proportional to the increase in hydrogen pressures. The same kinetic behavior with regard to the partial pressure of carbon monoxide was observed with propylene and 2-ethyl-1-hexene.

The effect of olefin structure on rate was presented in table 23. A further discussion of these results will be presented under Mechanism of Hydroformylation.

Although the reaction is first order with respect to olefin concentration at low pressures, the dependence of the rate on cobalt concentration varied with the carbon monoxide pressure. Above 50 atm. of carbon monoxide, the rate was approximately directly proportional to the cobalt concentration (first order). For lower carbon monoxide pressures, the apparent order decreased to a value of about one-half.

MECHANISM OF HYDRO-FORMYLATION

Function of Carbonyls

At least three carbonyls of cobalt are involved in the addition of carbon monoxide and hydrogen to an olefin. Their preparation and properties have been described earlier; their probable roles in the hydroformylation reaction will now be discussed.

Direct addition of carbon monoxide to an olefin is excluded because the rate of hydroformylation varies inversely with the pressure of carbon monoxide. Reaction occurs in the liquid phase, and carbon monoxide is transferred to the olefin from an intermediate, which contains carbon monoxide bound to at least one metal atom. The probable functions of the three carbonyls are as follows:

1. Carbon monoxide in the gas phase must be made available as a metal carbonyl in the liquid phase. This probably occurs by transformation of the tricarbonyl to the tetracarbonyl or to cobalt hydrocarbonyl.

$$Co_4(CO)_{12} + 4CO \rightleftharpoons 2Co_2(CO)_8$$

$$Co_4(CO)_{12} + 4CO + 2H_2 \rightleftharpoons 4HCo(CO)_4$$
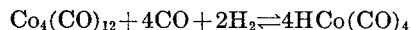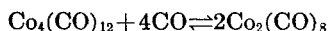
2. Hydrogen must be transferred from the gas phase to the liquid phase, and the hydrogen molecule must be split. Homogeneous activation occurs by the reaction of dicobalt octacarbonyl with hydrogen in the presence of synthesis gas to form cobalt hydrocarbonyl.

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \qquad (87)$$

3. Hydrogen and carbon monoxide must be transferred from some complex or complexes to the olefin, also in the liquid phase. All three reactants, olefin, carbon monoxide, and hydrogen, are probably gathered in one complex at some stage of the reaction.

Until recently, examples of homogeneous activation of hydrogen were rare. In 1938, Calvin (25) described a system for the homogeneous catalytic hydrogenation of benzoquinone in which the catalyst was cuprous acetate. Weller

and Mills (144) called attention to the striking analogy between the activation of hydrogen by cuprous acetate and that occurring under hydroformylation conditions. These workers corroborated Calvin's mechanism of the activation, which they wrote as follows:

$$(Cu^1)_2 + H_2 \rightleftharpoons (Cu^1)_2 \cdot H_2. \qquad (88)$$
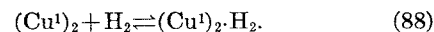
The cuprous dimer is required for the catalytic action, presumably because two strong copper-hydrogen bonds must be formed to compensate for the energy of dissociation of the hydrogen molecule. Reactions (87) and (88) have certain similarities: In both cases molecular hydrogen reacts with a dimeric metal complex to form a compound in which the hydrogen molecule has been split.

Weller (143) and Halpern (57) have written excellent discussions of the homogeneous activation of hydrogen in a number of systems.

Since, of the three carbonyls mentioned, cobalt hydrocarbonyl is the only one containing hydrogen, it must play an important role in the transfer of hydrogen to the olefin. Indeed, the hydrocarbonyl may provide both hydrogen and carbon monoxide; Wender, Sternberg, and Orchin have demonstrated that the hydroformylation of olefins can proceed at atmospheric conditions with molar proportions of pure cobalt hydrocarbonyl (159). In one experiment 4.0 g. (0.023 mole) of cobalt hydrocarbonyl was collected in a liquid nitrogen trap containing 7.0 g. (0.085 mole) of cyclohexene. On warming, the cobalt hydrocarbonyl dissolved in the olefin without noticeable decomposition. At about 15° C. the solution began to darken, a little gas was given off, and the mixture became warm. Addition of 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of cyclohexanecarboxaldehyde; the yield of aldehyde was 60 percent, based on the cobalt hydrocarbonyl present. When excess 1-hexene was similarly treated with pure hydrocarbonyl, C_7 aldehydes were secured, and the unconverted 1-hexene was completely isomerized to the thermodynamically more stable internal hexenes. Not only was hydroformylation conducted at atmospheric pressure with pure cobalt hydrocarbonyl, but hydrogenolysis reactions—known to occur under the usual oxo conditions—were likewise achieved at atmospheric pressure. Thus, treatment of triphenylcarbinol, benzhydrol, and benzyl alcohol with cobalt hydrocarbonyl gave, respectively, triphenylmethane, diphenylmethane, and toluene, products identical with those secured by treatment of the respective substrates at the usual oxo conditions of high temperatures and superatmospheric pressure.

There are many reactions in which carbon monoxide is transferred to organic compounds

by metal carbonyls. Cobalt hydrocarbonyl is unique in that it supplies both hydrogen and carbon monoxide to organic substrates.

Hydroformylation is also possible with dicobalt octacarbonyl as the sole source of carbon monoxide. A patent describes the reaction of olefins, dicobalt octacarbonyl, and hydrogen at 40 to 285 atm. and 25° to 150° C. (8); under these conditions, the olefin was converted to aldehydes and primary alcohols, and the carbonyl was decomposed to metallic cobalt. In 1955, Pino, Ercoli, and Calderazzo (110) showed that aldehydes could be synthesized from olefins, hydrogen, and dicobalt octacarbonyl. When an olefin is treated with stoichiometric amounts of dicobalt octacarbonyl under a high pressure of hydrogen at room temperature, approximately 2 moles of hydrogen is absorbed per mole of dicobalt octacarbonyl. The olefin is transformed into the next higher aldehydes, and appreciable amounts of well-crystallized cobalt tricarbonyl are also obtained. The reaction may be represented by

$$2RCH = CHR + Co_2(CO)_8 + 2H_2 \longrightarrow$$
$$2RCHCH_2R + \tfrac{1}{2}[Co(CO)_3]_4. \quad (89)$$
$$\underset{CHO}{|}$$
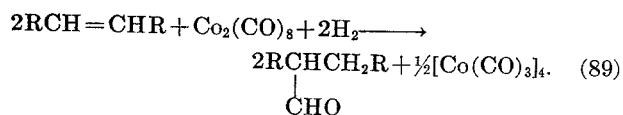
Experiments with cyclohexene and 200 atm. of hydrogen showed that the reaction is approximately first order with respect to the olefin in this stoichiometric synthesis of aldehydes. Small amounts of carbon monoxide inhibit the reactions in proportion to its partial pressure.

Since cobalt hydrocarbonyl and olefins react at room temperature to form aldehydes, it was wondered whether the stoichiometric synthesis of aldehydes from the octacarbonyl, hydrogen, and an olefin involves the formation and further reaction of the hydrocarbonyl. Tests showed that cobalt hydrocarbonyl is always formed in detectable amounts in the stoichiometric synthesis from the octacarbonyl. Cobalt hydrocarbonyl is also formed when dicobalt octacarbonyl is treated with hydrogen at room temperature in the absence of olefins, even at a hydrogen pressure as low as 70 atm. However, the formation of cobalt hydrocarbonyl does not appear to follow the simple scheme of equation (87). Again, the addition of carbon monoxide in small amounts (1 to 4 atm.) to 190 atm. of hydrogen in the presence of 48 millimoles of Co₂(CO)₈ slows up the absorption of hydrogen appreciably. Cobalt hydrocarbonyl may form at room temperature by reaction between hydrogen and a lower unstable carbonyl, which would be present in equilibrium with the octacarbonyl in concentrations which would depend on the carbon monoxide pressure (110). There may

be a readily reversible equilibrium with the lower carbonyl, $[Co_2(CO)_7]_2$:

$$2Co_2(CO)_8 \rightleftharpoons [Co_2(CO)_7]_2 + 2CO. \quad (90)$$
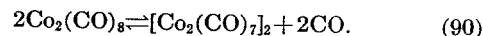
In any case, the inhibiting action of carbon monoxide on the synthesis of cobalt hydrocarbonyl and on the stoichiometric synthesis of aldehydes suggests that we are dealing with the same phenomenon in both instances.

The probable role of tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$, has been pointed out earlier. This compound is stable in solution at least up to 80° C. in an atmosphere of carbon monoxide and is fairly soluble in toluene at 90° C. ($\geq$ 5 percent). Natta, Ercoli, and Castellano (94) have shown that the tricarbonyl and octacarbonyl, in the absence of hydrogen, coexist at carbon monoxide pressures corresponding to the highest reaction rates (8 to 10 atm.).

Although few data exist on the equilibrium between dicobalt octacarbonyl and hydrogen and cobalt hydrocarbonyl (equation (87)), one may assume that, for a given partial pressure of hydrogen and a given concentration of dissolved dicobalt octacarbonyl, the hydrocarbonyl concentration depends on that of the octacarbonyl. As shown by equation (20), this latter concentration increases with the partial pressure of carbon monoxide. Pressures corresponding to the maximum concentration of cobalt hydrocarbonyl (high CO pressures) do not appear to coincide with those for which the rate of hydroformylation is highest (low CO pressures). However, this consideration does not eliminate a mechanism involving the formation of an intermediate from the olefin and hydrocarbonyl with the elimination of carbon monoxide.

Abundant evidence is available to show that cobalt hydrocarbonyl is present under oxo conditions of temperature and pressure *in the absence of olefins*. Hieber, Schulten, and Marin (67) prepared cobalt hydrocarbonyl from cobalt (II) sulfide and from cobalt (II) iodide by treatment with 140 to 200 atm. of carbon monoxide and water at 160° to 180° C.; they were able to obtain pure octacarbonyl only with completely anhydrous cobalt salts. The hydrocarbonyl was also prepared from metallic cobalt and from pure dicobalt octacarbonyl in the presence of carbon monoxide and hydrogen at 165° C.; it was identified by precipitation of the anion $Co(CO)_4^-$ with nickel o-phenanthroline cation (equation (10)) and by the formation of the yellow salt, $Co(CO)_4 \cdot HgCl \cdot \tfrac{1}{2}H_2O$, by treatment of the gas stream from the autoclave with an aqueous solution of $HgCl_2$. Keulemans (74) showed that cobalt hydrocarbonyl was formed when a mixture of carbon monoxide and hydrogen was passed over a bed

of cobalt on pumice at 50° to 180° C. and a total pressure of 100 to 200 atm. Workers at the Bureau of Mines found that the pyridinium salt of cobalt hydrocarbonyl is the sole product when a cobalt salt is treated with hydrogen and carbon monoxide under oxo conditions in the presence of pyridine (157).

There is some question, however, as to whether cobalt hydrocarbonyl is present as such under oxo conditions in the presence of an olefin. Orchin, Kirch, and Goldfarb (102) heated a solution of dicobalt octacarbonyl to 110° C. under a pressure of 110 atm. of carbon monoxide; hydrogen was then added rapidly to a total pressure of 220 atm. The autoclave was cooled as rapidly as possible to dry-ice temperatures, and the contents were poured into an aqueous nickel o-phenanthroline chloride solution to test for $Co(CO)_4^-$. At least 50 percent of the cobalt was present as the anion, presumably formed from cobalt hydrocarbonyl. In the presence of excess 1-hexene, however, no anion was found in the reaction products. When the hydroformylation was allowed to go to completion so that the 1-hexene present was very small, 62 percent of the cobalt was present as the anion. These results are interpretable on the basis that cobalt hydrocarbonyl is rapidly complexed in the presence of olefin and is therefore not present as such under the usual oxo operating conditions. The stabilizing effect of an olefin on the hydrocarbonyl had been demonstrated earlier at the Bureau of Mines (159); whereas cobalt hydrocarbonyl decomposes rapidly at minus 26° C. (equation (91))

$$2HCo(CO)_4 \rightarrow H_2 + Co_2(CO)_8 \qquad (91)$$
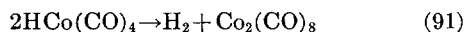
in saturated hydrocarbons, no reaction occurs in olefins until about 15° C.; at this temperature the hydrocarbonyl reacts with olefins to form aldehydes.
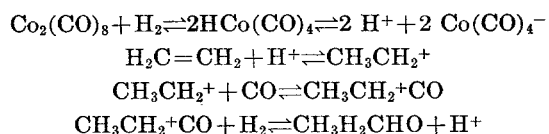
As was indicated earlier, 1-hexene is rapidly isomerized to a mixture of internal hexenes by pure cobalt hydrocarbonyl at 0° to 15° C. However, double-bond isomerization of terminal to internal olefins is very slow during the oxo reaction. Again, the inference is that hydrocarbonyl is not present as such during the reaction.

## Early Postulations as to Mechanism

Many of the mechanisms postulated during early work on hydroformylation involved the direct reaction between carbon monoxide and the olefin. If this were the case, hydroformylation would be favored kinetically by high pressures of carbon monoxide. Although erroneous, these postulations will now be considered briefly.

Cobalt hydrocarbonyl is a strong acid and may function as such in hydroformylation. A more or less conventional carbonium-ion mechanism has been postulated (93, 155) in which hydrocarbonyl acts as a protonic acid and the carbonium-ion intermediate reacts with carbon monoxide:

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \rightleftharpoons 2 H^+ + 2 Co(CO)_4^-$$
$$H_2C = CH_2 + H^+ \rightleftharpoons CH_3CH_2^+$$
$$CH_3CH_2^+ + CO \rightleftharpoons CH_3CH_2^+CO$$
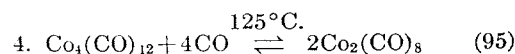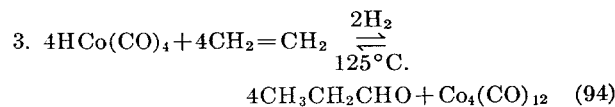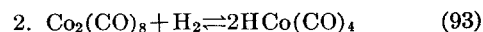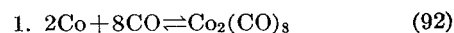$$CH_3CH_2^+CO + H_2 \rightleftharpoons CH_3H_2CHO + H^+$$

Alternately, the acyl carbonium ion may lose a proton to form a ketene, which, in the presence of hydrocarbonyl, is hydrogenated to an aldehyde:

$$CH_2CH_2^+CO \xrightarrow{-H^+} CH_3CH = C = O \xrightarrow{H_2} CH_3CH_2CHO.$$
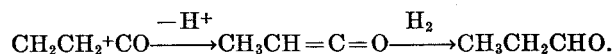
These pathways are at variance with results of kinetic experiments, and the distribution of products from a terminal olefin is not that expected from a carbonium-ion intermediate. Part of this difficulty may be avoided by assuming that the initial electrophilic attack on the olefin is made competitively by H^+ and by $\overset{+}{C}HO$ formed from H^+ and CO. The formyl carbonium-ion, $\overset{+}{C}HO$, has been assumed to be an intermediate in the Gatterman-Koch reaction, which is also an acid-catalyzed reaction involving carbon monoxide. The formation of a ketene as an intermediate was offered as an explanation for the finding that an olefin substituted at the second carbon atom (isobutylene) yielded only one alcohol (isoamyl alcohol) in the oxo reaction. However, the finding that isobutylene reacts to give, in addition to isoamyl alcohol, about 5 percent of neopentyl alcohol (146) and the fact that perfluoroolefins (150) undergo the oxo reaction make this mechanism extremely improbable.

The same type of reasoning indicates that the addition of carbon monoxide to a radical formed by reaction of an olefin with a cobalt carbonyl radical is unlikely.

A mechanism of aldehyde formation involving the attack of hydrocarbonyl on the olefin was given in the first American article on hydroformylation. Adkins and Kresk (1) proposed that the usual hydroformylation proceeds in at least four steps:

$$1. \quad 2Co + 8CO \rightleftharpoons Co_2(CO)_8 \qquad (92)$$

$$2. \quad Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \qquad (93)$$

$$3. \quad 4HCo(CO)_4 + 4CH_2 = CH_2 \underset{125°C.}{\overset{2H_2}{\rightleftharpoons}}$$
$$4CH_3CH_2CHO + Co_4(CO)_{12} \qquad (94)$$

$$4. \quad Co_4(CO)_{12} + 4CO \overset{125°C.}{\rightleftharpoons} 2Co_2(CO)_8 \qquad (95)$$
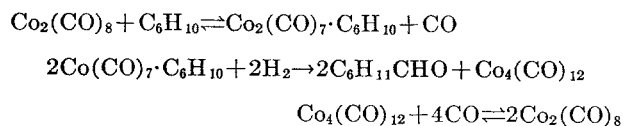
The discovery of the hydroformylation of olefins with pure hydrocarbonyl (but at 0° to 20° C. and in the absence of added hydrogen) confirms the essentials of equation (94). However, the activation of molecular hydrogen in this step is not explained, and this series of equations implies that the rate of the reaction would be directly proportional to the pressure of carbon monoxide.
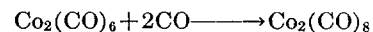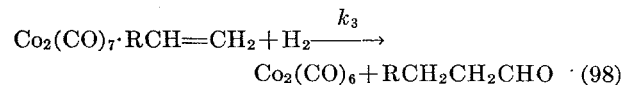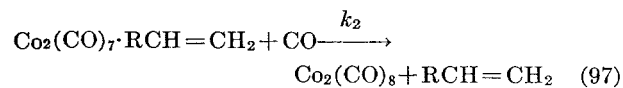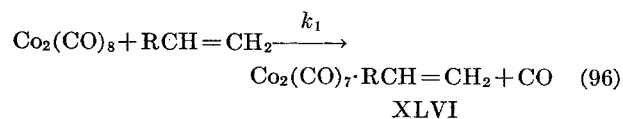
Later Work

The fact that the rate of the hydroformylation reaction varies inversely with the carbon monoxide pressure may be explained if, in the initial stages, some reaction occurs between a carbonyl of cobalt (possibly dicobalt octacarbonyl or cobalt hydrocarbonyl) and the olefin, the latter displacing some of the CO in the carbonyl.

On the basis of kinetic data, several workers (50, 82, 95) have postulated that the first step in the synthesis involves the reaction of the olefin with dicobalt octacarbonyl to form an olefin-carbonyl complex and carbon monoxide. The following scheme has been suggested for the reaction with cyclohexene (95):

$$Co_2(CO)_8 + C_6H_{10} \rightleftharpoons Co_2(CO)_7 \cdot C_6H_{10} + CO$$

$$2Co(CO)_7 \cdot C_6H_{10} + 2H_2 \rightarrow 2C_6H_{11}CHO + Co_4(CO)_{12}$$

$$Co_4(CO)_{12} + 4CO \rightleftharpoons 2Co_2(CO)_8$$

Although this scheme predicts that the rate of hydroformylation would be inversely proportional to the CO pressure, it does not lead to a simple explanation of the variation of reaction rates with changes in the hydrogen-to-carbon monoxide ratio (H_2:CO).

Martin (82) showed that the following sequence of equations led to a kinetic expression that fits the data obtained with different ratios of gases at elevated pressures quite well:

$$Co_2(CO)_8 + RCH=CH_2 \xrightarrow{k_1}$$
$$Co_2(CO)_7 \cdot RCH=CH_2 + CO \quad (96)$$
$$\text{XLVI}$$

$$Co_2(CO)_7 \cdot RCH=CH_2 + CO \xrightarrow{k_2}$$
$$Co_2(CO)_8 + RCH=CH_2 \quad (97)$$

$$Co_2(CO)_7 \cdot RCH=CH_2 + H_2 \xrightarrow{k_3}$$
$$Co_2(CO)_6 + RCH_2CH_2CHO \quad (98)$$

$$Co_2(CO)_6 + 2CO \longrightarrow Co_2(CO)_8$$

which gives the following equation:

$$\text{initial rate} = \frac{k_1 k_3 p_{H_2}}{k_2 p_{CO} + k_3 p_{H_2}} [Co_2(CO)_8][RCH=CH_2]$$
$$(99)$$

This sequence is similar to that originally suggested, except that equilibrium is not maintained between dicobalt octacarbonyl and olefin, on the one hand, and complex I and carbon monoxide, on the other. If this equilibrium is maintained, the kinetic equation above reduces to

$$\text{initial rate} = \frac{k_1 k_3 p_{H_2}}{k_2 p_{CO}} [Co_2(CO)_8][RCH=CH_2].$$

Martin's results show that, although the initial rate of reaction increases with increase in the ratio of hydrogen to carbon monoxide partial pressure, it does so at a diminishing rate of increase as this ratio increases.

Martin's equation (99) can be rearranged:

$$\text{initial rate, } r = \frac{k_1 k_3}{k_2 \dfrac{p_{CO}}{p_{H_2}} + k_3}$$

whence

$$\frac{1}{r} = \frac{k_2 \dfrac{p_{CO}}{p_{H_2}}}{k_1 k_3} + \frac{1}{k_1}.$$

This equation predicts a linear relationship between $\frac{1}{r}$ and the ratio of partial pressures of CO and H_2. That this is the case is shown in figure 14; the data in this figure were obtained by Wender, Metlin, Ergun, and Greenfield with cyclohexene (160). Figure 15 was obtained by plotting the ratios of these specific reaction-rate constants to that for equimolar ratios of the gases, $r/r_{1:1}$, as a function of the H_2:CO ratio. This curve indicates that six is about the maximum possible increase in rate over that with $1H_2 + 1CO$ in going to higher ratios of H_2:CO.

This mechanism ignores the role of cobalt hydrocarbonyl. Martin suggested that reaction (98) might occur in more than one step, but stated that there appeared to be no reason why this reaction is not as simple as the equation indicates. However, the complex or intermediate I is a large molecule and is not likely to acquire a molecule of hydrogen and then undergo the complex molecular rearrangements necessary to form aldehyde in one step. More likely, I reacts with hydrogen before aldehyde is formed (153):

$$Co_2(CO)_7 \cdot RCH=CH_2 + H_2 \rightarrow$$
$$\text{XLVI}$$
$$[Co_2(CO)_7 \cdot RCH=CH_2 \cdot 2H]. \quad (100)$$
$$\text{XLVII}$$
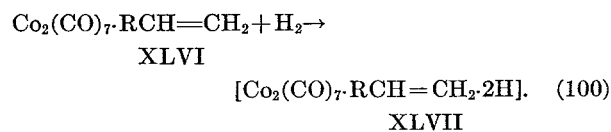
An idea of the structure of XLVI may be gained from the complex obtained by reacting acetylene with dicobalt octacarbonyl (51, 130). The stoichiometry of this reaction indicates

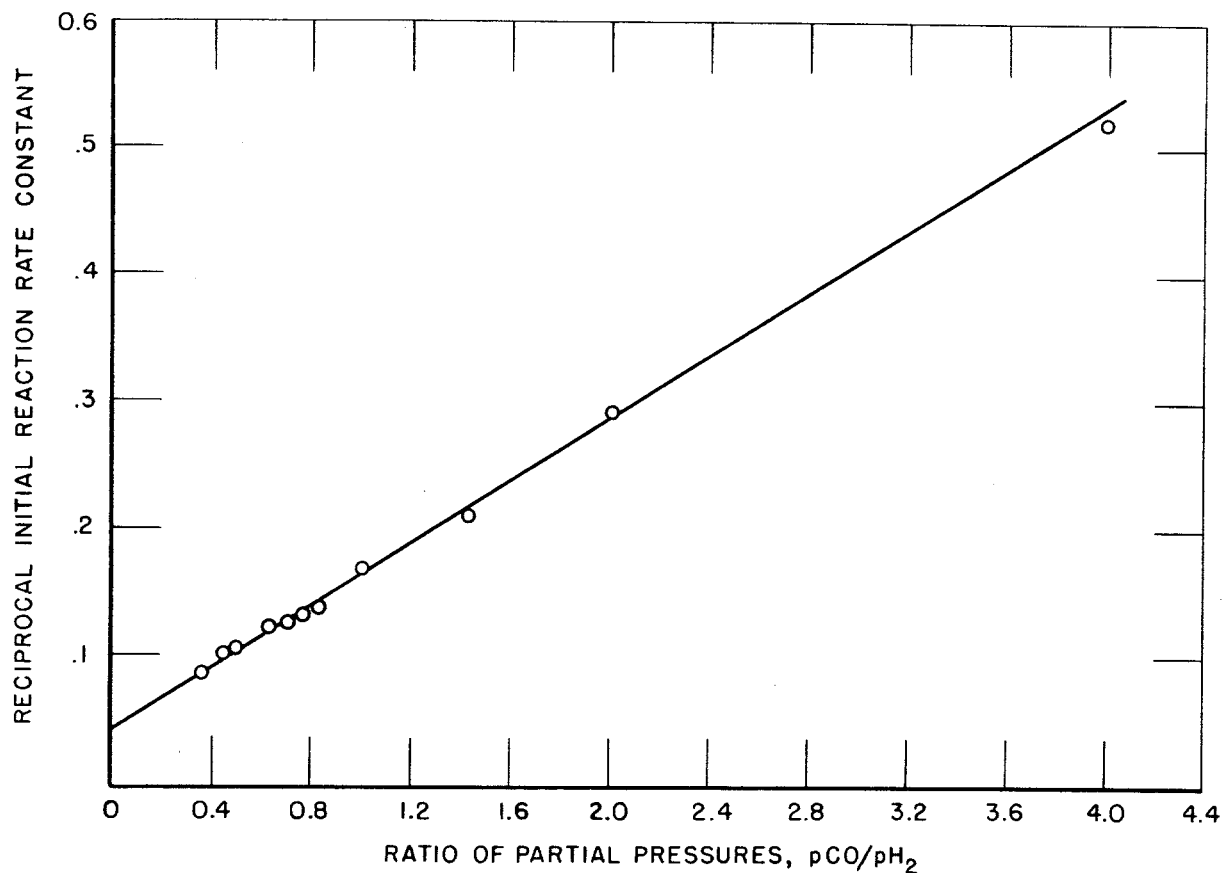FIGURE 14.—Rate Constants for Oxo Reaction of Cyclohexene at 110° C. Fitted to Martin's Equation (82).
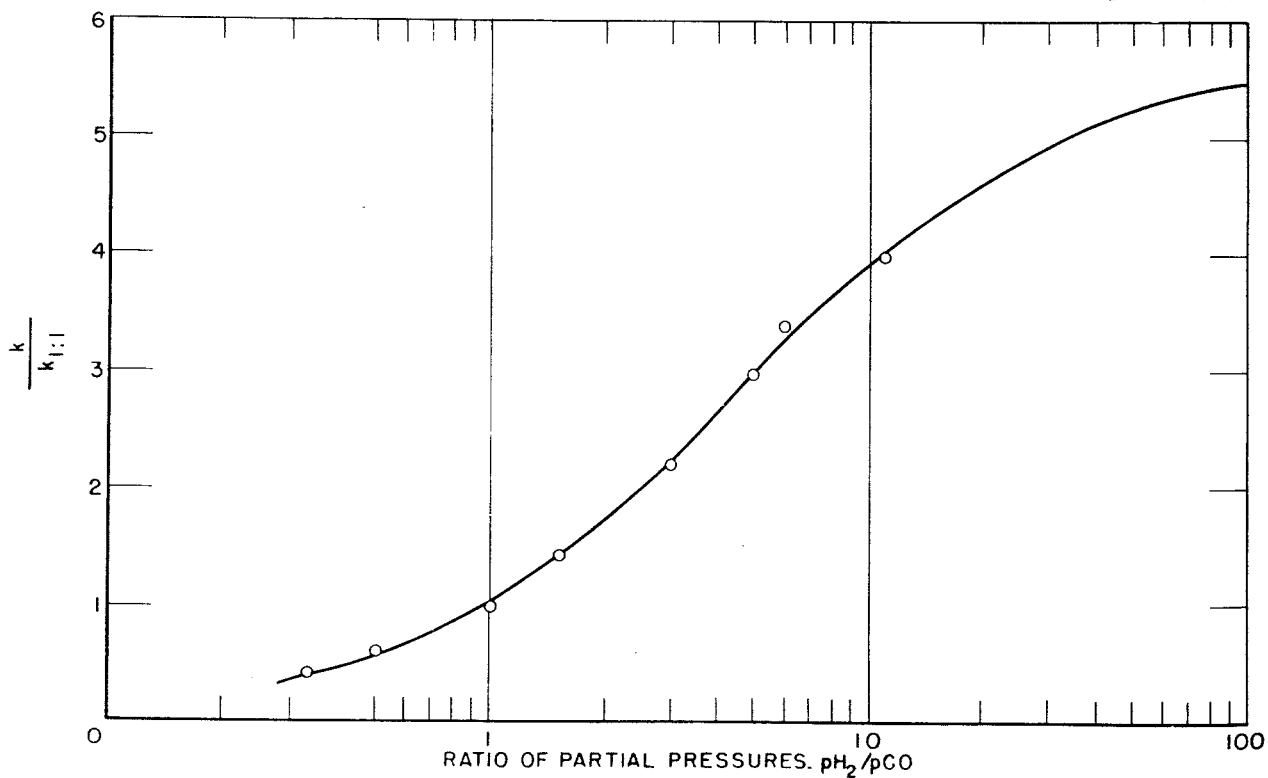

FIGURE 15.—Use of Martin's Equation (82) and Experimental points (131) To Determine Effect of Composition of Synthesis Gas on Rate of Oxo Reaction; Cyclohexene at 110° C.

that the acetylene complex XLVIII is formed as follows:

$$(CO)_3Co\text{---}Co(CO)_3 + C_2H_2 \longrightarrow (CO)_3Co\text{---}Co(CO)_3 + 2CO \quad (101)$$

XLVIII

The analytical, spectroscopic, magnetic, and dipole moment data are compatible with the structure written for XLVIII. Since an olefin, RCH=CHR', presumably displaces only 1 mole of carbon monoxide, the olefin-carbonyl complex XLVI probably has the following structure:

XLVI

The ease of formation of XLVI (or any similar complex) should be influenced by the steric requirements of the olefin, so the rates of reaction of various olefins should depend on the configuration about the double bond. The effect of olefin structure on the rate of hydroformylation at 110° C. with $1H_2 + 1CO$ at 233 atm. is as follows:

Olefin	Specific reaction rate, k 10^3 minute^{-1}
C—C—C—C—C=C	66
C—C—C—C=C—C	19
C—C—C—C=C—C—C	19
C—C—C—C=C—C—C (with branches)	6.2
C—C—C=C—C (with branch)	4.9
C—C—C=C—C (with branches)	2.3
C—C=C—C (with branches)	1.4

The straight-chain terminal olefin is least hindered and reacts most rapidly; the corresponding internal olefins react at about one-third this rate. However, the position of the double bond, as long as it is internal, has no effect upon the rate. Although 2,6-dimethyl-3-heptene is doubly branched and has a double bond far removed from the terminal position, it reacts more rapidly than olefins lower in the table because there are no substituents at the double bond to offer steric interference to complex formation with the carbonyl. The other olefins offer increased steric hindrance at the site of reaction and react at correspondingly lower rates.

The minimum in the rate of reaction of cyclic olefins (table 24) for the C_6 ring may be explained in terms of complex formation with a carbonyl. Traynham and Sehnert (140) have calculated the strain energy of cyclopentene to be 4.4 and that of cycloheptene to be 4.1 kcal./mole relative to cyclohexene. The more strained a cyclic compound, the more reactive it is as an electron donor. Tirpak, Wotiz, and Hollingsworth (138), however, observed that the relative reactivities of various acetylenes with dicobalt octacarbonyl could not be correlated with possible electronic effects. Cyclopentene and cycloheptene may thus be hydroformylated so rapidly because of their great tendencies to form complexes with $Co_2(CO)_8$ or $HCo(CO)_4$.

The formation of XLVII has been postulated to explain the dissociation of hydrogen by the catalyst. There is other evidence for the existence of a complex such as XLVII: Cobalt hydrocarbonyl, $HCo(CO)_4$, reacts with olefins at room temperature (in the absence of synthesis gas) to form aldehydes. Since cobalt hydrocarbonyl is the source of both hydrogen and carbon monoxide in this reaction, at least two molecules of hydrocarbonyl must react with one molecule of olefin. A trimolecular reaction between two molecules of hydrocarbonyl and one of olefin or two consecutive bimolecular reactions must occur (equation (102)) to furnish the aldehyde; the latter is more likely.

$$2HCo(CO)_4 \rightleftharpoons (CO)_3CoH \quad HCo(CO)_3 \xrightarrow{RCH=CH_2} (CO)_3CoH \quad HCo(CO)_3 + CO \quad (102)$$

XLIX   XLVII

Therefore, both the stoichiometric reaction with cobalt hydrocarbonyl and autoclave runs with catalytic amounts of dicobalt octacarbonyl probably proceed via the same intermediate, XLIX. Cobalt hydrocarbonyl may not be present under hydroformylation conditions because of its rapid reaction with olefins according to equation (102).

Natta, Ercoli, and Castellano (94) have written two other mechanisms for the oxo reaction. The first involves the formation of a complex from cobalt hydrocarbonyl and the olefin:

$$HCo(CO)_4 + C_6H_{10} \rightleftharpoons HCo(CO)_3 \cdot C_6H_{10} + CO \quad (103)$$

$$HCo(CO)_3 \cdot C_6H_{10} + HCo(CO)_4 \xrightarrow{slow} C_6H_{11}CHO + Co_2(CO)_6 \quad (104)$$

$$2Co_2(CO)_6 \rightleftharpoons Co_4(CO)_{12}, \text{ and so forth.} \quad (105)$$

TABLE 27.—*Product distribution from hydroformylation of isomeric pentenes*

Catalyst	Tem-pera-ture, ° C.	Pres-sure, atm.	Hexanol, percent		2-Methyl-1-pentanol, percent		2-Ethyl-1-butanol, percent	
			From 1-pentene	From 2-pentene	From 1-pentene	From 2-pentene	From 1-pentene	From 2-pentene
Reduced cobalt [1]	120–160	100–200	50	55	40	35	10	10
Do.[2]	145–155	80–180	48	44	46	46	6	10
Co₂(CO)₈, in ben-zene [2]	145–150	80–180	67	52	30	39	3	9
CO₂(CO)₈, in hex-ane [3]	112	210–220	80	70	17	27	3	3

[1] See reference (75).
[2] See reference (90).
[3] See reference (48).

The composition shown on the left side of equation (104) corresponds to complex XLVII, which may be postulated as an intermediate in this case also. The variation in rate of reaction of cyclohexene at 120° C. with the partial pressure of CO (at constant hydrogen pressure) agreed with theoretical curves based on an assumed equilibrium constant for equation (87). To date, however, not even approximate data for this equilibrium are available. The agreement was not so good for data obtained at 110° C.

The second mechanism involves the formation of complex XLVI according to equation (106)

$$Co_2(CO)_6 + C_6H_{10} + CO \rightleftharpoons Co_2(CO)_7 \cdot C_6H_{10} \quad (106)$$
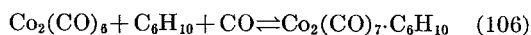
and resembles a scheme proposed earlier (95). This mechanism assigns no role to cobalt hydrocarbonyl and does not appear to fit all the kinetic data.

Nature of the Olefin in the Intermediate Complexes

Although double bonds are isomerized at a significant rate under oxo conditions, workers at the Bureau of Mines (153) and the University of Cincinnati (48) found this rate to be considerably slower than that of hydroformylation. During hydroformylation of 1-pentene little or no 2-pentene was formed until the reaction was 75 percent complete; only small amounts of 1-pentene were formed when 2-pentene was the starting olefin. Isomerization may occur when the olefin-carbonyl complex XLVI reacts with carbon monoxide to regenerate the carbonyl and the (isomerized) olefin (equation (97)).

Although internal olefins are thermodynamically more stable than terminal olefins under reaction conditions, the products from hydroformylation are largely derived by addition to the terminal carbons. Three papers have appeared on the product distribution obtained from the isomeric pentenes; the results are summarized in table 27. The results are difficult to compare because the experiments were not carried out under identical conditions and because the analytical procedures differed in each case, but some general conclusions may nevertheless be drawn from the data. With reduced cobalt catalysts, approximately equal amounts of alcohols were derived by addition to the first and second carbon atoms. With dicobalt octacarbonyl, the straight-chain alcohol predominated from both 1- and 2-pentenes. Two interpretations of the data are possible: (1) Essentially the same products are obtained from both of the isomeric pentenes and (2) the product distribution from 1-pentene is significantly different from that obtained with 2-pentene. Goldfarb and Orchin favor the latter conclusion, although their results show that the product distribution is qualitatively the same. The work of Keulemans, Kwantes, and van Bavel lends credence to the first interpretation; these workers obtained the same distribution of products from the isomeric methylbutenes:

2-methyl-1-butene ⎫ 55 percent 4-methyl-1-pentanol
2-methyl-2-butene ⎬ 45 percent 3-methyl-1-pentanol
3-methyl-1-butene ⎭ 5 percent 2,3-dimethyl-1-butanol

The results in table 27 indicate that lower temperatures favor the production of straight, rather than branched, alcohols. This view is supported to some extent by the work of Schreyer (119), who prepared a mixture of butyl (28 percent) and isobutyl (72 percent) acetates by treating propylene with $1H_2 + 1CO$

at 250° C. and 700 atm. in the presence of acetic acid.

A recent paper (153) has explained the distribution of products in the oxo reaction on the basis that different isomers yield essentially the same products: Because of steric hindrance, 2-pentene reacts with dicobalt octacarbonyl to form a complex more slowly than 1-pentene, and this accounts for the differences in rates observed with these olefins. The energy required for the rearrangement of the complex subsequent to its formation is small; therefore, essentially the same complex is obtained from terminal and internal olefins. Structure XLVI probably represents the complex initially formed from a terminal or an internal olefin. The structure of the olefin-carbonyl complex as it exists a moment later is uncertain, because the position of attachment of the unsaturated entity to the carbonyl is probably not fixed.

Some mechanism must exist for the facile movement of hydrogen in these complexes. Hydrogen atoms are probably transferred from one part of the chain to another by interaction with cobalt atoms. This idea is supported by the observation that allenes with at least one hydrogen atom $(R_2C=C=CHR)$ are polymerized by dicobalt octacarbonyl at room temperature (52). Similarly, acetylene, or any compound with the formula $RC\equiv CH$, is polymerized by the acetylene-cobalt carbonyl complex XLVIII at room temperature; complexes derived from acetylenes with no hydrogen atom $(RC\equiv CR)$ do not catalyze these polymerizations.

Whereas the intimate mechanism of hydroformylation awaits further study, the course of the reaction and the nature of the intermediates appear fairly well defined. The concept of a carbonyl-olefin complex such as XLVII being (1) the only immediate source of hydrogen and carbon monoxide and (2) the locus of transfer of hydrogen and carbon monoxide to the olefin aids in understanding the nature and role of intermediates in catalytic reactions.
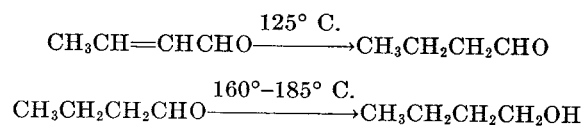
Hydrogenation of Organic Compounds With Synthesis Gas

HOMOGENEOUS CHARACTER OF THE HYDROGENATION

The conversion of olefins to aldehydes in the presence of a cobalt catalyst and synthesis gas was the first stage in the German oxo plants. The second stage consisted of the hydrogenation of the aldehydes with pure hydrogen to their corresponding alcohols. The catalyst used in this second step was often the same as that used in the first stage. Cheaper and more readily

available solid hydrogenation catalysts later replaced cobalt for hydrogenating aldehydes. It was necessary to remove all carbon monoxide and cobalt carbonyl before hydrogenation, because carbon monoxide poisoned the catalyst.

Although the Fischer-Tropsch catalyst was used by the Germans, Roelen's study of the hydroformylation reaction led him to postulate that the first stage was probably a homogeneous catalytic process with dicobalt octacarbonyl or cobalt hydrocarbonyl as the catalyst. It was known that sulfur need not be removed from synthesis gas and that small amounts of the starting olefins and the product aldehyde are hydrogenated during the hydroformylation stage. Adkins and Krsek (2) demonstrated that certain unsaturated compounds react exclusively by hydrogenation rather than by hydroformylation. Crotonaldehyde treated with dicobalt octacarbonyl and synthesis gas at 125° C. gave butyraldehyde in about 50-percent yield; the addition of small amounts of diphenyl sulfide did not interfere with the hydrogenation. Wender, Levine, and Orchin later showed that if the temperature was raised from 125° to 160° to 185° C., crotonaldehyde was reduced to butanol:

$$CH_3CH=CHCHO \xrightarrow{125° C.} CH_3CH_2CH_2CHO$$

$$CH_3CH_2CH_2CHO \xrightarrow{160°-185° C.} CH_3CH_2CH_2CH_2OH$$

Greenfield, Metlin, Orchin, and Wender (49) also demonstrated that thiophenes could be reduced to thiolanes under hydroformylation conditions.

Strong evidence for the homogeneous character of hydrogenation under oxo conditions was provided by the experiments of Wender, Orchin, and Storch (156). The basis of these experiments was the supposition that either dicobalt octacarbonyl or cobalt hydrocarbonyl, both of which are soluble in organic solvents, was the catalyst for the hydrogenation. Mond, Hirtz, and Cowap, in an early paper (86), showed that at 150° C. a partial pressure of carbon monoxide of at least 40 atm. was necessary to keep the dicobalt octacarbonyl from decomposing. Since metallic cobalt is poisoned as a hydrogenation catalyst by carbon monoxide, hydrogenation should be retarded or inhibited if an insufficient partial pressure of carbon monoxide is present in a synthesis gas mixture to keep the cobalt in the form of a carbonyl at reaction temperature.

Bureau of Mines personnel performed a series of three experiments at 185° C. with reduced cobalt as the catalyst and butyraldehyde as the substrate. The catalyst was prepared by treating 9.3 g. of cobaltous formate and 50 ml. of cyclohexane with 2,000 p.s.i. hydrogen at 185° C. for 2 hours in a stainless steel autoclave of 500-ml. capacity. An initial partial

pressure of 2,000 p.s.i. of hydrogen was used in each of the three experiments, and the partial pressure of carbon monoxide was varied.

In the first experiment no carbon monoxide was present. The reduction proceeded smoothly, and the calculated pressure drop was observed; a 77-percent yield of 1-butanol was obtained. In a second experiment 1,000 p.s.i. of carbon monoxide was added (total pressure, 3,000 p.s.i.). Approximately 1 mole of gas was again absorbed, and a 66-percent yield of 1-butanol was obtained. The reaction was presumably homogeneous, with the soluble dicobalt octacarbonyl, $Co_2(CO)_8$, or cobalt hydrocarbonyl, $HCo(CO)_4$, functioning as the catalyst.

In a third experiment 300 p.s.i. of carbon monoxide was added ($8H_2:1CO$). The mixture was heated at 185° C. for 2 hours and at 200° C. for 1 hour, but no gas was absorbed. Distillation gave three fractions: A low-boiling portion containing unchanged butyraldehyde (83 percent); a small middle fraction which infrared spectroscopy showed to be free of 1-butanol; and a residue, part of which depolymerized to butyraldehyde on heating to 240° to 270° C. In this case carbon monoxide was sufficient to poison the heterogeneous catalysis, but insufficient to form $Co_2(CO)_8$ or $HCo(CO)_4$, the catalyst in the second experiment.

In another experiment butyraldehyde was treated with a clear benzene solution of $Co_2(CO)_8$ at 185° C. and 2,000 p.s.i. of hydrogen. No hydrogenation occurred; the carbonyl was reduced to cobalt, which did not function as a catalyst because of carbon monoxide poisoning. Fifty-four percent of the butyraldehyde was recovered; no 1-butanol was found in the residue. In a series of concluding experiments with freshly reduced cobalt at 185° C., thiophenecarboxaldehyde and butyraldehyde containing thiopene reacted rapidly in the presence of synthesis gas, but with hydrogen alone the hydrogenations were greatly retarded.

HYDROGENATION OF DOUBLE BONDS IN CONJUGATED SYSTEMS

All simple aliphatic olefins react with synthesis gas at 100° to 150° C. in the presence of a cobalt catalyst to yield principally an aldehyde or a mixture of isomeric aldehydes containing one carbon atom more than the starting olefin. At 150° to 190° C. the aldehyde or aldehydes initially formed are reduced, and their corresponding alcohols are the chief products of the reaction. Although hydrogenation of a double bond in a simple olefin is thermodynamically favored over its hydroformylation, hydrogenation begins to compete with hydroformylation only when the double bond is conjugated with another unsaturated linkage.

α, β-Unsaturated Aldehydes and Ketones

Compounds possessing an olefinic bond conjugated to a carbonyl group of an aldehyde or ketone are reduced to the saturated aldehyde or ketone under the usual oxo conditions, providing the temperature is below about 125° C. Thus, crotonaldehyde gives butyraldehyde and methyl vinyl ketone gives methyl ethyl ketone (2). The reason why conjugation leads to hydrogenation of the olefinic linkage rather than

hydroformylation has not been satisfactorily explained. It is especially noteworthy that esters of crotonic acid (conjugation with carbethoxy) are largely hydroformylated (although an appreciable amount of hydrogenation to butyrate esters does occur) (58), whereas conjugation of the double bond with an aldehyde group (crotonaldehyde) results in hydrogenation. As is well known, an ester group conjugates with a double-bond linkage to a lesser extent than with an aldehyde function; the resonance energy of crotonaldehyde is about 2.4 kcal. greater than the resonance energy of ethyl crotonate.

Esters such as ethyl acrylate and ethyl fumarate react more rapidly with synthesis gas under oxo conditions than do any olefinic hydrocarbons. Specifically, diethyl fumarate or maleate reacts about five times as rapidly as 1-hexene.

Conjugated Diolefins and Styrenes

Introduction of two formyl or related groups by hydroformylation of a conjugated diolefin would lead to commercially useful products. Thus, treatment of butadiene could yield a C_6 dialdehyde and thence a C_6 dibasic acid. However, the major product on treatment of a conjugated diolefin is a saturated aldehyde containing only one carbon atom more than the starting material. With such substrates, one double bond is hydrogenated and the other hydroformylated. Thus, 1,3-butadiene gives approximately equal amounts of valeraldehyde and α-methylbutyraldehyde; 2,3-dimethyl-1,3-butadiene gives 3,4-dimethyl-valeraldehyde (3).

Although Adkins and Krsek reported that furan, which may be regarded as a conjugated ether, did not react with synthesis gas at 125° C., Wender, Levine, and Orchin (152) found that this compound behaved at 160° to 185° C. as though it were a conjugated diene; both hydrogenation and hydroformylation took place to give 2-tetrahydrofurfuryl alcohol:
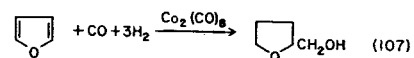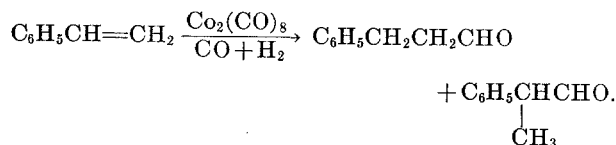

Similar treatment of 2,5-dimethylfuran gave 2,5-dimethyl-3-tetrahydrofurfuryl alcohol.

Aliphatic α,β-unsaturated esters such as ethyl acrylate react by hydroformylation; however, when the double bond is conjugated with an aromatic ring, the unsaturated ester is hydrogenated. Thus, as major products, ethyl cinnamate gives ethyl β-phenylpropionate,

$$C_6H_5CH=CHCOOC_2H_5 + H_2 \xrightarrow[CO]{Co_2(CO)_8}$$

$$C_6H_5CH_2CH_2COOC_2H_5$$
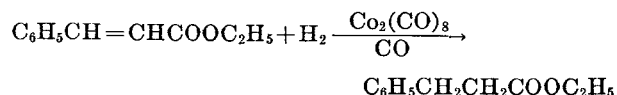
and cinnamyl alcohol gives hydrocinnamyl alcohol (3-phenyl-1-propanol). This behavior is in accord with the generalization that the more the double bond is involved in conjugation, especially with an aromatic ring, the larger is the tendency towards hydrogenation rather than hydroformylation.

Adkins and Krsek reported isolation of hydratropaldehyde (2-phenylpropionaldehyde) from the hydroformylation of styrene; Wetzel, McKeever, and Levesque (162) found the product to be a mixture of hydratropaldehyde and 3-phenylpropionaldehyde:

$$C_6H_5CH{=}CH_2 \xrightarrow{\text{Co}_2(\text{CO})_8}{\text{CO}+\text{H}_2} C_6H_5CH_2CH_2CHO$$

$$+ C_6H_5\underset{\underset{CH_3}{|}}{C}HCHO.$$

Bureau of Mines workers found a mixture of the two aldehydes, but also a 25-percent yield of the reduction product ethylbenzene (155). Although Adkins and Krsek have reported that 1-vinylnaphthalene reacts with synthesis gas to give about 30 percent of β-(1-naphthyl)-propionaldehyde, an appreciable quantity of 1-ethylnaphthalene is also likely to be formed. Isopropylbenzene is synthesized from α-methylstyrene in high yield under hydroformylation conditions:

$$C_6H_5C{=}CH_2 + H_2 \xrightarrow{\text{Co}_2(\text{CO})_8}{\text{CO}+\text{H}_2} C_6H_5\underset{\underset{CH_3}{|}}{C}HCH_3.$$
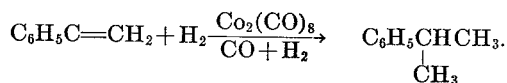
Polynuclear Aromatic Compounds

Adkins and Krsek treated phenanthrene with carbon monoxide, hydrogen, and a cobalt

catalyst at 125° C., but found no appreciable reaction. Wender, Levine, and Orchin treated phenanthrene at a higher temperature, where it was slowly hydrogenated. After 2 hours at 180° to 185° C., a 7-percent yield of 9,10-dihydrophenanthrene and a 1-percent yield of 1,2,3,4-tetrahydrophenanthrene were obtained; 81 percent of the starting compound was recovered unchanged.

In later work, Friedman, Metlin, Svedi, and Wender discovered that anthracene, the linear isomer of phenanthrene, reacted smoothly with synthesis gas at 135° C. to give 9,10-dihydroanthracene in quantitative yield (47). This prompted a study of other polynuclear hydrocarbons, the results of which are summarized in table 28.

The data show that polynuclear aromatic hydrocarbons may be selectively hydrogenated under hydroformylation conditions. Benzene and simple alkyl-substituted benzenes serve as solvents for hydroformylation reactions and have not been observed to undergo any reduction. Naphthalene, on the other hand, is reduced slowly. The specificity of this reducing system is most strikingly shown by the fact that anthracene is reduced rapidly to 9,10-dihydroanthracene at about 135° C., whereas phenanthrene is reduced slowly even at 200° C.

This behavior of aromatic systems extends to the larger molecules. Naphthacene, similar to anthracene in structure and behavior, is readily reduced to 9,10-dihydronaphthacene under conditions identical with those used for reducing anthracene.
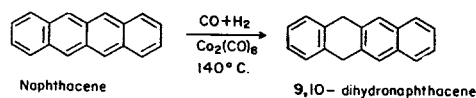

Naphthacene   9,10- dihydronaphthacene

TABLE 28.—*Hydrogenation of polynuclear aromatic hydrocarbons with* $1H_2 + 1CO$ *and* $Co_2(CO)_8$ *as catalyst*

| Compound	Weight, g.	Benzene, ml.	Co₂(CO)₈, g.	Initial pressure, p.s.i.g.	Temperature ° C.	Products	Yield, percent
Anthracene	10.0	80	2.0	2,900	150	9,10-Dihydroanthracene	99
Naphthacene	2.8	85	2.0	3,000	140	----do----	90
Phenanthrene	5.0	¹85	1.6	2,500	185	Mixture of hydrophenanthrenes	8
						Phenanthrene	92
Chrysene	1.0	80	3.4	3,500	150	No reaction	
Do	1.0	80	2.0	3,000	200	5,6-Dihydrochrysene	30
						Chrysene	70
Perylene	.4	85	2.0	3,000	150	1,2,3,10,11,12-Hexahydroperylene	80
						Perylene	20
Pyrene	1.0	80	1.9	3,600	150	No reaction	
Do	1.0	80	1.5	3,000	200	1,2-Dihydropyrene	80
						Pyrene	20
Fluoranthene	1.0	80	1.4	3,200	200	1,2,3,4-Tetrahydrofluoranthene	60
						Fluoranthene	40
β-Methylnaphthalene	7.0	----------	7.5	3,500	185	Methyltetralin	30
						β-Methylnaphthalene	70
Naphthalene	25.0	----------	2.5	3,100	200	Tetralin	16
						Naphthalene	84
Fluorene	2.0	80	1.0	3,600	200	No reaction	
Dinaphthyl	25.0	70	1.0	3,500	200	----do----	
Triphenylene	.6	100	2.0	1,400	150	----do----	

¹ Ethanol used as solvent.

The product contains benzene and naphthalene systems, both stable toward further reduction.

Chrysene, resembling phenanthrene in structure and chemical behavior, is slowly hydrogenated at 200° C. to the 5,6-dihydro compound.

Chrysene   5,6-dihydrochrysene
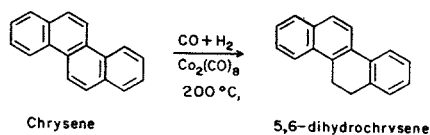
Further proof of the stability of the phenanthrene system is shown by the reduction of perylene to 1,2,3,10,11,12-hexahydroperylene and of pyrene to 1,2-dihydropyrene.


Perylene   Hexahydroperylene

Pyrene   1,2-dihydropyrene
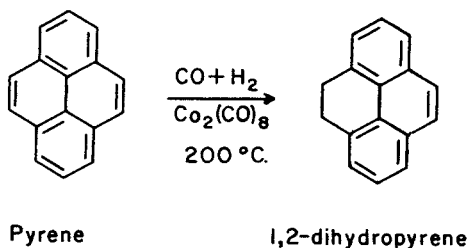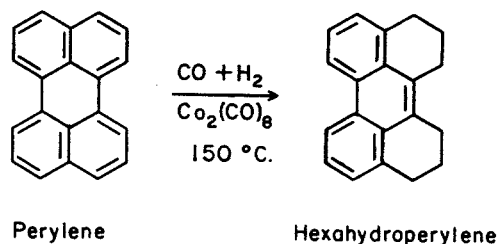
In both cases the product is a phenanthrene derivative and inert to further hydrogenation.

1,1-dinaphthyl, though resembling perylene except for one bond, cannot be reduced.

Triphenylene, which is a benzphenanthrene as well as a compound containing three separate substituted benzene rings, is also inert to reduction.

Triphenylene
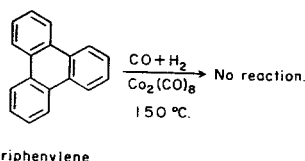
The hydrogenation of fluoranthene to tetrahydrofluoranthene indicates that the fluorene system is also stable to further hydrogenation.

Fluoranthene   1,2,3,4,—tetrahydrofluoranthene
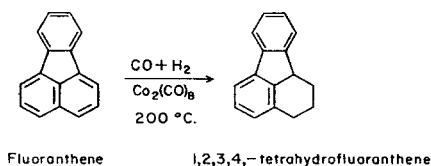
This is confirmed by the resistance to reduction shown by fluorene.

Thus, in reduction of a polynuclear aromatic system catalyzed by dicobalt octacarbonyl, benzene rings are most stable; angularly condensed systems (phenanthrene, chrysene) are relatively stable, though reduced slowly at higher temperatures; peri-condensed systems (perylene, pyrene) are easily reduced; linearly cata-condensed systems (anthracene, naphthacene) are also readily reduced to give isolated benzene and naphthalene systems. The latter ring structure is slowly reduced further to benzene derivatives.

REDUCTION OF AROMATIC ALCOHOLS AND KETONES

The hydrogenation of aliphatic aldehydes and ketones with synthesis gas leads to primary and secondary alcohols (acetone gives isopropyl alcohol). However, in the aromatic series, the hydroxyl group attached to a carbon atom carrying one or more phenyl groups is readily lost, and hydrocarbons are formed (149). In some instances the hydrocarbon may be isolated in more than 90-percent yield. Aromatic ketones like acetophenone, benzophenone, and fluorenone are also reduced to hydrocarbons under hydroformylation conditions. The results of experiments conducted at the Bureau of Mines with aromatic alcohols and ketones are summarized in table 29.

Benzyl alcohol reacts with synthesis gas at 185° C. to give a 50- to 60-percent yield of toluene (hydrogenation) and a 25- to 30-percent yield of 2-phenylethanol; this latter reaction (homologation or chain lengthening of alcohols) will be discussed in a later section. Substitution of one of the nonnuclear hydrogen atoms of benzyl alcohol by a methyl group increases the proportion of hydrocarbon. Substitution by phenyl groups results in exclusive production of the reduced product; no homologous alcohol is obtained.

$$C_6H_5CHOHC_6H_5 + 2H_2 \xrightarrow[CO]{Co_2(CO)_8} C_6H_5CH_2C_6H_5 + H_2O$$
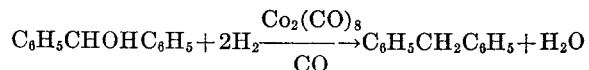
Substitution of the phenyl group in benzyl alcohol by a napthyl group also results in a larger yield of hydrogenated product; a yield of 72 percent of 1-methylnaphthalene was obtained from 1-naphthalene-methanol. Nuclear hydrogenation also occurred in this case: Mass spectrometric analysis showed that 1-methyl and 5-methyl-1,2,3,4-tetrahydronaphthalene were produced.

Aromatic ketones are probably hydrogenated via the carbinol, since the alcohol was isolated occasionally as a minor constituent, and in other cases (benzhydrol, triphenylcarbinol) the carbinol was employed as the start-

TABLE 29.—*Reaction of aromatic alcohols and ketones with synthesis gas[1] and cobalt catalyst[2] at 180°–185° C.*

Starting compound	Mole	Benzene, ml.	Synthesis gas, H_2:CO	Time, hours	Composition	Yield, percent
Benzyl alcohol	0.78	0	1	3	Toluene	49
					2-Phenylethanol	26
					Water	99
Do	.60	50	.2	5	Toluene	63
					2-Phenylethanol	32
					Water	100
1-Naphthalenemethanol	.45	65	2	3	1-Methylnaphthalene [3]	72
1-Phenylethanol	.75	0	2	3	Ethylbenzene	70
Benzhydrol	.05	70	1	3	Diphenylmethane	95
Triphenylcarbinol	.04	94	1	3	Triphenylmethane	94
Benzopinacol	.03	93	1	3	Diphenylmethane	89
Acetophenone	1.0	0	1	1	Benzophenone	5
					Ethylbenzene	53
					Acetophenone	14
Do	.69	0	2	3	Ethylbenzene	67
					Acetophenone	9
p-Methoxyacetophenone	.70	20	2	4	p-Ethylanisole	91
					2-(p-Methoxyphenyl)-propanol-1 [4]	6
Benzophenone	.60	90	1	2	Diphenylmethane	86
Fluorenone	.06	60	2	4	Benzophenone	8
					Fluorene	95
Benzanthrone	.07	50	1	3	9-Fluorenol	2
					1,10-Trimethylenephenanthrene	59

[1] The total initial pressure, measured at room temperature, was always between 3,000 and 3,500 p.s.i.
[2] In each experiment, 1.5-2.5 g. of cobalt was added as cobalt (II) carbonate, cobalt (II) acetate tetrahydrate, or dicobalt octacarbonyl.
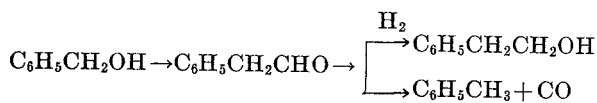[3] An authentic sample of this alcohol was prepared by lithium aluminum hydride reduction of the corresponding aldehyde; α-naphthylure-than, melting point, 109.1-110.0° C., identical with that prepared from the isolated alcohol. Analytically calculated for $C_{21}H_{21}NO_2$: C, 75.20; H, 6.31. Found: C, 75.28; H, 6.41.
[4] Some 1-methyl and 5-methyl-1,2,3,4-tetrahydronaphthalene were also present.

ing material. Conversion of benzopinacol, $Ph_2C(OH)C(OH)Ph_2$, to diphenylmethane may be explained by the fact that the pinacol decomposes on heating to benzophenone and benzhydrol, both of which are readily reduced to diphenylmethane under oxo conditions.

Formation of hydrocarbons from benzyl alcohols may involve the formation of an aldehyde and its subsequent decarbonylation under reaction conditions. From benzyl alcohol one obtains a mixture of toluene and the homologous alcohol, 2-phenylethanol. Both products may be derived from the intermediate formation and reaction of phenylacetaldehyde:

$$C_6H_5CH_2OH \rightarrow C_6H_5CH_2CHO \rightarrow \begin{cases} \xrightarrow{H_2} C_6H_5CH_2CH_2OH \\ \rightarrow C_6H_5CH_3 + CO \end{cases}$$

The question arises as to whether the toluene results from the direct hydrogenolysis of benzyl alcohol or from the decarbonylation of phenylacetaldehyde; analogous decarbonylations are well known. To establish the validity of the decarbonylation path, phenylacetaldehyde was treated under conditions similar to those that result in the conversion of benzyl alcohol to toluene and 2-phenylethanol; the phenylacetaldehyde, however, polymerized very readily, and no identifiable reaction products were secured. The attempted decarbonylation was repeated with diphenylacetaldehyde (table 30), which is less readily polymerized than phenylacetaldehyde. A small yield of the hydrocarbon diphenylmethane was secured, but the major product of the reaction was 2,2-diphenylethanol. Since reduction of benzhydrol under similar conditions gives diphenylmethane exclusively, this hydrocarbon is unlikely to be formed to any great extent via diphenylacetaldehyde, according to $Ph_2CHOH \rightarrow Ph_2CHCHO \rightarrow Ph_2CH_2$. In an attempted decarbonylation of 2-phenylpropionaldehyde (table 30), a small yield of ethylbenzene was secured, but the principal reaction was hydrogenation to 2-phenyl-1-propanol. The evidence indicates that the hydrocarbons listed in table 29 probably result from direct hydrogenolysis of the aromatic alcohol.

TABLE 30.—*Decarbonylation experiments (185° C. for 3 hours)*

Starting compound	Mole	Benzene, ml.	Synthesis gas, H_2:CO	Initial pressure, p.s.i.	Composition	Yield, percent
2-Phenylpropionaldehyde [1]	0.75	0	0.25	2,000	Ethylbenzene	3
					2-Phenyl-1-propanol	38
					2-Phenylpropionaldehyde	18
Diphenylacetaldehyde [2]	.03	100	.125	1,800	Diphenylmethane	7
					2,2-Diphenylethanol	87
Do.[2]	.05	100	1	2,500	Diphenylmethane	8
					2,2-Diphenylethanol	88

[1] 7 g. of cobalt (II) acetate tetrahydrate was used as the catalyst.
[2] 5 g. of cobalt (II) carbonate was used as the catalyst.

Conversion of benzanthrone to 1,10-trimethylenephenanthrene under oxo conditions is an example of nuclear hydrogenation:
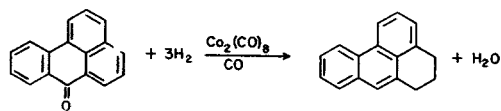

Benzanthrone   1,10— trimethylenephenanthrene

Attempts (149) to prepare this hydrocarbon from benzanthrone by the Wolff-Kishner method or its modifications, by Raney nickel reduction, by the Clemmensen procedure, and by zinc-dust distillation were unsuccessful or gave the desired hydrocarbon in poor yield. The product of this reaction is a phenanthrene derivative; as has been shown, polynuclear hydrocarbons yield phenanthrene derivatives or compounds with isolated benzene rings under oxo conditions.

When substituted benzyl alcohols of the type $C_6H_5CRR'OH$ (when R and/or R' are alkyl or aromatic groups) are treated with synthesis gas under hydroformylation conditions, the corresponding hydrocarbon is formed exclusively. A kinetic study of the reduction of such alcohols with synthesis gas and dicobalt octacarbonyl was made in batch autoclaves to gain information on the mechanism of this hydrogenation (150).

After alcohol and solvent were placed in the autoclave, the bomb and gas compressor were purged three times with nitrogen and three times with synthesis gas to cylinder pressure and boosted with the compressor to the desired pressure. To prevent plugging of the lines leading from the autoclave with solid alcohols, the rocking mechanism was not started until the internal temperature had reached 75° C.

Each alcohol reacted with synthesis gas and catalytic amounts of dicobalt octacarbonyl to yield the corresponding hydrocarbon with the absorption of 1 mole of hydrogen per mole of alcohol. With benzhydrol, this hydrogenolysis reaction may be written:

$$(C_6H_5)_2CHOH + H_2 \rightarrow (C_6H_5)_2CH_2 + H_2O.$$
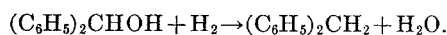
The change in alcohol concentration during the reaction was assumed to be proportional to the change in the gas pressure at constant temperature. That is, $C_0/C_t = (P_0 - P_t)/(P_t - P_f)$, where C_0 is the initial concentration of aromatic alcohol, C_t is the concentration of alcohol at time t, P_0 is the calculated initial pressure at reaction temperature, P_f is the calculated final pressure at reaction temperature, and P_t is the pressure at reaction temperature at time t. Thus, the rate of reduction could be followed by observing the change of pressure with time. Plots of log $(P_0 - P_t)/(P_t - P_f)$ as a function of time gave good straight lines (see figure 16),

indicating that the reaction rate is first order with respect to the concentration of aromatic alcohol. The first-order specific reaction-rate constants for a number of aromatic alcohols are listed in table 31.

TABLE 31.—Specific reaction-rate constants, k, for reduction of aromatic alcohols [1]

Alcohol	Temperature ° C.	k 10^{-3} minute^{-1}
Benzhydrol	125	3. 9
	130	5. 2
	135	6. 8
	140	8. 9
	145	11. 2
p-Methylbenzhydrol	115	8. 3
	120	10. 7
	125	13. 4
	130	17. 4
p-Methoxybenzhydrol	95	2. 6
	100	3. 7
	105	6. 0
	110	9. 9
	115	15. 8
p-Chlorobenzhydrol	160	7. 9
	165	10. 3
	170	15. 3
	175	16. 8
p,p'-Dichlorobenzhydrol	177	7. 8
Triphenylcarbinol	125	40. 7
Phenylmethylcarbinol	150	2. 2
	160	3. 6

[1] 0.167 mole aromatic alcohol, 2.8 g. (8.2$\times10^{-3}$ mole) dicobalt octacarbonyl, 50 ml. benzene, and 3,500 p.s.i. initial pressure at room temperature of $1H_2 + 1CO$ in 200-ml. autoclave.

The rate of hydrogenation of benzhydrol at 135° C. was independent of the pressure of carbon monoxide in the range investigated (700 to 2,600 p.s.i.). The rate increased with increasing pressures of hydrogen, though not as a simple function.

The specific reaction rate for hydrogenating benzhydrol at 135° C. was approximately proportional to the initial concentration of dicobalt octacarbonyl from about 4.5 to 28 mole-percent cobalt per mole benzhydrol.

The effect of solvents on the rate of reduction of benzhydrol (table 32) is considerably greater than that observed in the hydroformylation of olefins (153).

An investigation of the effect of bases on the rate of the benzhydrol reduction at 135° C. showed that small amounts of pyridine in benzene (3 percent by volume) increase the rate, whereas larger amounts (20 to 50 percent by volume) decrease the rate. In one experiment with a solvent consisting of 79 percent benzene and 21 percent triethylamine, no gas absorption was observed. When dimethylformamide was used as solvent, gas absorption did not begin until the temperature was raised to
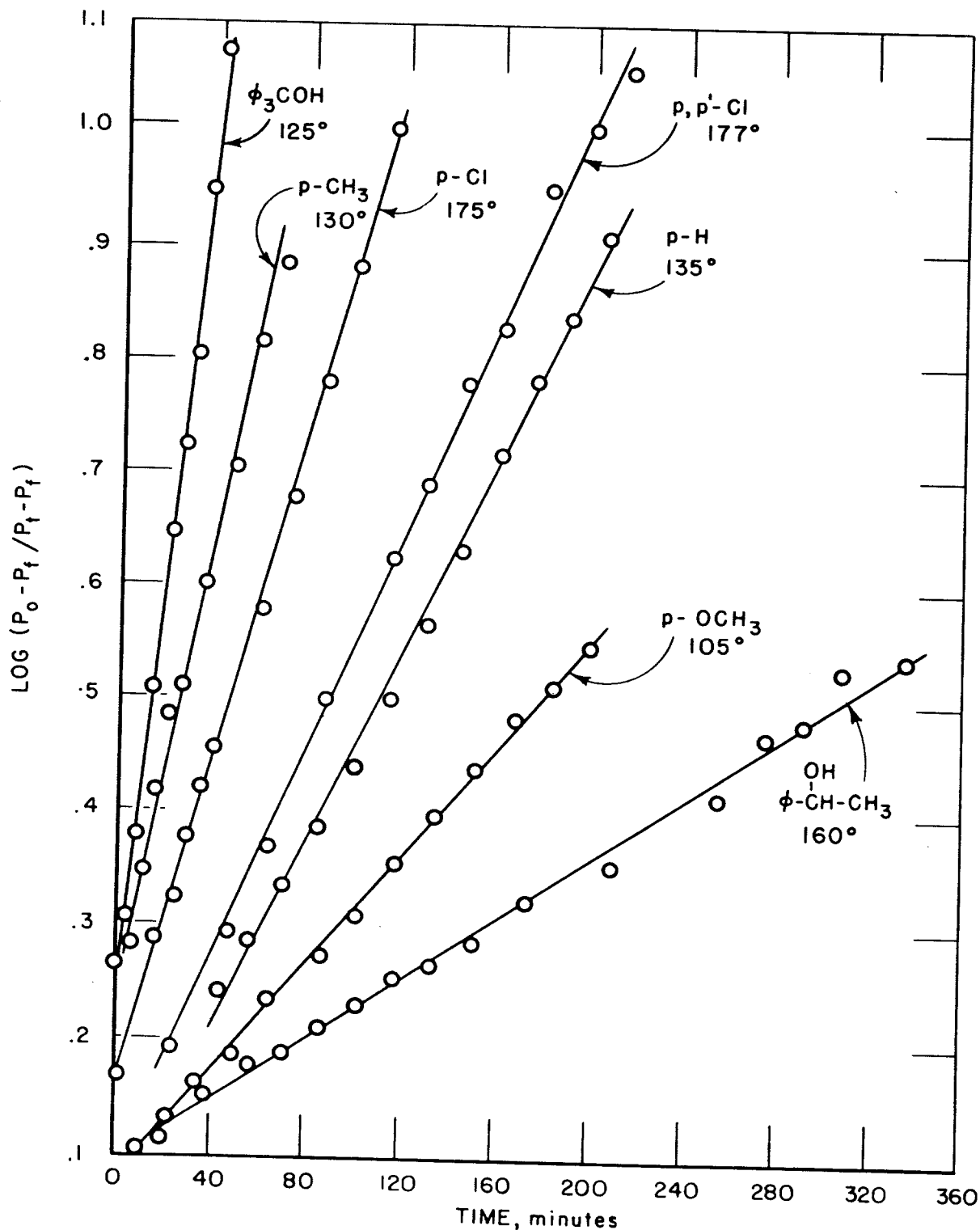
FIGURE 16.—Rates of Reduction of Aromatic alcohols.

about 145° C. Similar results have been obtained in the hydroformylation of olefins (153).

The effect of substituents on the rate of reduction of benzhydrols to hydrocarbons is $p\text{-}CH_3O > p\text{-}CH_3 > H > p\text{-}Cl > p,p'di\text{-}Cl$, as

shown in table 31. However, it may not be possible to interpret the increase in rate with increased electron-releasing capacity of the nuclear substituent in terms of a seemingly appropriate mechanism, such as an acid-catalyzed

TABLE 32.—*Effect of solvent on specific reaction-rate constant, k, of reduction of benzhydrol* [1]

Solvent	Temperature, ° C.	$k\ 10^{-3}$ minute^{-1}
Benzene	135	6. 8
Butyl ether	135	6. 9
Ethyl ether	135	8. 2
Isopropyl ether	135	8. 2
Chlorobenzene	135	10. 5
Benzene+diphenylmethane (1:1)	135	10. 8
Benzene+ethanol (97:3)	135	8. 5
Ethanol	80	4. 9
	85	6. 4
	90	8. 4
	95	11. 1
	100	14. 9
	105	19. 6
Methanol	96. 5	21. 1
Acetone	110	56. 8

[1] 0.167 mole benzhydrol, 2.8 g. (8.2×10⁻³ mole) dicobalt octacarbonyl, 50 ml. solvent, and 3,500 p.s.i. initial pressure at room temperature of 1H₂+1CO in 200-ml. autoclave.

reaction involving formation of a carbonium ion in the rate-determining step. The apparent heats and entropies of activation, shown in table 33, indicate the importance of the pre-exponential factor. For example, p-methoxy-benzhydrol is very reactive despite its relatively high heat of activation. No correlation is obvious between the electron-releasing capacity of the nuclear substituents and apparent heat or entropy of activation. Hence, the correlation of electron-releasing capacity with rate may be fortuitous. Also, heats and entropies of activation obtained over different temperature ranges in this system may not be directly comparable; the equilibria between the various cobalt carbonyls and hydrogen and carbon monoxide may well be a function of temperature.
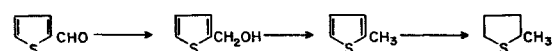
The rate of hydrogenation of benzhydrol was markedly increased by the presence of small amounts of metallic copper; a tenfold increase in rate could be secured in this manner. The significance of this fact is yet to be explained, but copper may function as an electron donor

Cu°→Cu⁺1(e), or as a one-electron transfer agent.

HYDROGENATION OF THIOPHENE AND SUBSTITUTED THIOPHENE

As most conventional hydrogenation catalysts are poisoned by compounds containing sulfur, no method existed for reducing thiophene until the procedure using palladium catalysts at low pressures was developed (87). This method, though useful, has its limitations: Very high ratios of catalyst to thiophene are usually required, and the method has not been applied to more than a few grams of substrate. Campaigne and Diedrich (26) reported that 2-acyl-thiophenes were reduced to the corresponding alkyl thiophenes and alkyl thiacyclopentanes when treated with 100 to 150 atm. of hydrogen in the presence of a cobalt polysulfide catalyst at temperatures up to 225° C. However, these workers were unable to reduce alkyl thiophenes or thiophene by this procedure.

Since hydrogenations which occur under hydroformylation conditions are homogeneously catalyzed, surface poisoning of the catalyst by sulfur is impossible. Wender, Levine, and Orchin (152) were able to reduce 2-thiophene-carboxaldehyde to a mixture of 2-thenyl alcohol and 2-methylthiophene and to reduce 2-acetyl-thiophene to 2-ethylthiophene. Later work (49) showed that the thiophene nucleus is reduced if the amount of catalyst (dicobalt octacarbonyl) and the time of reaction are increased. Conversion of a substituted thiophene to the reduced thiacyclopentane appears to be a step-by-step process which, for 2-thiophene-carboxaldehyde, may be represented as follows:

Experiments with various substrates containing the thiophene nucleus are summarized in table 34.

TABLE 33.—*Apparent heats and entropies of activation for hydrogenation of benzhydrols under oxo conditions*

	Solvent	Temperature range, ° C.	ΔH^{++}, kcal./mole	Preexponential factor, second^{-1}	ΔS^{++} [1]
Benzhydrol	Benzene	125–145	17. 3	1. 90×10⁵	−35. 1
Do	Ethanol	80–105	14. 8	1. 21×10⁵	−35. 8
p-Methylbenzhydrol	Benzene	115–130	14. 9	3. 30×10⁴	−47. 7
Do	do	95–115	26. 1	1. 22×10¹¹	−8. 5
p-Chlorobenzhydrol	do	160–175	20. 1	1. 85×10⁶	−30. 8

[1] Entropy units.