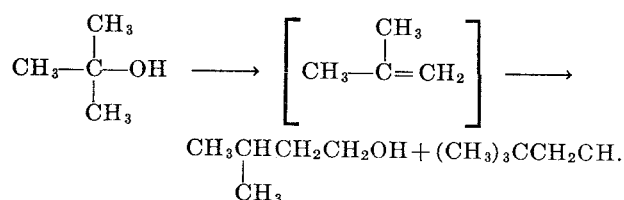


## Lengthening the Carbon Chain (Homologation) of Alcohols

Workers at the Bureau of Mines found that alcohols were converted to the primary alcohol containing one carbon atom more than the original (homologation), when treated with a cobalt catalyst and synthesis gas at 185° to 190° C. This homologation is a general reaction applicable to tertiary, secondary, and primary aliphatic alcohols and, as has been shown earlier, to benzyl alcohol.

t-Butyl alcohol reacts rapidly at 150° to 180° C. to give isoamyl alcohol, together with small amounts of neopentyl alcohol (146, 151). This reaction undoubtedly involves dehydration of t-butyl alcohol to isobutylene, followed by an oxo reaction on the olefin:



Isobutylene was identified in the tail gas of this reaction. If the reaction is conducted below 150° C., the chief product is isovaleraldehyde.

Isopropyl alcohol reacts much more slowly under oxo conditions to give an 11-percent yield of a mixture of isobutyl and n-butyl alcohols. Propyl alcohol reacts very slowly under the same conditions to give a 6-percent yield of a mixture of n-butyl and isobutyl alcohols. Traces of alcohols containing five carbon atoms were also present in the reaction products.

An important discovery was made, however, when it was found that the simplest primary alcohol, methyl alcohol, is anomalous in that it reacts with synthesis gas more rapidly than do secondary alcohols (147). Ethyl alcohol is the chief product of the reaction, and the conversion presents a new route to this alcohol that may have important theoretical and commercial implications. Interest in the reaction from a mechanism point of view arises from the fact that methanol cannot react via an olefin intermediate.

In one experiment 2 moles (64.1 g.) of methyl alcohol and 4 g. of dicobalt octacarbonyl were placed in a 500-ml. stainless steel autoclave. Synthesis gas (1H<sub>2</sub>+1CO) was added until the pressure reached 3,500 p.s.i. The autoclave was then heated with rocking to 185° C. within 65 minutes. The maximum pressure obtained was 5,100 p.s.i. at 181° C.; it dropped to 2,410 p.s.i. while the temperature was held at 183° to 185° for 4 hours. The reaction vessel was cooled to room

temperature and then repressured to 3,000 p.s.i. with 1H<sub>2</sub>+1CO. The temperature was raised once more to 185° C. (maximum pressure, 4,560 p.s.i. at 167° C.) and held at this temperature for 4 hours, during which time the pressure dropped to 3,150 p.s.i. The total pressure drop corresponded to approximately 3.6 moles of gas, or 2.3 moles of gas per mole of methyl alcohol converted. After cooling to room temperature overnight, gas samples were taken, and the residual gases were vented to the atmosphere. Mass spectrometric analysis of the fractionated mixture showed that 49.0 g. (76.4 percent) of the methyl alcohol had reacted to give the following products:<sup>13</sup>

Compound	Yield, percent
Methyl formate.....	2.0
Methyl acetate.....	9.0
Ethyl alcohol.....	38.8
Ethyl acetate.....	6.3
Propyl alcohol.....	4.7
Butyl alcohol.....	.9
Methane.....	8.5
Propyl acetate.....	.1
Total.....	70.3
Water.....	90.8

Approximately 2 g. of the distilled product could not be identified. Acetaldehyde was identified in the lower boiling fractions as its 2,4-dinitrophenylhydrazone, melting point, 148.3° to 149.2° C., but no estimate of its total concentration could be made. A semisolid residue (6.4 g.) containing metallic cobalt and organic material was left in the distillation flask.

The variety and distribution of the products have certain similarities to the oxygenated products secured in the Fischer-Tropsch process (107). Ethanol is the chief oxygenated product from the Fischer-Tropsch reaction, and relatively small quantities of methyl, propyl, and butyl alcohols are found. The preponderance of ethanol and the relatively small amounts of methanol, n-propanol, and butanols in the Fischer-Tropsch process products may be related to the rapid conversion of methanol and the slow reaction of ethanol in hydroformylation.

This study of the conversion of alcohols to the next higher homologs by treatment with synthesis gas has been extended by Ziesecke (163).

Earlier work had shown that treatment of benzyl alcohol with 2H<sub>2</sub>+1CO and a cobalt catalyst gives a mixture of toluene and the homologous alcohol, 2-phenylethanol, in a ratio of about 2:1 (149). When substituted benzyl alcohols of the type C<sub>6</sub>H<sub>5</sub>CR'R''OH (where R' and R'' are alkyl and/or aryl groups) are similarly treated, the corresponding hydrocarbons are formed almost exclusively. This study was extended to nuclear-substituted benzyl alcohols to determine (1) the relative proportions of the hydrogenated and homologated products and (2) the effect of different substituent groups on the rates of the two reactions. All reactions were conducted at

<sup>13</sup> Yields are based on converted methanol.

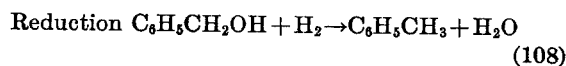
TABLE 34.—*Reduction of thiophene compounds with synthesis gas (2H<sub>2</sub>:1CO) and a cobalt catalyst at 180°–190° C.<sup>1</sup>*

Starting compound	Moles	Benzene, ml.	Cobalt, g. <sup>2</sup>	Time, hours	Product	Yield, percent
Thiophene.....	1.5	20	6	5	{Thiolane.....	50
Do.....	1.01	80	10	4	{Thiophene.....	25
2-Methylthiophene.....	.89	20	1.4	4	{Thiolane.....	66
Do.....	1.00	80	2.6	5	{Thiophene.....	24
2-Ethylthiophene.....	.40	80	2.6	3	{2-Methylthiolane.....	51
2,5-Dimethylthiophene.....	.44	50	1.4	5	{2-Methylthiophene.....	39
2-Thenyl alcohol.....	.36	50	1.4	4	{2-Methylthiolane.....	77
2-Acetylthiophene.....	.72	20	2.7	3	{2-Methylthiophene.....	5
Do.....	1.0	20	2.7	1	{2-Ethylthiolane.....	82
2-Thiophenecarboxaldehyde.....	.37	35	.8	.75	{2-Ethylthiophene.....	6
					{2,5-Dimethylthiolane.....	22
					{2,5-Dimethylthiophene.....	53
					{2-Methylthiophene.....	24
					{2-Methylthiolane.....	57
					{2-Ethylthiophene.....	52
					{2-Ethylthiolane.....	26
					{2-Acetylthiophene.....	25
					{2-Ethylthiophene.....	66
					{2-Thenyl alcohol.....	41
					{2-Methylthiophene.....	26
					{2-Thiophenecarboxaldehyde.....	17

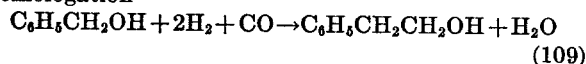
<sup>1</sup> Initial pressure, 3,500–4,000 p.s.i. at room temperature.<sup>2</sup> As Co<sub>2</sub>(CO)<sub>8</sub> or as a cobalt salt.<sup>3</sup> Hexane used as solvent; 1H<sub>2</sub>+1CO used in this experiment.

185° to 190° C., with an initial pressure of 238 atm. of 2H<sub>2</sub>+1CO.

Alcohols, solvent benzene, and dicobalt octacarbonyl were heated in an autoclave from room temperature to 190° C. in 110 minutes. The rates with which the various substituted alcohols reacted with synthesis gas were followed by observing the drop in pressure (tables 35 and 36). Although the stoichiometry of reduction (equation (108)) is quite different from that of homologation (equation (109)), both reactions

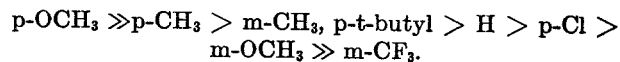


Homologation



usually proceed simultaneously, and the rate of gas absorption can be used as a rough measure of the speed of the overall reaction.

The time interval required to absorb 1 mole of gas per mole of starting alcohol was used qualitatively to compare reaction rates. The temperatures at which this absorption occurred varied; table 36 gives time and temperature data. Thus, p-methoxybenzyl alcohol had absorbed 1 mole-equivalent of gas 6 minutes after the temperature reached 80° C.; the temperature at the end of this time interval was only 92° C. p-Methylbenzyl alcohol absorbed this amount of gas between 80° and 166° C. in 44 minutes. Table 36 also shows that the rates of uptake of gas were in the following order:

TABLE 35.—*Reaction of substituted benzyl alcohols with 2H<sub>2</sub>+1CO<sup>1</sup>*

Substituent	Weight-percent				Recovered starting alcohol	Other products
	Hydrocarbon	Homologated alcohol	Homologated hydrocarbon	Recovered starting alcohol		
p-Methoxy.....	16	44	4.9	0	0	Approximately 34 percent high-boiling polymer, probably aldol of p-methoxyphenylacetaldehyde. <sup>3</sup>
p-Hydroxymethyl.....	27	39	1.9	0	0	
p-Methyl.....	58	24	.6	0	0	8 percent of high-boiling polymer, probably aldol. <sup>3</sup>
m-Methyl.....	52	36	.7	0	0	1–2 percent m-methylbenzaldehyde.
p-t-Butyl.....	54	28	.5	0	0	<1 percent p-t-butylbenzaldehyde.
Benzyl.....	63	31	.5	0	0	
2,4,6-Trimethyl.....	58	18	.3	0	0	
p-Chloro.....	41	16	.4	31	4	4 percent p-chlorobenzaldehyde.
m-Methoxy.....	23	42	.1	56	4	4 percent m-methoxybenzaldehyde.
m-Trifluoromethyl.....	5			78	4	4 percent m-trifluoromethylbenzaldehyde.
p-Carboethoxy.....	27					High-boiling products.
p-Nitro.....				44		Polymer of p-aminobenzyl alcohol.

<sup>1</sup> Initial total pressure of gas was 238 atm. Maximum time allowed for reaction was 5 hours at 185°–190° C.<sup>2</sup> This product added to yield of homologated product in column 4.<sup>3</sup> A yield of 12 was obtained for dihomologated alcohol, p-phenylene-β,β'-diethanol.<sup>4</sup> Approximately.

TABLE 36.—Relative rates of reaction of substituted benzyl alcohols

Substituent	Time, minutes <sup>1</sup>	Temperature, °C <sup>2</sup>	Relative reaction rate <sup>3</sup>
p-Methoxy.....	6	92	10,000
p-Methyl.....	44	166	200
m-Methyl.....	67	188	50
p-t-Butyl.....	67	188	50
Hydrogen.....	82	190	1
p-Chloro.....	109	190	.8
p-Carboxy <sup>4</sup> .....	231	190	.4
m-Methoxy <sup>4</sup> .....	254	190	.3
m-Trifluoromethyl.....	<sup>5</sup> 10,000	190	.01

<sup>1</sup> Time required to absorb 1 mole of gas per mole of starting alcohol after the temperature reached 80° C.

<sup>2</sup> Temperature reached at the end of time interval in column two. The last four alcohols started to react at 190° C.; benzyl alcohol started to absorb gas slowly at 180° C.

<sup>3</sup> On the assumption that the reaction rate doubles for each 10° rise this column indicates the ratio of time necessary for 1 mole of gas to be absorbed per mole of benzyl alcohol at 190° C. to the time required for the substituted benzyl alcohol at 190° C. The average of the temperature recorded in column three and 80° C. is taken as the temperature at which the reaction started.

<sup>4</sup> The rate data for p-carboxy and for m-methoxybenzyl alcohols are for 0.35-mole runs and are therefore not strictly comparable with the other data, which are for 0.6-mole runs.

<sup>5</sup> Only 5 percent of the alcohol reacted in 5 hours, and several days would probably be required to absorb 1 mole equivalent of gas.

This sequence of substituents is in the order of their ability to release electrons. All the benzyl alcohols having electron-releasing substituents started to react between 80° and 166° C. Benzyl alcohol started to absorb gas at 180° C. The alcohols having electron-attracting substituents reacted so slowly at 100° C. that starting alcohol was recovered after 5 hours; some dehydrogenation of the starting alcohol occurred, and significant quantities of the corresponding aldehydes were identified in the reaction products from these experiments.

Table 35 shows that, in general, as the relative speed of the reaction decreased, the quantity of product derived from homologation decreased as compared with that from hydrogenolysis. For example, after 5 hours at 190° C., more than half of the original m-methoxybenzyl alcohol was recovered unchanged, and nearly all of the reacted portion was reduced. However, p-methoxybenzyl alcohol reacted more than 10 times as fast as m-methoxybenzyl alcohol, and most of the p-methoxy compound reacted by homologation, although considerable p-methoxytoluene (hydrogenation) was secured.

2,4,6-Trimethylbenzyl alcohol reacted rapidly with synthesis gas to yield 58 percent of hydrocarbon and 18 percent of homologated alcohol. Evidently the o-methyl groups did not impose any serious steric restriction on hydrogenolysis or homologation.

The reaction of p-nitrobenzyl alcohol illustrates the retarding effect of an electron-attracting group in the para position upon the reduction and homologation reactions. Almost half of the starting alcohol (40 percent) was

recovered unchanged. After removal of the liquid products from the autoclave, a brown solid was left, the ultimate analysis of which was consistent with polymeric p-aminobenzyl alcohol. Reduction of the nitro group was evidently the fastest reaction; the aminobenzyl alcohol formed is known to polymerize very rapidly in the presence of traces of acids. The possibility of reducing nitro groups with synthesis gas and a cobalt catalyst suggested by this experiment was realized by the reduction of nitrobenzene to aniline.

The rate measurements listed in table 36 were semiquantitative, and the determination of product distribution (table 35) was frequently difficult. Nevertheless, the data indicate that (1) electron-releasing substituents in the meta and para positions markedly increase the rates of reduction and homologation, and (2) the proportion of homologation product increases in the order in which the substituent is capable of releasing electrons. However, this effect is not nearly as pronounced as the effect on the reaction rates. Thus, homologation and reduction may proceed via a common intermediate (possibly a carbonium ion) by reaction of the alcohol with the acid  $\text{HCo}(\text{CO})_4$ , and this intermediate is transformed to the various final products at different rates.

## Rearrangements Under Hydroformylation Conditions

Cobalt hydrocarbonyl is a strong acid and, under hydroformylation conditions, may function as an acid catalyst. Only one instance is reported of an acid-catalyzed rearrangement under oxo conditions: Pinacol gave, among other products, some pinacolyl alcohol and pinacolone (154). These compounds are known to form when pinacol is treated with an acid. Other reaction products identified were 3,4-dimethyl-1-pentanol and 2,2,3-trimethyltetrahydrofuran. All these products may be derived from the postulated intermediate (A), according to the scheme outlined in figure 17, by a series of reactions involving acid catalysis. The suggested mode of formation of pinacolone is apparent from figure 17. Previous work has shown that aliphatic ketones are reduced slowly to alcohols in the presence of dicobalt octacarbonyl and synthesis gas; a similar reduction of pinacolone accounts for the formation of pinacolyl alcohol. Loss of a proton from A before rearrangement could give the unsaturated alcohol B. This alcohol was not isolated, but dehydration to 2,3-dimethylbutadiene is likely under the acidic conditions of the reaction. Hydroformylation of 2,3-dimethylbutadiene is known to yield 3,4-dimethyl-1-

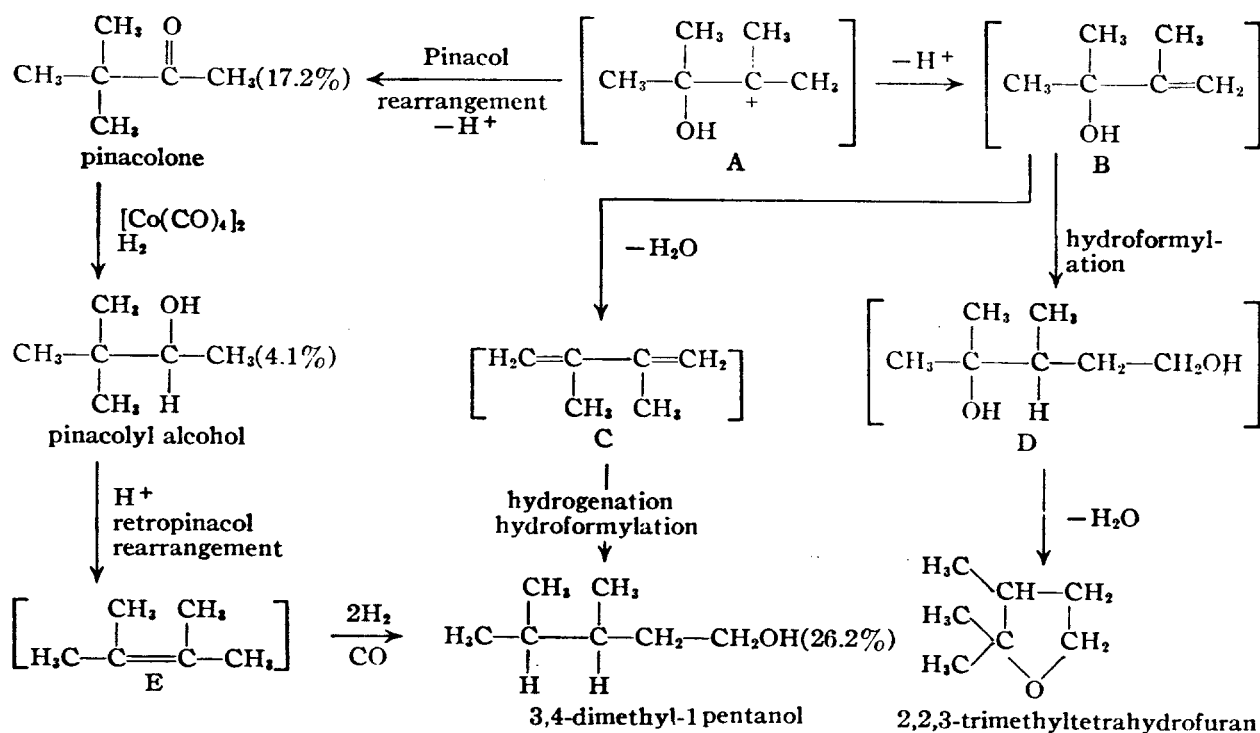
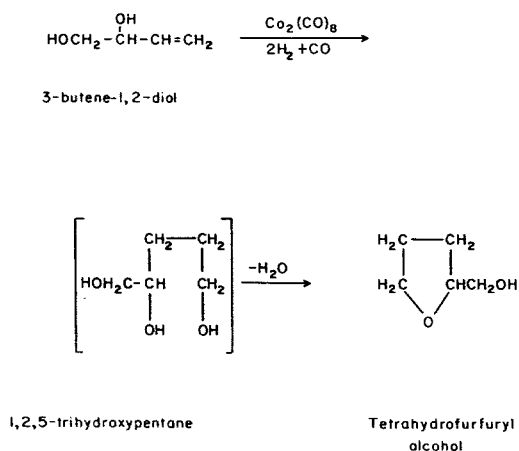


FIGURE 17.—Hydroformylation of Pinacol.

pentanol (3). As the conditions of the present reaction were nearly identical with those for hydroformylation, the postulated series of reactions (fig. 17) accounts for the formation of 3,4-dimethyl-1-pentanol. An alternate but less likely route to this alcohol consists of the retro-pinacol rearrangement of pinacolyl alcohol, followed by hydroformylation of the resulting tetramethylethylene (75).

The formation of a tetrahydrofuran system from an acyclic compound has been reported: 3-butene-1,2-diol, an unsaturated alcohol structurally similar to B, gave tetrahydrofurfuryl alcohol, according to the following postulated series of reactions (33).



Corroboration for this transformation was obtained by Wender, Metlin, and Orchin (154). 1,2,5-Trihydroxypentane was synthesized and treated with synthesis gas and dicobalt octacarbonyl at 185° C.; tetrahydrofurfuryl alcohol (25.5-percent yield) was indeed obtained. If B is an intermediate in the reaction of pinacol with synthesis gas, a similar reaction should yield the diol D, which, by a mechanism analogous to the conversion of 1,2,5-trihydroxypentane to tetrahydrofurfuryl alcohol, could lose water to yield 2,2,3-trimethyltetrahydrofuran. Examination in the mass spectrometer of the fraction boiling from 106° to 129° C. showed (1) no mass peaks above 120, (2) peaks at 102 (pinacolyl alcohol) and 100 (pinacolone), and (3) a large peak at 99. The 99 peak was not present in the spectra of pure pinacolyl alcohol or pinacolone. This peak probably resulted from an ionization process, as no compound containing carbon (atomic mass 12), hydrogen (atomic mass 1), and oxygen (atomic mass 16) can have an odd number as its molecular weight. The loss of CH<sub>3</sub> (mass 15) from 2,2,3-trimethyltetrahydrofuran, molecular weight 114, would give a 99 peak. The failure to obtain a peak at 114 corresponding to a molecular weight of 2,2,3-trimethyltetrahydrofuran is not unexpected, as many compounds fail to give peaks corresponding to their molecular weight.

To eliminate the possibility that a thermal rearrangement of pinacol to pinacolone occurred

at 185° C., pinacol was heated at this temperature with 3,200 p.s.i. of nitrogen in the presence of a cobalt catalyst. No rearrangement occurred, and 85 percent of the starting material was recovered unchanged.

The evidence strongly indicates that acid-catalyzed reactions can occur in the system comprising synthesis gas and a cobalt catalyst at about 185° C. This acid is very likely cobalt hydrocarbonyl, which is in equilibrium with dicobalt octacarbonyl.

All the rearranged materials, however, contain the same number of carbon atoms as the starting material. Accordingly, there is as yet no example in which a hydroformylation product has been secured which arose from a skeletal rearrangement of the olefin.

## The Reactions of Acetylenes

### POLYMERIZATION OF ACETYLENES BY DICOBALT OCTACARBONYL

When dicobalt octacarbonyl is treated with acetylene at room temperature, carbon monoxide is evolved, and the dicobalt hexacarbonyl acetylene complex XLVIII, a dark-red oil, is formed according to equation (101). When the complex XLVIII is allowed to remain in contact with acetylene, acetylene is slowly taken up, and the red oil is changed into a dark red-brown solid. At room temperature the uptake of acetylene is slow, about 0.2 mole of acetylene in 24 hours per mole of complex XLVIII. At elevated temperature the rate of uptake of acetylene is considerably faster, but it decreases rapidly with time. At 80° C., for example, the rate of acetylene uptake per mole of acetylene complex (at a constant acetylene pressure of 1 atm.) dropped from 1 mole in the first hour to 0.25 mole in the second hour and to 0.20 mole in the fourth hour.

In one experiment the reaction was interrupted when 5 moles of acetylene had been absorbed per mole of acetylene complex. The reaction product was a dark-red brittle resin, soluble in pyridine, slightly soluble in benzene and acetone, and insoluble in absolute alcohol. The fact that 5 moles of acetylene were absorbed per mole of acetylene complex indicates that polymerization has occurred.

Acetylene is also absorbed when the acetylene complex is present in solution. In one experiment a 0.35 molar solution of the acetylene complex in heptane was treated with acetylene until 0.3 mole of gas had been taken up per mole of complex. The uptake of acetylene was accompanied by the formation of a dark brown precipitate. The infrared spectrum of the solution showed, in addition to the three bands characteristic for the three terminal carbonyl

groups in the acetylene complex, a sharp strong band at 5.31  $\mu$ , that is, in the bridge carbonyl region.

Monosubstituted acetylenes, such as methylacetylene, phenylacetylene, and 1-pentyne, also react with the acetylene complex. The reaction of methylacetylene, for example, is analogous to that of acetylene. After formation of the corresponding methylacetylene complex according to equation (101), methylacetylene is absorbed with the formation of a heptane-insoluble precipitate. The spectrum of the heptane-soluble portion is similar to that obtained in the corresponding acetylene experiment, except that the bridge carbonyl band at 5.31  $\mu$  is missing. The heptane-insoluble portion does not contain any metal carbonyl group. This is demonstrated by the fact that no carbon monoxide is evolved when a sample is treated with a solution of iodine in pyridine. Moreover, the spectrum of a solution of the heptane-insoluble portion in pyridine showed no bands attributable to metal carbonyl.

The reactions of 1-pentyne and phenylacetylene with the corresponding acetylene complexes can be followed spectroscopically and also by observing the formation of a precipitate.

In contrast to acetylene and the monosubstituted acetylenes previously mentioned, the disubstituted acetylene, 2-pentyne, does not react with the 2-pentyne dicobalt hexacarbonyl complex. Even after standing for several weeks in excess 2-pentyne, the spectrum of the solution remained that of the pure hexacarbonyl complex, and there was no evidence that any precipitate had formed.

In the preceding experiments the polymerization of the various acetylenes was always carried out in the presence of the corresponding acetylene cobalt carbonyl complex. A study was also made to determine whether or not polymerization will take place in the presence of a complex whose acetylene portion differed from the acetylene to be polymerized.

Two complexes, phenyl and diphenyl acetylene, dicobalt hexacarbonyl, were tested as catalysts for the polymerization of acetylene. No acetylene was absorbed in the presence of the diphenylacetylene complex, even at elevated temperature. However, in the presence of the phenylacetylene complex, acetylene was absorbed at a rate comparable with that observed when the acetylene complex was used. The reaction was interrupted after 1 mole of acetylene had been absorbed per mole of phenylacetylene complex at 75° C. Analysis of the gas revealed that a little carbon monoxide (0.2 mole of carbon monoxide per mole of phenylacetylene complex) had been evolved, an indication that some (3.3 percent) of the complex had been destroyed.

Despite the exploratory nature of these ex-

periments, they permit some interesting conclusions. In the presence of acetylene or monosubstituted acetylenes, dicobalt octacarbonyl reacts to form the corresponding acetylene dicobalt hexacarbonyl complex. When this acetylene complex is treated with excess acetylene, the following two reactions take place: A new acetylene complex is formed, and the acetylene is polymerized. The polymerized product contains little if any cobalt carbonyl complex. The rate of acetylene uptake is slow at room temperature and fast at elevated temperature. At elevated temperature the rate of polymerization decreases rapidly with time, probably owing to decomposition of the complex. Acetylene, or any derivative of the formula  $RC\equiv CH$ , is polymerized by the acetylene cobalt carbonyl complex XLVIII at room temperature; complexes derived from acetylene derivatives with no hydrogen atom ( $RC\equiv CR$ ) do not catalyze these polymerizations.

### REACTIONS OF ACETYLENES UNDER HYDROFORMYLATION CONDITIONS

Although hydroformylation of olefins has received considerable attention because of its industrial importance, little work has been done on acetylenes. A mixture of high-boiling, unidentified products was produced by the reaction of acetylene with carbon monoxide and hydrogen in the presence of metallic cobalt catalysts at 120° to 150° C. and 200 to 300 atm. This reaction takes place at a slower rate than the hydroformylation of olefins.

Greenfield, Wotiz, and Wender (53) investigated the reactions of 1-pentyne and of diphenylacetylene under hydroformylation conditions. They studied the effect of small amounts of alkynes on several reactions of nonacetylenic compounds that occur under hydroformylation conditions, and they also reacted acetylene with stoichiometric amounts of cobalt hydrocarbonyl at room temperature and atmospheric pressure.

#### Reaction of 1-Pentyne Under Hydroformylation Conditions

The 1-pentyne began to absorb gas at about 130° C. The temperature was then raised to about 185° C. to convert any aldehydes into the corresponding alcohols (152) which are less reactive and easier to isolate. A 6-percent yield of 1-hexanol and a 5.5-percent yield of 2-methyl-1-pentanol were obtained; the remainder of the product was higher boiling material. Infrared and mass spectroscopic analyses showed the presence of  $C_{12}$  esters in a fraction distilling at 113° to 116° C. at 20 mm. Such esters could be formed by the reaction of 1-pentyne with

carbon monoxide and a  $C_6$  alcohol (96, 97, 111).

1-Hexanol and 2-methyl-1-pentanol may be formed from 1-pentyne by one of two likely reaction paths. In the first case, if the 1-pentyne were hydrogenated to 1-pentene, the olefin would react further to yield the usual hydroformylation products, hexanal and 2-methyl-pentanal. These aldehydes would then be hydrogenated to the corresponding alcohols. In the second case, if the alkyne were first hydroformylated to give  $\alpha$ ,  $\beta$ -unsaturated aldehydes, both the conjugated olefinic linkages and the carbonyl groups would be hydrogenated to yield 1-hexanol and 2-methyl-1-pentanol.

Whereas 1-pentyne began to react at about 130° C., the corresponding olefin, 1-pentene, under similar conditions starts to react at about 90° C. This confirms the earlier observation that acetylene reacts more slowly than olefins under hydroformylation conditions. The double bond generally is more reactive than the comparably situated triple bond toward electrophilic reagents, as in electrophilic halogen additions, and toward free radicals, such as the trichloromethyl radical, whereas the reverse holds true for nucleophilic reagents, such as the methoxide ion. With regard to hydroformylation, however, mechanistic inferences based on the relative reactivities of alkenes and alkynes are complicated by the fact that alkynes, in contrast to alkenes, react readily with dicobalt octacarbonyl at room temperature. As shown earlier, the alkyne replaces two carbonyl groups in dicobalt octacarbonyl and forms an acetylenic dicobalt hexacarbonyl, a stable organometallic compound.

#### Alkynes As Inhibitors of Hydroformylation Reactions

Dicobalt octacarbonyl is probably the catalyst, or the catalyst precursor, for reactions occurring under hydroformylation conditions. A possible explanation of the fact that acetylene and 1-pentyne appear less reactive than the corresponding olefins is that the catalyst has been removed by reaction with the alkynes to form acetylenic dicobalt hexacarbonyls (equation (101)). If the organometallic compound thus formed were not a catalyst, no hydroformylation or hydrogenation should occur until it was transformed into an active catalyst. This point was investigated by using acetylenic dicobalt hexacarbonyls instead of dicobalt octacarbonyl in the following reactions under hydroformylation conditions: Hydroformylation of cyclohexene, hydroformylation of 1-heptene, hydrogenation of crotonaldehyde to butyraldehyde, hydrogenolysis of *p*-methoxybenzhydrol to *p*-methoxydiphenylmethane, and hydrogenolysis and homologation of *p*-methoxy-

benzyl alcohol to p-methoxytoluene and 2-(p-methoxyphenyl) ethanol.

In each of the above cases, the temperature of initial reaction was increased when an acetylenic dicobalt hexacarbonyl was used instead of dicobalt octacarbonyl. The temperature at which reaction took place was different for the various acetylenic dicobalt hexacarbonyls. The effect of acetylenes on hydroformylation of cyclohexene with 233 atm. of  $1\text{H}_2:1\text{CO}$  is shown as follows:

<i>Cobalt added as</i>	<i>Approx. temperature of initial reaction, °C.</i>
Dicobalt octacarbonyl.....	105
1-Hexyne dicobalt hexacarbonyl.....	115
Phenylacetylene dicobalt hexacarbonyl.....	130
Diphenylacetylene dicobalt hexacarbonyl.....	140
Diphenylacetylene dicobalt hexacarbonyl plus dicobalt octacarbonyl.....	105

These results suggest that the reactions just mentioned did not occur until the acetylenic dicobalt hexacarbonyl had been converted to an active catalyst. It is not clear whether this transformation occurs by thermal decomposition, reaction of acetylenic dicobalt hexacarbonyl with carbon monoxide and/or hydrogen, or reaction of acetylenic dicobalt hexacarbonyl with the organic substrate. Experiments with nonacetylenic substrates in the presence of both an acetylenic dicobalt hexacarbonyl and dicobalt octacarbonyl did not show any inhibition. Thus, the previously observed inhibition was due to the absence of dicobalt octacarbonyl rather than to any inhibiting effect of the acetylenic dicobalt hexacarbonyl as such.

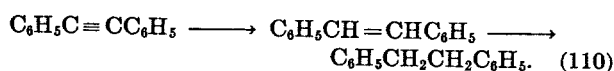
Addition of catalytic amounts of an alkyne makes it possible to run reactions in batch autoclaves above the usual hydroformylation temperature. Such a procedure should change the product distribution and in certain cases might be used to obtain higher yields of desired products.

This effect of alkynes on reactions that are homogeneously catalyzed by cobalt carbonyls has an analog in heterogeneous catalysis. Alkynes inhibit the metal-catalyzed, heterogeneous hydrogenation of olefins (15, 31). Apparently the alkyne monopolizes the catalyst surface because of stronger chemisorption. The similarity is remarkable between intermediates produced by associative adsorption of unsaturated hydrocarbons on dual surface sites of metals (14, 78) and complexes formed in the reaction of dicobalt octacarbonyl with alkynes and olefins.

#### Reaction of Diphenylacetylene Under Hydroformylation Conditions

Diphenylacetylene began to react at approximately 170° C. The temperature was maintained at 180° to 195° C. for about 2 hours.

An 80-percent yield of 1,2-diphenylethane was obtained. Presumably, the course of the reaction was



Cis-stilbene also yields 1,2-diphenylethane as the major product under similar conditions.

#### Stoichiometric Reaction of Acetylene With Cobalt Hydrocarbonyl

Some catalytic reactions which take place under hydroformylation conditions also can be effected by stoichiometric amounts of cobalt hydrocarbonyl at atmospheric pressure and room temperature (150, 159). It was therefore of interest to determine whether alkynes as well as alkenes undergo a stoichiometric reaction with cobalt hydrocarbonyl.

Acetylene gas was allowed to stand for 24 hours with cobalt hydrocarbonyl, carbon monoxide, and hydrogen at room temperature and atmospheric pressure. Infrared and mass spectroscopic analyses showed the absence of cobalt hydrocarbonyl and the presence of acetylene, acetylene dicobalt hexacarbonyl, and propionaldehyde. Presumably, the acetylene dicobalt hexacarbonyl arose from the reaction of acetylene and dicobalt octacarbonyl, the latter being the known product of the decomposition of cobalt hydrocarbonyl (66).

#### Reaction of Allenes With Dicobalt Octacarbonyl

The report that alkynes react with dicobalt octacarbonyl to give a new type of organometallic compound (equation (101)) prompted an investigation of the reaction of allenes with the same carbonyl. Certain allenes were found to react with dicobalt octacarbonyl at room temperature with the evolution of carbon monoxide (52); the primary product of this reaction, which has not been identified, then catalyzes the polymerization of allenes. That the polymerization catalyst is probably an organometallic complex is supported by the isolation of organometallic compounds from the reaction of acetylenes with dicobalt octacarbonyl and by the accumulation of evidence that olefins also form organometallic complexes with dicobalt octacarbonyl under hydroformylation conditions.

Allenenes having a hydrogen atom bonded to an allenic carbon atom (allene, 1,2-heptadiene, 2-butyl-2,3-butadienoic acid, and 2-butyl-2,3-pentadienoic acid) reacted with dicobalt octacarbonyl at room temperature. Tetraphenyl-

allene, which does not have a hydrogen atom on an allenic carbon atom, did not react. No reaction took place at room temperature between dicobalt octacarbonyl and a monoolefin, 1-dodecene, and between the carbonyl and a conjugated diolefin, 1,4-diphenyl-1,3-butadiene.

The results of gasometric experiments with excess allene and with excess 1,2-heptadiene indicate that terminal allenes displace 1 mole of carbon monoxide from 1 mole of dicobalt octacarbonyl. The excess terminal allene polymerizes, either after the reaction with dicobalt octacarbonyl or concurrently with this reaction. For example, the infrared spectrum of the product of the reaction with a fiftyfold molar excess of 1,2-heptadiene showed the absence of any 1,2-heptadiene. In the reaction with excess allene, the polymerization was demonstrated directly by the absorption of large quantities of gaseous allene to form first a liquid and then a solid product. Because of the polymerization, the number of moles of an allene associated with the evolution of 1 mole of carbon monoxide from 1 mole of dicobalt octacarbonyl could not be determined.

An infrared spectrum was obtained from the dark, viscous oil resulting from the reaction of dicobalt octacarbonyl with allene after approximately 8 moles of the allene had been absorbed per mole of dicobalt octacarbonyl. The spectrum indicated the absence of dicobalt octacarbonyl and an allenic group. The spectrum had bands at 6.06  $\mu$ , characteristic of the C=C stretching frequency, and at 11.14  $\mu$ , characteristic of a terminal methylene group. Bands at 4.86 and 5.04  $\mu$  could not be accounted for by any of the known carbonyls of cobalt.

The reaction mixture obtained from treating dicobalt octacarbonyl with excess 1,2-heptadiene was also subjected to infrared analysis. As in the case with allene, the spectrum indicated the absence of dicobalt octacarbonyl and an allenic group. It had bands at 6.08 and 11.18  $\mu$  and also at 4.88, 4.95, 4.97, and 5.04  $\mu$ . This latter group of bands and the absorption

at 4.86 and 5.04  $\mu$  for the product obtained from allene suggest the presence of compounds possessing terminal carbonyl groups of the type found in dicobalt octacarbonyl and the acetylenic dicobalt hexacarbonyls.

In one experiment gaseous allene was allowed to react with dicobalt octacarbonyl until about 5.5 moles of allene had been absorbed per mole of dicobalt octacarbonyl. An attempt was made to distill the reaction mixture, a dark, viscous oil. None of the material was volatile at 45° C. and 1-mm. pressure, suggesting the absence of any hydrocarbons possessing less than 12 to 13 carbon atoms. Thus, the polymer derived from allene apparently did not contain any dimers, trimers, or tetramers.

The results of the investigation of the reactions of dicobalt octacarbonyl with allene and with 1,2-heptadiene suggest that the initial product is an organocobalt compound that can catalytically polymerize allenes under very mild conditions. The polymerization products appear to be high-molecular-weight substances. The progressive transformation of octacarbonyl and gaseous allene from an oil to a solid suggests that the degree of polymerization increases with further addition of allene.

An infrared spectrum was obtained of the reaction mixture resulting from the treatment of 2-butyl-2,3-butadienoic acid with excess dicobalt octacarbonyl. The spectrum showed the presence of unreacted dicobalt octacarbonyl and the absence of any absorption bands that could be attributed to allenic or carboxyl groups. Hence, the reaction of allenic acid with dicobalt octacarbonyl apparently involved the allenic and the carboxylic acid groups.

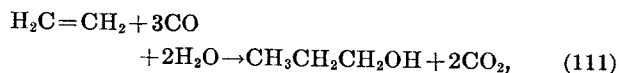
A product of the reaction of allene and dicobalt octacarbonyl was able to catalyze the polymerization of additional allene in several days. Experiments with propylene and with ethylene showed that the catalyst for the polymerization of allene was inactive for polymerizing simple monoolefins under the same reaction conditions.

## SOME CATALYTIC PROPERTIES OF IRON CARBONYLS

The work presented to this point has shown that cobalt carbonyls and their derivatives function as catalysts for many reactions. Iron catalysts have supplanted cobalt in the Fischer-Tropsch reaction, and it was therefore of interest to explore the catalytic possibilities of iron carbonyl. Although metal carbonyls as a class have catalytic properties, the conditions under which the various carbonyls function as catalysts vary with the electronic character of the metal.

An examination of the literature revealed that solutions obtained by treating iron pen-

tacarbonyl with aqueous alkali have intriguing chemical and catalytic properties, which include the conversion of olefins to the next higher alcohols (116),

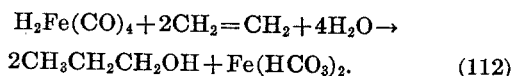


reduction of nitrobenzene to aniline (89), benzil to benzoin (89), quinone to hydroquinone (89), and acetylene to ethylene (129). The fact that alkali is important in these reactions was considered significant, because addition of



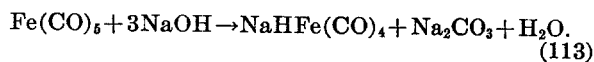
alkali to Fischer-Tropsch iron catalysts constituted one of the most important steps in their development (135). A program to elucidate the nature of the catalytic species involved in the reactions catalyzed by the iron pentacarbonyl-aqueous alkali system was therefore initiated; the results are summarized below.

Reppe and Vetter (116) have shown that aqueous solutions, prepared by treating iron pentacarbonyl with alkali, react with olefins at elevated temperature to form the next higher alcohols. This reaction was thought to be due to the presence of iron hydrocarbonyl,  $\text{H}_2\text{Fe}(\text{CO})_4$ , and is formulated as



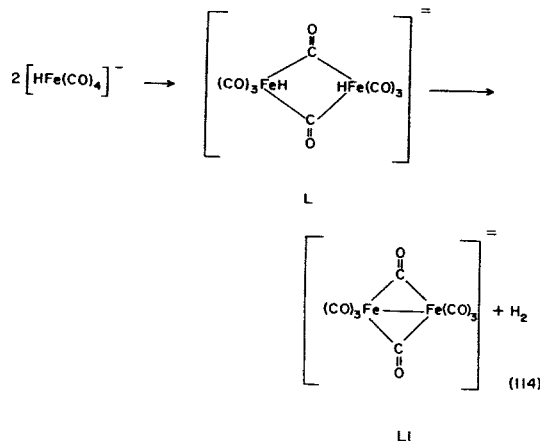
The reaction requires stoichiometric amounts of iron pentacarbonyl. A modification of this reaction, using carbon monoxide at elevated pressures and catalytic amounts of iron pentacarbonyl in alkaline solutions, was also reported by Reppe and Vetter and expressed by equation (111). Since hydrogen and the hydroxymethyl group ( $-\text{CH}_2\text{OH}$ ) are added across the double bond, this may be termed a hydrohydroxymethylation reaction; for convenience we shall refer to it as the hydroxymethylation of olefins. The reaction resembles the hydroformylation of olefins in that carbon monoxide and hydrogen are added to the double bond; it differs in several ways: (1) A carbonyl of iron rather than cobalt is used as the catalyst; (2) the reaction is carried out in aqueous alkali rather than in an organic solvent; (3) water rather than molecular hydrogen is the source of hydrogen, and (4) in contrast to hydroformylation, which yields about 50 percent each of straight- and branched-chain alcohols, the hydroxymethylation reaction, like the Fischer-Tropsch process, yields primarily straight-chain alcohols.

Since the catalyst for hydroxymethylation is obtained by treating iron pentacarbonyl with aqueous alkali, it was first necessary to consider the reactions that occur when iron pentacarbonyl is treated with this reagent. Krumholz and Stettiner (76) have shown that when 1 mole of iron pentacarbonyl is treated with 3 moles of sodium hydroxide in aqueous solution, iron hydrocarbonyl anion,  $[\text{HFe}(\text{CO})_4]^-$ , is formed:

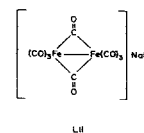


As shown earlier, the ion  $[\text{HFe}(\text{CO})_4]^-$  dimer-

izes to yield L; complex L readily loses 1 mole of hydrogen to form LI:

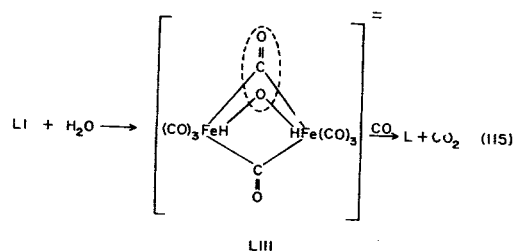


From neutral or weakly alkaline aqueous solutions, a monosodium salt (LII) of the acid derivative of LI can be obtained by extraction with ether:



This salt is a dark-red solid which forms stable 1:1 adducts with water, methanol, and diethyl ether. The solvent in these complexes is tightly held and is only removed by heating in vacuum. These molecules ( $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ) are utilized in a number of metal carbonyl catalyzed reactions, as a source of hydrogen or to furnish hydroxide or methoxide radicals or ions.

At elevated pressures of carbon monoxide, anion LI functions as a catalyst for the water-gas shift, as shown by the fact that the formation of hydrogen and carbon dioxide from water and carbon monoxide takes place. In the presence of excess carbon monoxide, a bridge carbonyl splits out oxygen from the water in the complex with the simultaneous formation of two iron-hydrogen bonds:

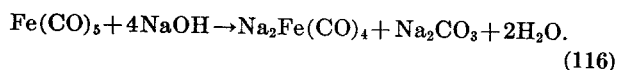


In the absence of an olefin, L loses hydrogen to form LI. In the presence of a reducible substrate (olefin or aldehyde), hydrogen is transferred from L to the unsaturated linkage.

Despite the striking similarity between iron complexes L and LI and the corresponding cobalt complexes (dicobalt octacarbonyl and XLIX), there is one important difference: The iron complexes are anions, whereas the cobalt complexes are uncharged. This difference explains the course of hydroxymethylation in a manner analogous to that postulated for hydroformylation.

Hydroxymethylation may be divided into two separate steps. The first is addition of —H and —CHO to the double bond just as in hydroformylation. The second is hydrogenation of the aldehyde to the corresponding alcohol; this same reduction to alcohols occurs in hydroformylation above 150° C.

Reppe and Vetter did not report the presence of aldehydes in their reaction products. This may be partly because they used strongly basic solutions; when a mole of iron pentacarbonyl is treated with 4 or more moles of sodium hydroxide,  $[\text{Fe}(\text{CO})_4]^-$  rather than  $[\text{HFe}(\text{CO})_4]^-$  is formed:

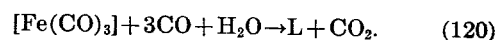
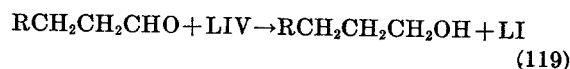
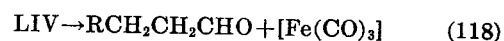
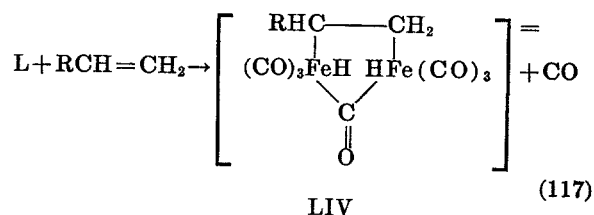


Sternberg, Markby, and Wender found that aldehyde is formed exclusively under certain conditions. Thus, when cyclopentene was treated at 155° C. and 160 atm. carbon monoxide pressure with an aqueous solution prepared from  $\text{Fe}(\text{CO})_5$  and NaOH in a molar ratio of 1:3, the reaction product contained

only cyclopentanecarboxaldehyde and unchanged cyclopentene.

That aldehydes are indeed reduced to alcohols under reaction conditions was shown by adding benzaldehyde to a solution obtained by treating pentacarbonyl with aqueous alkali prepared according to equation (113); the aldehyde was readily reduced to benzyl alcohol.

The course of the hydroxymethylation reaction may be pictured in approximately the following manner:



The cobalt carbonyl-catalyzed isomerization of olefins also finds its parallel in the iron carbonyl system. When 1-hexene is shaken with an aqueous solution containing the anions L and LI, it is converted to a mixture of 2- and 3-hexenes. Double-bond isomerization also takes place under the conditions of hydroxymethylation; when 1-octene is hydroxymethylated at 160° to 175° C. and 160 atm. of carbon monoxide, all the unreacted olefin is converted to a mixture of internal olefins.