2) occurs, but more slowly than in the hydroformylation of propene; the higher the temperature, the larger the amount of butyl alcohol produced[6)] (Fig. 2 - - -,).

Effect of the Propene Concentration. As is shown in Fig. 3, [aldehydes] increased with the initial increase from 25 to 150 mmol of propene, but a further increase of propene resulted in a decrease in the yields. On the other hand, the total amounts of dipropyl ketones ((5), [ketones]) drastically increased, and it turned out, as a result, that the ketones were obtained as the principal products in the reaction of propene with CO and H_2O. Under these conditions, the product molar ratio of 4-heptanone: 2-methyl-3-hexanon: 2,4-dimethyl-3-pentanone was *ca* 1:1.8:0.8; this ratio depends little on the propene concentration.

Generally, dipropyl ketones can be produced under normal oxo conditions in the presence of $Co_2(CO)_8$; the formation of the ketones is favored not only by a high concentration of propene, but also by the use of such hydrogen donors as H_2O, alcohols instead of H_2.[7)] Taking into account the fact that H_2O is used as a hydrogen donor in our $Co_2(CO)_8$–diphos system, the findings in Fig. 3 are analogous to those in the normal $Co_2(CO)_8$ system. In the normal system, however, the formation of the ketones does not predominate over that of the aldehydes (or esters,

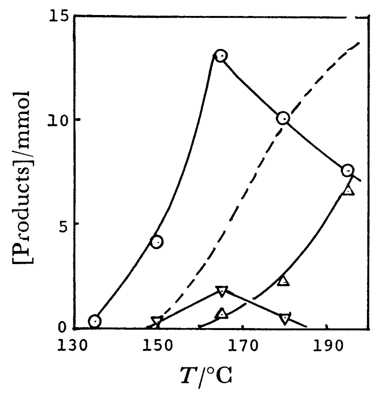


Fig. 2. Effect of temperature.
$Co_2(CO)_8$ 2 mmol, diphos 2 mmol, H_2O 60 mmol, dioxane 50 ml, CO 50 kg/cm^2, propene 25 mmol, time 5 h.
Marks (○,△,▽): See footnote of Fig. 1, dotted line: reduction of butyraldehyde to butyl alcohol.

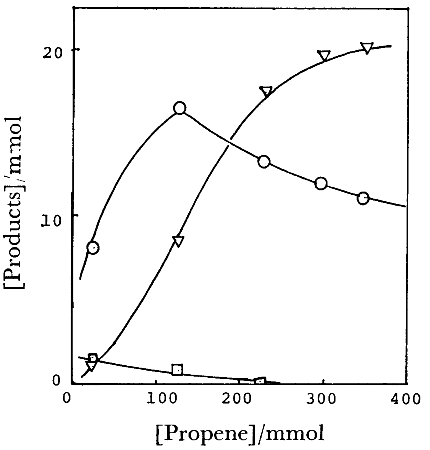


Fig. 3. Effect of propene concentration.
$Co_2(CO)_8$ 2 mmol, diphos 2 mmol, H_2O 60 mmol, dioxane 50 ml, CO 70 kg/cm^2, temp 165 °C, time 5 h.
Marks (○,▽,□): See footnote of Fig. 1.

acids). In this point, the catalytic behavior of $Co_2(CO)_8$ and that of $Co_2(CO)_8$–diphos was quite different. An obvious explanation cannot be obtained from the data shown in Fig. 3; further work is required.

In recent reports on metal carbonyl (cluster)-catalyzed hydroformylation with CO and H_2O, ketone formation has not been referred to at all.[3)] According to our additional experiments, an $RhCl_3$– or $RuCl_3$–Et_3N catalyst system can give dipropyl ketones only as minor product under the conditions shown in Fig. 3. Thus, the $Co_2(CO)_8$–diphos system appears to be more desirable for the exclusive formation of dipropyl ketones from propene; the details will be described in the succeeding paper.[8)]

Catalytic Behavior as a Function of Time. The hydroformylation of propene was repeated under the conditions where C_4 aldehydes are predominantly formed, and aliquots of the catalyst solutions were withdrawn from the autoclave at several reaction times and analyzed. The results are illustrated in Fig. 4(○), where an induction period of *ca.* 1 h was observed. In our catalyst system, under the conditions employed, aldol condensation, by which butyraldehyde is converted to C_8 aldehyde, occurs to only a slight extent with the progress of the reaction (see Fig. 4(○,●)), partly because alkali or organic amine is absent in the solution.[9)]

The presence of an induction period is of interest in connection with the intermediates present in the catalyst solutions. The period disappears on the pretreatment of the solution ($Co_2(CO)_8$–diphos–dioxane) with both CO (50 kg/cm^2) and H_2O (60 mmol) at 165 °C for 1 h in the absence of propene (Fig. 4, □),[10a)] whereas it does not disappear on the similar pretreatment of the solution with only CO (Fig. 4, △).[10b)] These findings indicate that the H_2O molecule is required for the production of intermediates, which are themselves responsible for the hydroformylation with CO and H_2O. Considering that the catalytic behavior of $Co_2(CO)_8$–diphos system using CO–H_2O is relatively similar to those of normal $Co_2(CO)_8$ using CO–H_2 (Figs. 1, 2, and 3), cobalt carbonyl hydride complexes ($(HCo(CO)_m(diphos)_n$, (A))[11)] may be probable candidates as the key intermediates necessary for the catalysis of the reaction. Rhodium or ruthenium carbonyl hydrides have already been proposed as intermediates active in hydroformylation using CO–H_2O.[3b)]

In the absence of propene, the $Co_2(CO)_8$–diphos system is active in the water-gas-shift reaction (WGSR), thoguh its catalytic activity is *ca.* ten times lower than that of the hydroformylation.[1)] Therefore, there is a possibility that the catalytic intermediates which catalyze the hydroformylation participate in the WGSR.[12)] In fact, the catalyst solutions derived from the $Co_2(CO)_8$–diphos system show the same absorptions in the metal carbonyl regions in both the presence and absence of propene.[13)]

Unfortunately, attempts to isolate (A) were not successful.[14)] Also, it is not obvious from our data that the catalytic intermediates, (A), which are necessary for the catalysis of the hydroformylation, are in fact involved in the catalysis of the WGSR. However, undoubtedly, intermediates active in the hydroformylation of propene, as well as in the WGSR, can be formed only from $Co_2(CO)_8$, diphos, and H_2O (Fig. 4).

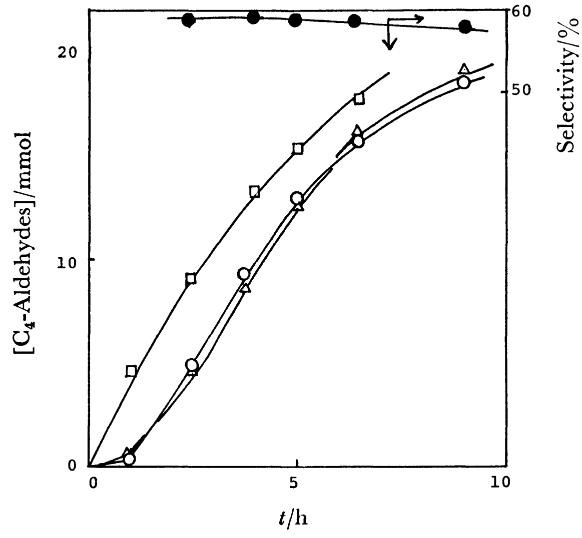


Fig. 4. Cobalt-catalyzed hydroformylation as a function of time.

$Co_2(CO)_8$ 2 mmol, diphos 2 mmol, H_2O 60 mmol, dioxane 50 ml, CO 50 kg/cm^2, temp 165 °C, propene 25 mmol. Products other than C_4-aldehydes are omitted.

—○—: Standard reaction, —□—: reaction after the pretreatment with CO and H_2O, —△—: reaction after the pretreatment with only CO, —●—: selectivity to linear aldehyde.

References

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3) a) H. Kang, C. H. Mauldin, T. Cole, W. Slegeir, K. Cann, and R. Pettit, *J. Am. Chem. Soc.*, **99**, 8323 (1977); b) R. M. Laine, *ibid.*, **100**, 6451 (1978).

4) The catalytic activity rather decreased at a CO pressure of 20 kg/cm^2 because of the partial decomposition of $Co_2(CO)_8$.

5) B. R. James, "Homogeneous Hydrogenation," Wiley, New York (1973), p. 158.

6) The rate of the reduction of isobutyraldehyde to isobutyl alcohol was approximately the same as that of butyraldehyde under these conditions.

7) I. Wender and P. Pino, "Organic Synthesis *via* Metal Carbonyl," Wiley, New York (1977), Vol. 2, p. 215.

8) K. Murata and A. Matsuda, *Bull. Chem. Soc. Jpn.*, **54**, 249 (1981).

9) The preferential condensation of aldehyde occurs during the ruthenium-catalyzed hydroformylation using CO–H_2O in the presence of KOH.[3b)]

10) a) After this pretreatment, propene (25 mmol) was introduced at room temp; the reaction was then carried out under conditions identical with those shown in Fig. 4(○); b) In this run, propene (25 mmol) and H_2O (60 mmol) were introduced at room temp.

11) When either $CH_3CCo_3(CO)_9$ or $Co_4(CO)_{12}$ was used as a catalyst precursor, a longer induction period resulted.

12) Thus, if this is so, the following ideal catalytic cycles, for example, can be surmised in comparison with Heck's mechanism: the intermediates (A) formed during the course of the shift reaction could be trapped by propene (hydride addition), followed by CO insertion, accompanied by the elimination of aldehyde to reform (A). R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

13) These include ν_{CO} 2062(ms), 2922(m, sh), 1986(s), and 1887(m) cm^{-1}.

14) More recently, we have found that the ^{1}H-NMR spectrum of an active water-gas-shift catalyst solution consisting of $Co_2(CO)_8$, diphos, H_2O, and dioxane displays a characteristic resonance at δ -17.2. Further studies of this will be discussed elsewhere.