

# REACTIONS CATALYZED BY THE COBALT CARBONYLS

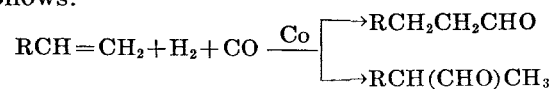
## The Oxo Reaction

### INTRODUCTION

The earliest recorded experiments in which oxygenated compounds were produced from hydrogen-carbon monoxide mixtures were those performed by Mittasch and Schneider and incorporated into patents issued to the Badische Anilin und Soda Fabrik in 1913 (7, 84, 85). They found that hydrogen and carbon monoxide reacted at 100 to 200 atm. and 300° to 400° C. in the presence of alkali-activated cobalt and osmium oxides to form a liquid product containing alcohols, aldehydes, ketones, acids, and saturated and unsaturated hydrocarbons. Further development of this line of investigation, in particular the use of difficultly reducible oxides such as zinc oxide as catalysts, led eventually to the establishment of the commercial methanol synthesis. Investigations along a different line, in which the iron-group metals were used as catalysts, had equally important consequences. In 1923, Fischer and Tropsch (45), working at the Kaiser-Wilhelm Institut für Kohlenforschung, discovered that hydrogen and carbon monoxide, when passed over alkalized iron turnings at 100 to 150 atm. and 400° to 450° C., formed an oily liquid which they called "synthol" (synthetic oil). Under these conditions the oil was chiefly oxygenated, but in experiments (1925) in which the pressure was lowered to about 7 atm., "synthol" consisted chiefly of olefinic and paraffinic hydrocarbons suitable for motor fuel. This process for the production of synthetic fuels (or chemicals) from carbon monoxide-hydrogen mixtures has since become known as the Fischer-Tropsch reaction.

The industrial importance of the Fischer-Tropsch synthesis stimulated much research in the industrialized countries of the world. In 1926, Elvins and Nash (40) in England called attention to the fact that the product from the low-pressure hydrocarbon synthesis always contained small quantities of oxygenated compounds. In 1929, Smith, Hawk, and Golden (127), at the Bureau of Mines, added ethylene to the carbon monoxide-hydrogen mixture before passing it over a cobalt catalyst and found that the yield of oxygenated compounds

was increased. Meanwhile research on the synthesis was being pursued in Germany, especially at Ruhrchemie A. G., where one of Fischer's former students, Otto Roelen, was directing a group of research workers. In 1937, they studied the effects of recycling tail gas and adding substances to the tail gas before recycling. Added olefins were partly hydrogenated, partly incorporated into higher molecular weight hydrocarbons, and partly converted to oxygenated compounds. The experiment of Smith, Hawk, and Golden was repeated, and the aldehydic portion of the product was separated by 2,4-dinitrophenylhydrazine. Only the phenylhydrazone of propionaldehyde was found. Roelen felt that the small quantity of propionaldehyde had been formed from the added ethylene and reasoned that such a reaction, involving the condensation of 3 moles of gas, would be highly dependent on pressure. Furthermore, earlier work had shown that temperatures lower than those for the Fischer-Tropsch reaction were desirable to increase the yield of oxygenated materials with a cobalt catalyst. In July and August of 1938, experiments were performed with water gas (1H<sub>2</sub>:1CO), ethylene, and a cobalt catalyst at 100 atm. and 50° to 150° C. The product consisted principally of propionaldehyde, together with some diethyl ketone. Thus, Roelen's study of the Fischer-Tropsch reaction, in which hydrocarbons were the main product and oxygenated compounds a minor constituent, led to the discovery of a new reaction in which oxygenated compounds were the only product. Roelen considered the reaction to be a general one for all olefins (117, 118). In the patent applications and correspondence the reaction was called an "oxo" synthesis, and the linguistic appeal of the simple short word has won it a permanent place in the literature of chemical technology. The overall reaction is most easily visualized as involving the addition of a hydrogen atom and a formyl group (H-CHO) across the double bond of an olefin, and therefore the name "hydroformylation" has been proposed (2). The general reaction can be represented as follows:



In the discussion which follows the names oxo and hydroformylation will be used interchangeably to denote the just shown reaction. Hydrogenation reactions will be shown to occur in lieu of, in competition with, or subsequent to the oxo reaction. Hence "oxo" or "hydroformylation" conditions denote the conditions of temperature, pressure, and catalyst required for the oxo and related reactions. These conditions are approximately 50° to 200° C., 100 to 400 atm. of synthesis gas,<sup>12</sup> and a cobalt catalyst (reduced metallic cobalt, a cobalt salt, or a carbonyl of cobalt). Dicobalt octacarbonyl, cobalt hydrocarbonyl, and tetracobalt dodecacarbonyl may all be present under these conditions.

## THE PRINCIPAL REACTION

### Commercial Charge Stocks and Products

The starting materials for the oxo synthesis, as operated in the United States, are propylene, butylenes, heptenes, nonenes, and dodecenes; the higher olefins are obtained by polymerizing propylene or propylene-butylene mixtures. Oxo production in the United States started in late 1948, and capacity rose to over 150 million pounds in 6 years (28). The largest manufacturing capacity is devoted to the production of "isooctyl" alcohols from mixed heptylenes. The isooctyl alcohol produced is a mixture of at least 10 different C<sub>8</sub> primary alcohols, including 3,5-, 3,4-, and 4,5-dimethylhexanol and 3-, 4-, and 5-methylheptanol. The dimethylhexanols are the principal components. Isooctyl alcohol is mostly converted to isooctyl phthalate, a plasticizer in polyvinyl chloride formulations. Propylene is the feed material in one large oxo plant which produces butyraldehyde and isobutyraldehyde. This is one of the few operations in which the aldehyde is isolated and purified; usually the aldehyde mixture is reduced immediately to the corresponding mixture of alcohols. Isolation of aldehydes is particularly feasible when they are low boiling. In another large oxo plant, butylenes are converted to amyl alcohols. Those are all primary alcohols and thus differ from the C<sub>5</sub> alcohols made by fermentation processes.

In Germany the main interest in the oxo process during World War II was production of alcohol sulfates as washing and wetting agents. The charge stock was an olefinic mixture in the C<sub>11</sub> to C<sub>17</sub> range secured by thermal cracking of the soft wax produced in the Fischer-Tropsch process. The process was never oper-

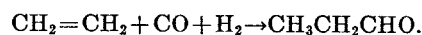
ated on a large scale. In Italy early interest in the oxo reaction was directed toward the manufacture of propionaldehyde from ethylene.

In a typical commercial oxo operation, a mixture of heptylenes boiling at 76° to 99° C. is mixed with a recycle product and enough cobalt naphthenate (or other form of soluble cobalt) to give a concentration of 0.2 weight-percent cobalt, based on the total feed. The solution is pumped through a preheater and into a reactor where the liquid passes upward concurrently with synthesis gas. The reactor may be an empty tube, or it may be filled with an inert material such as Raschig rings. The temperature of the reactor is about 175° C., and the pressure of synthesis gas (1H<sub>2</sub>:1CO) is about 200 atm. The reaction is exothermic; the conversion of ethylene to propionaldehyde is accompanied by the liberation of 34.8 kcal./mole. A recycle product helps in removing the heat of reaction.

### Scope and Limitations of the Reaction

#### THERMODYNAMICS

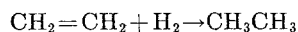
The feasibility of the oxo reaction can be determined by evaluating the magnitude of the free-energy change,  $\Delta F^\circ$ , which is the thermodynamic driving force for the reaction. Rather extensive data are available for the oxo reaction involving ethylene:



The heats of formation,  $\Delta H$ , for ethylene, carbon monoxide, and propionaldehyde are plus 12,496, minus 26,416, and minus 48,707 cal./mole at 25° C., respectively, from which  $\Delta H$  of the reaction is minus 34,787 cal./mole. Substitution of this value in the free-energy equation,  $\Delta F^\circ = \Delta H - T\Delta S^\circ$ , where  $T$  is expressed in ° K. and  $\Delta S^\circ$  is change in entropy, yields  $\Delta F = -34,787 + 58.1 T$  (161), from which the equilibrium constant  $K$  was calculated from the usual relationship,  $\Delta F^\circ = -RT \ln K_p$ . The values obtained in this manner by Wenner and somewhat different values secured by Natta, Pino, and Mantica (99) are shown in table 22. These data show that the formation of propionaldehyde from ethylene and synthesis gas is favored at 1 atm. and moderate temperature. The reaction obviously is not subject to equilibrium restrictions. Although the oxo synthesis does not proceed at atmospheric pressure with a dicobalt octacarbonyl catalyst, measurable rates have been observed at only 10 atm., and indeed the reaction has been shown to occur readily at room conditions when cobalt hydrocarbonyl is mixed with an olefin. An olefin is usually hydroformylated to the almost complete exclusion of hydrogenation, even though the

<sup>12</sup> Synthesis gas is the general name given to all mixtures of carbon monoxide and hydrogen. When a particular synthesis gas is discussed, the ratio H<sub>2</sub>:CO is usually given in parentheses.

free-energy change,  $\Delta F^\circ$ , for the reaction



at 25° C. is minus 22,608 cal./mol (91), compared with minus 14,460 for the oxo synthesis. Hydrogenation becomes competitive only when the olefinic linkage is conjugated.

TABLE 22.—Free energy and equilibrium values for the hydroformylation of ethylene

Temperature, °C.	$\Delta F^\circ$ , cal./mole		$K_p$	
	Reference (161)	Reference (99)	Reference (161)	Reference (99)
25.....	-17,473	-14,460	$6.5 \times 10^{12}$	$4.05 \times 10^{10}$
100.....	-13,116	-8,930	$4.8 \times 10^7$	$1.71 \times 10^3$
150.....	-10,211	-5,220	$1.9 \times 10^5$	$4.99 \times 10^2$
200.....	-7,306	-1,390	$2.4 \times 10^3$	4.39

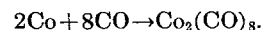
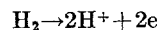
### CATALYSTS

The first catalyst to be used in the oxo synthesis was one containing cobalt, thoria, magnesia, and kieselguhr in the proportions 100:5:8:200. This was the standard Fischer-Tropsch cobalt catalyst used by Ruhrchemie and was thus available in large quantity. When reduced, this catalyst is very active in the oxo synthesis, but the last three components, although important in the Fischer-Tropsch synthesis, are superfluous for the oxo reaction. The Fischer-Tropsch synthesis is a heterogeneously catalyzed reaction, and the condition of the surface of the catalyst, its method of preparation, and the manner in which it is activated are of utmost importance. On the other hand, the oxo synthesis is a homogeneous reaction in which soluble cobalt carbonyls are the catalysts. When metallic cobalt is used in the oxo synthesis, its efficiency depends, therefore, on the ease with which it is transformed to the carbonyl.

Although dicobalt octacarbonyl may be formed from activated cobalt by reaction with carbon monoxide, the conversion of cobalt salts to the carbonyl usually requires hydrogen. In fact, when an oxo reaction is catalyzed by cobalt salts, somewhat higher temperatures are required than when cobalt carbonyl is added. For example, 1-octene is hydroformylated at 200 to 300 atm. of  $1\text{H}_2:1\text{CO}$  with cobalt acetate at 150° to 160° C. However, when the same concentration of cobalt is introduced as dicobalt octacarbonyl, the reaction is rapid at 115° to 125° C. Obviously the formation of the carbonyl from the salt requires the higher temperature.

The reaction of a cobalt salt is illustrated by the conversion of cobaltous acetate to dicobalt octacarbonyl. The valence of cobalt in the

carbonyls is zero; in cobaltous (II) acetate it is, of course, two. The reduction of cobalt (II) to cobalt (0) requires two electrons; in this system they are furnished by hydrogen. In the presence of synthesis gas, cobalt (II) is probably reduced to zerovalent cobalt simultaneously with the formation of cobalt carbonyl, the carbon monoxide helping the conversion along:



In support of such a concerted mechanism, it may be noted that high temperatures and long times are needed for reducing cobalt salts to metallic cobalt in the presence of hydrogen alone. Furthermore, conversion to the carbonyl of metallic cobalt, even in as active a state as Raney cobalt, appears to require a longer time than does cobaltous acetate or carbonate under comparable conditions.

Thus, virtually any form of cobalt may be used as a catalyst for the oxo synthesis, since dicobalt octacarbonyl is formed under the usual conditions. This is also true of organic cobalt salts such as cobalt octanoate or naphthenate; the crude salts (sold as accelerators for drying oils) are suitable for the oxo reaction.

Cobalt and rhodium carbonyls are catalysts for the oxo reaction; iron pentacarbonyl functions as a catalyst at somewhat higher temperatures. Nickel carbonyl is not an oxo catalyst. Early writers stated that cobalt and iron were oxo catalysts because these metals form hydrocarbonyls, whereas nickel did not form a hydrocarbonyl and hence was not a catalyst. However, a hydrocarbonyl of nickel,  $[\text{NiH}(\text{CO})_3]_2$ , has been prepared (9).

### EFFECT OF OLEFIN STRUCTURE

All simple olefins submitted to the oxo synthesis have been shown to react. Their rates of reaction, however, vary appreciably.

Rates of hydroformylation of 26 olefins at 110° C. were studied in a batch system under the following conditions (153):

A solution of, for example, 41.0 g. (0.50 mole) of cyclohexene, 65 ml. of methylcyclohexane, and 2.8 g. ( $8.2 \times 10^{-3}$  mole) of dicobalt octacarbonyl was placed in a 500-ml., stainless steel, rocking autoclave. The autoclave and gas compressor were purged three times with 20 atm. of synthesis gas. The unit was filled with  $1\text{H}_2:1\text{CO}$  to cylinder pressure and then boosted to 233 atm.; then the autoclave was isolated from the compressor by a high-pressure valve. The rocking mechanism was started, and heating of the autoclave was begun. It took 56 minutes to heat the autoclave from room temperature to 110° C.; the temperature was controlled to  $\pm 1^\circ$  C. The pressure could be read to within 0.33 atm. on a gage mounted inside the stall. The experiment was continued until the end of

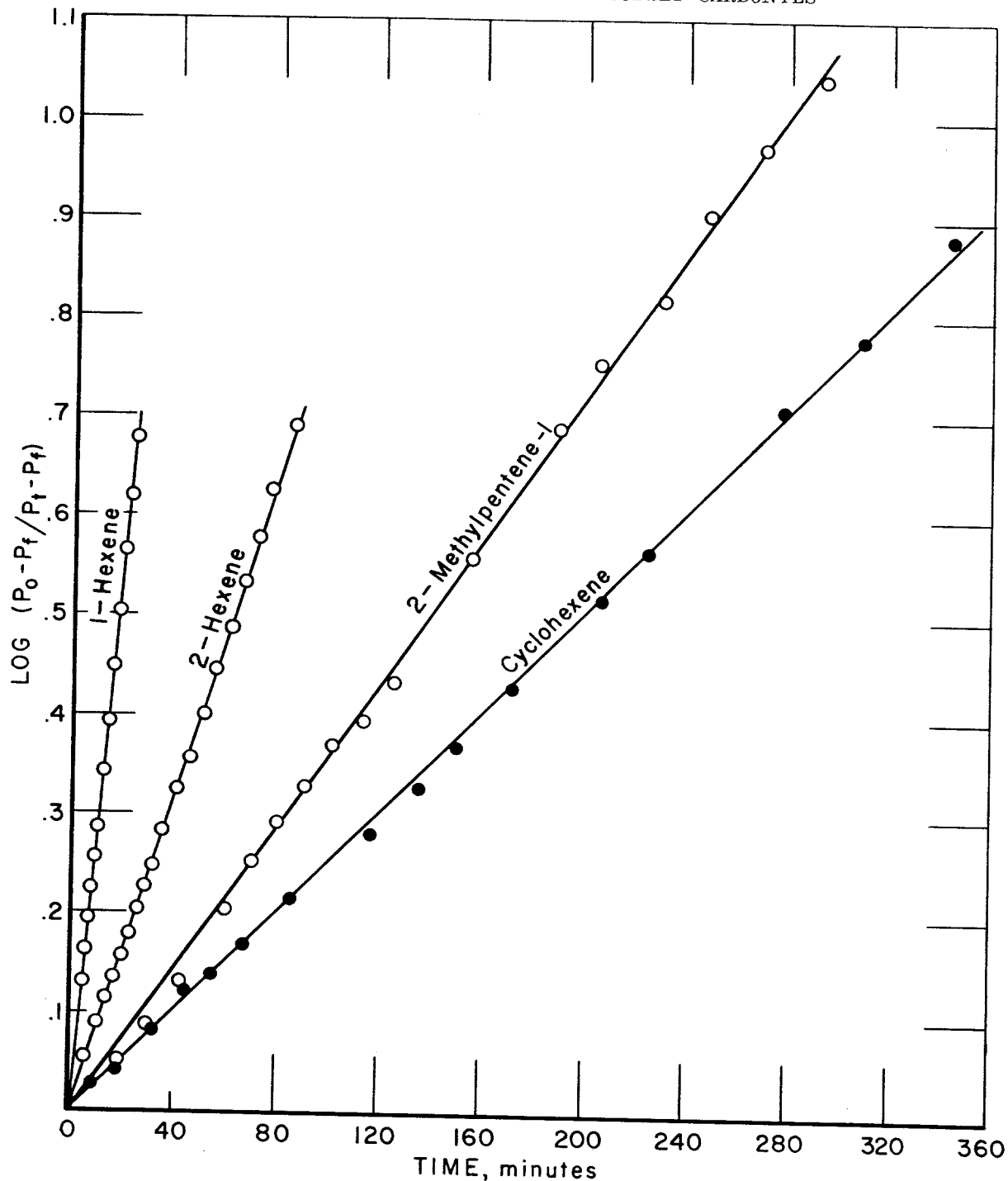


FIGURE 11.—Rates of Hydroformylation of Olefins at 110° C. and 233 atm. With  $1\text{CO} + 1\text{H}_2$ .

the working day, when the heat was turned off and the rocking stopped. Final pressure and temperature readings were taken the following morning. The same autoclave was used for each run.

The reproducibility of the results was determined in duplicate runs and in additional runs with cyclohexene at random intervals. A statistical analysis of 55 runs yielded a standard deviation from the mean of  $\pm 1.5$  percent. The method of least squares was used in calculating the rate constants from the data.

The original pressure at room temperature was not taken as the initial pressure because of an appreciable drop after rocking was begun. This drop, which occurred before the material reacted, did not reach a constant value until the autoclave had been heated to about 80° C. Consequently, the initial pressure at room temperature was calculated from the observed pressures during rocking of the autoclave at elevated temperatures. Gas was taken up by the liquid; this was demonstrated during blank runs in the absence of

a catalyst. In these runs the initial pressures, calculated from observed pressures at elevated temperatures during rocking, agreed well with the observed pressures after rocking was stopped and the autoclave had been cooled to room temperature. The initial pressure at reaction temperature,  $P_0$ , was then calculated from the calculated initial pressure at room temperature. Approximately 2.2 moles of gas was used per mole of olefin; the same value was obtained by Natta and Ercoli (93) for moles of gas absorbed per mole of reacted olefin. This excess gas absorption over the theoretical value is probably due to some hydrogenation of the aldehydes and of aldehyde condensation products.

Plots of  $\log(P_0 - P_t/P_t - P_t)$  as a function of time yielded straight lines ( $P_t$ =final pressure at reaction temperature after complete reaction,  $P_t$ =pressure at time  $t$ ), indicating that the rate of decrease of pressure was linear with the total pressure. Several such plots are given in figure 11; time corrections for the reaction that occurred on heating to 110° C. were found by extrapolating conversion-time plots to zero conversion.

The kinetic data, summarized in table 24, show a fiftyfold variation between the fastest and slowest rates. The olefins listed in table 23 are conveniently divided into five structural classes for purposes of comparison.

TABLE 23.—Rates of hydroformylation of olefins at 110° C.<sup>1</sup>

Olefin, structural class	Specific reaction rate, $k \times 10^3 \text{ min.}^{-1}$ <sup>2</sup>
<b>Straight-chain terminal:</b>	
1-Pentene.....	68.3
1-Hexene.....	66.2
1-Heptene.....	66.8
1-Octene.....	65.6
1-Decene.....	64.4
1-Tetradecene.....	63.0
<b>Straight-chain internal:</b>	
2-Pentene.....	21.3
2-Hexene.....	18.1
2-Heptene.....	19.3
3-Heptene.....	20.0
2-Octene.....	18.8
<b>Branched terminal:</b>	
4-Methyl-1-pentene.....	64.3
2-Methyl-1-pentene.....	7.82
2,4,4-Trimethyl-1-pentene.....	4.79
2,3,3-Trimethyl-1-butene.....	4.26
Camphene.....	2.2
<b>Branched internal:</b>	
4-Methyl-2-pentene.....	16.2
2-Methyl-2-pentene.....	4.87
2,4,4-Trimethyl-2-pentene.....	2.29
2,3-Dimethyl-2-butene.....	1.35
2,6-Dimethyl-3-heptene.....	6.23
<b>Cyclic:</b>	
Cyclopentene.....	22.4
Cyclohexene.....	5.82
Cycloheptene.....	25.7
Cyclooctene.....	10.8
4-Methyl-1-cyclohexene.....	4.87

<sup>1</sup> Conditions: 0.50 mole of olefin, 65 ml. of methylcyclohexane as solvent, 2.8 g. ( $8.2 \times 10^{-3}$  mole) of dicobalt octacarbonyl, and an initial pressure at room temperature of 233 atm. of  $\text{H}_2$ :1CO.

<sup>2</sup> Every olefin was run at least twice, except camphene and cyclooctene.

### Straight-Chain Terminal Olefins

This type of olefin reacts most rapidly. There is a small drop in rate with increase in chain length, but the effect becomes smaller with increase in carbon number. The decrement may be due to the increased difficulty of orienting the double bond in the higher molecular weight olefins towards dicobalt octacarbonyl.

### Straight-Chain Internal Olefins

Two conclusions may be drawn from the data: (1) The rate of hydroformylation of straight-chain internal olefins is about one-third that of the corresponding terminal olefin, and (2) the position of the double bond, as long as it is internal, has little or no effect on the rate; that is, 2-heptene and 3-heptene react with essentially the same speed. Steric effects are important, since the accessible terminal double bond reacts faster in all cases. The isomerization of double bonds catalyzed by dicobalt octacarbonyl under hydroformylation conditions will be discussed later.

### Branched Terminal Olefins

Within the range of olefins studied, branching always results in a decrease in rate. The largest decrease was observed for olefins with a methyl group at one of the carbon atoms of the double bond (compare 1-hexene and 2-methyl-1-pentene). Further branching along the chain results in a further decrease in rate; even a single methyl branch on the  $\beta$ -carbon atom (4-methyl-1-pentene) results in a small, but probably significant, decrease. Camphene, which has an exocyclic bond attached to a bulky and highly branched carbon chain is an extreme case; its rate of reaction is less than one-thirtieth that of 1-hexene.

### Branched Internal Olefins

Internal olefins that are branched react most slowly. Although 1-hexene and 2,3-dimethyl-2-butene are isomeric, the former reacts about fifty times as fast as the latter. A methyl branch at the carbon atom  $\alpha$  to the double bond decreases the rate (compare hexene-2 and 4-methyl-pentene-2). 2,6-Dimethyl-3-heptene reacted more rapidly than 2-methyl-2-pentene or 2,3-dimethyl-2-butene. The explanation for this surprising fact will be offered later.

### Cyclic Olefins

Since all cyclic olefins are internal olefins, they may be compared with straight-chain internal olefins. As is shown in table 24,

however, both cyclopentene and cycloheptene react more rapidly than the corresponding straight-chain internal olefins. In addition, there is a minimum in the rate of reaction at the six-membered ring.

Thus, although all simple olefins can be hydroformylated, the rates of reaction are dependent on structure. Later discussions will deal with the significance of these facts and will also treat the effect of conjugation of the olefinic linkage with another unsaturated center.

Most of the straight-chain olefins studied in the oxo reaction have the double bond in the terminal position. The product from such olefins is usually a mixture of aldehydes consisting of about 60 percent of the straight-chain isomers and 40 percent of the branched-chain isomers. Straight-chain olefins with the double bond in other positions yield almost identical products. For example, the distribution of alcohols secured from 1-pentene and 2-pentene at 120° to 160° C. is about the same (75): 50 to 55 percent hexanol, 35 to 40 percent 2-methyl-1-pentanol, and 10 percent 2-ethyl-1-butanol.

In general, therefore, a straight-chain olefin yields about 60 percent normal and 40 percent  $\alpha$ -branched aldehyde or alcohol, no matter where the double bond is located.

Branched olefins submitted to the oxo reaction also yield products that are almost the same, regardless of the location of the double bond (75). Thus, essentially the same products result from 2-methyl-2-butene as from 3-methyl-1-butene or 2-methyl-1-butene: 55 percent 4-methyl-1-pentanol, 45 percent 3-methyl-1-pentanol, and 5 percent 2,3-dimethyl-1-butanol (75).

Early investigators stated that addition of the formyl group to a tertiary carbon atom does not occur, so no quaternary carbon atoms are formed in the oxo reaction (75). Workers at the Bureau of Mines (146), however, obtained 1.2 percent neopentyl alcohol upon hydroformylation of isobutylene in an autoclave; this alcohol was isolated by distilling the reaction products in a column of high efficiency. Others may have failed to isolate or identify neopentyl alcohol, owing to the difficulty of isolating a compound that is present in minor quantities in a small sample.

A higher yield of neopentyl alcohol (4.1 percent) was obtained from *t*-butyl alcohol in a continuous unit. Previous work had shown that *t*-butyl alcohol reacts rapidly at 150° C. to give isoamyl alcohol in good yield (151); presumably the alcohol is dehydrated (21, 163) to isobutylene, which then undergoes hydroformylation.

*t*-Butyl alcohol was treated in a small continuous unit under conditions as follows: Pressure, 267 atm.;

volume of reactor, 295 ml.; volume of catalyst, 106 ml.; free space, 189 ml.; temperature, 200° C., feed rate of 1H<sub>2</sub>: 1CO, 102 l. 1 hr.; liquid feed rate, 200 ml. 1 hr.; and residence time, 1.1 hour. The reaction vessel was partly filled with a cobalt-thoria-magnesia-kieselguhr catalyst. Twenty grams per liter of dicobalt octacarbonyl was added with the liquid feed, which consisted of equal volumes of *t*-butyl alcohol (1 liter., 789 g., 10.7 moles) and solvent (2-ethylhexanol), corresponding to a mole ratio of alcohol to solvent of 1.66. Tail gas samples were taken periodically. Water was separated mechanically from the product.

The product was hydrogenated in a batch autoclave at 160° to 180° C. over Raney nickel at 200 atm. of hydrogen. The hydrogenated material was dried over Drierite and distilled at atmospheric pressure in a 6-foot Heli grid column at an efficiency of approximately 30 theoretical plates. A product boiling at 113° C. was identified as neopentyl alcohol (52 to 53° C., melting point) by its infrared and mass spectra; enough of this alcohol was obtained (7 g., 4.1 percent) to plug the takeoff condenser. Essentially all of the solvent was recovered unchanged. Only 1.19 moles (11.2 percent) of the 10.6 moles of *t*-butyl alcohol charged was recovered unchanged.

The distributions of products formed from isobutylene and *t*-butyl alcohol with synthesis gas are compared in table 24.

TABLE 24.—Distribution of hydrogenated products from the cobalt-carbonyl-catalyzed reaction of isobutylene and *t*-butyl alcohol with synthesis gas

Product	Yield, percent	
	From isobutylene <sup>1</sup>	From <i>t</i> -butyl alcohol <sup>2</sup>
Isobutylene.....		3.0
Isobutane.....		3.2
Neopentyl alcohol.....	1.2	4.1
Isoamyl alcohol.....	46.8	60.0
Higher boiling material calculated as isovaleraldehyde polymer.....	29.7	26.3
Total.....	77.7	96.6

<sup>1</sup> Based on starting isobutylene. Some isobutylene was lost on flushing the autoclave.

<sup>2</sup> Based on converted *t*-butyl alcohol. Reaction run in a flow system.

## OTHER REACTIONS OCCURRING UNDER OXO CONDITIONS

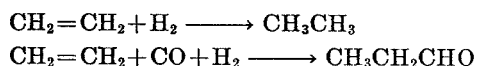
As might be expected from a reaction in which aldehydes are produced, extensive side reactions may occur, thus adversely affecting the yield of desired product. From a process standpoint, the most extensively studied oxo reaction is the two-stage conversion of mixed C<sub>7</sub> olefins to iso-octyl alcohol. In this process a small amount of low-boiling material is obtained, but the bottoms (material remaining after the alcohols are distilled) constitute 20 to 30 percent of the product. Among the products, other than al-

cohols, can be (114):  $C_7$ , olefins and paraffins;  $C_8$ , olefins;  $C_8$ , paraffins;  $C_8$ , aldehydes;  $C_{24}$ , acetals;  $C_{15}$ , ketones;  $C_{16}$ ; hemiacetals; acids; esters; aldols; and ketols.

Some of these side reactions are discussed in the following paragraphs.

### Hydrogenation of Olefins

The hydrogenation of an olefin is thermodynamically favored over its hydroformylation. For example, the standard state free energy changes at 25° C. for the two reactions with ethylene



are -22,608 cal./mole for the hydrogenation and -14,460 cal./mole for the hydroformylation (91). Nevertheless, simple olefins yield virtually no saturated hydrocarbons, especially when reacted at low temperatures (110° to 140° C.).

Saturated hydrocarbons, however, have been produced occasionally in oxo reactions. Thus, for example, a  $C_7$  feed, reacted above 125° C. with 0.5 $\text{H}_2$ :1CO to 2 $\text{H}_2$ :1CO at 200 at., yielded some  $C_7$  saturated hydrocarbons (114).  $C_8$  and higher olefins, treated in acetic acid solution at 250° to 270° C. at 700 atm. of 1 $\text{H}_2$ :1CO, yielded as much as 30 percent as hydrocarbon (119).

This discussion has been confined to simple olefins. When the double bond is conjugated with another unsaturated center (double bond, carbonyl group, phenyl group, and so forth), hydrogenation of the double bond not only becomes of importance, but in certain instances, it becomes the chief reaction. Such examples will be discussed under the section dealing with modifications of the principal reaction.

### Polymerization of Olefins

Although the presence of the strongly acidic cobalt hydrocarbonyl  $\text{HCo}(\text{CO})_4$  has been frequently postulated, no good evidence is published for the polymerization of olefins during the oxo reaction. An olefin such as isobutylene, prone to polymerize in the presence of strong acids, might yield some  $C_9$  aldehyde owing to dimerization followed by hydroformylation.

### Hydrogenation of Aldehydes

Hydrogenation occurs under oxo conditions, especially during relatively long contact times and at temperatures near the upper end of the oxo range (170° to 200° C.). Thus, for example, butyraldehyde has been hydrogenated

in good yield to butanol (152) at 180° C. and 200 atm. of 2 $\text{H}_2$ :1CO. When the oxo reaction is operated to secure alcohols as a final product, the partial hydrogenation of the aldehyde to alcohol during hydroformylation is of little consequence. However, when the process is operated to secure aldehydes as principal products, temperatures should be as low as compatible with efficient reaction rates and contact times.

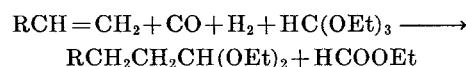
Although aldehydes can be converted to alcohols under somewhat more drastic oxo reaction conditions, this procedure is usually not preferred, since higher temperatures, longer contact times, and the acidic catalyst cause a loss of aldehydes through side reactions.

### Acetal Formation

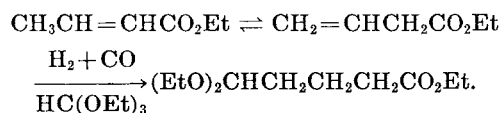
Because aldehydes and alcohols coexist in the oxo reaction, acetal formation occurs:



Acetals can be isolated after the hydrogenation stage of the two-step oxo process. The bottoms from alcohol distillation may contain up to 50 percent of acetals that can be hydrolyzed with steam or with 5 percent sulfuric acid to increase the yield of the desired alcohol (128). In fact, acetal formation has been recommended for minimizing side reactions of aldehydes. Thus, for example, when olefins were hydroformylated in the presence of ethyl orthoformate, excellent yields of the ethyl acetals of the aldehydes were secured (109).



This reaction has also been performed with  $\alpha,\beta$ -unsaturated esters, and ester acetals have been secured in high yield. Originally ethyl crotonate was thought to form only a  $\beta$ -formyl ester acetal, but subsequent work showed that this assignment of structure was incorrect and that the  $\gamma$ -formyl acetal ester, ethyl 5,5-diethoxyvalerate, was formed, presumably by prior isomerization (56, 112).



### Aldol Formation

One of the most important yield-reducing reactions in the hydroformylation synthesis is aldolization of the aldehydes; under certain conditions an appreciable portion of the product can be accounted for by aldolization of the aldehydes initially produced. Thus, treatment of





However, several workers (50, 82, 95) later demonstrated that the rate of hydroformylation increases with increasing hydrogen pressure (at constant carbon monoxide pressure) and decreasing carbon monoxide pressure (at constant hydrogen pressure). The previous observation of the independence of rate and pressure for equimolar mixtures of carbon monoxide and hydrogen was due to the approximately equal, but opposite, effects of increasing the partial pressures of the two gases.

Martin (82) measured the initial rate of hydroformylation of diisobutylene at 150° C. over a range of ratios of partial pressures of hydrogen to carbon monoxide from 1 to 3 (50 atm. of hydrogen and 150 atm. of carbon monoxide) to 11 to 1 (275 atm. of hydrogen and 25 atm. of carbon monoxide) and at several concentrations of cobalt (added as naphthenate) for each combination of gas pressures. The initial rate of reaction was always proportional to the quantity of cobalt and to the olefin concentration in a series of olefin-paraffin mixtures. The results are summarized in table 25.

TABLE 25.—Variation in rate of hydroformylation of diisobutylene with composition of synthesis gas

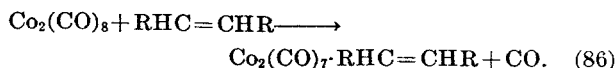
Initial pressure, atm.		Initial rate calculated from pressure drop, atm./hr.	Initial rate observed from pressure drop, atm./hr.	Rate calculated—rate observed (atm./hr. percent)
H <sub>2</sub>	CO			
50	50	225.4	204	+9.5
50	150	85.4	94	-10.0
150	150	225.4	248	-10.0
100	200	123.9	138	-11.4
150	100	310.2	323	-4.1
150	50	497.0	499	-0.4
150	25	711.2	759	-6.7
250	50	654.8	668	-2.0
275	25	884.5	812	+8.2

The initial rates of hydroformylation in the fourth column could be represented quite as well by the equation:

$$\text{Initial rate} = \frac{275 p_{H_2}}{0.220 p_{H_2} + p_{CO}} \quad (85)$$

However, the initial rate also appears to increase with the total pressure (for a given ratio of partial pressures); this phenomenon is not represented by the equation.

The fact that the rate varies inversely with the partial pressure of carbon monoxide led Natta, Ercoli, Castellano, and Barbieri (95); Greenfield, Metlin, and Wender (50); and Martin (82) to postulate that the first step is the reaction of the olefin with dicobalt octacarbonyl to form an olefin-carbonyl complex and carbon monoxide:



The rate of formation and the nature of this complex will be discussed under Mechanism of Hydroformylation, but this concept will prove useful in the interpretation of the results of other kinetic investigations.

### Effect of Temperature

The reaction rate doubles for a temperature rise of 7° to 8° C. According to the temperature region considered, the apparent energy of activation with cyclohexene appears to lie between 34 kcal. (100° to 110° C.) and 29 kcal. (110° to 120° C.) (93).

### Effect of Solvent

The effect of solvents on the rate of hydroformylation of cyclohexene at 110° C. and 233 atm. of 1H<sub>2</sub>+1CO (153) follows:

Solvent	Specific reaction rate constant, $k \cdot 10^{-3} \text{ minute}^{-1}$
Methylcyclohexane.....	5.8
Heptane.....	5.9
Methyl ethyl ketone.....	5.7
n-Butyl ether.....	5.9
Acetone.....	6.1
2-Ethyl-1-hexanol.....	6.5
Chlorobenzene.....	6.5
Benzene.....	6.7
Anisole.....	7.5
1-Methylnaphthalene.....	7.9
Ethyl alcohol.....	8.7
Methyl alcohol.....	8.9

The solvent effect, though not large, appears significant; the rate is about 1½ times as great when methyl or ethyl alcohol is substituted for a saturated hydrocarbon. The rate in aromatic solvents is greater than in aliphatic solvents; this effect may be due to the greater polarizability of the aromatic molecule or to the greater basicity of the aromatic hydrocarbons. The variations in specific reaction rates with solvent probably do not reflect any difference in solubilities of hydrogen and carbon monoxide in the reaction media; hydrogen, for instance, is more soluble in paraffins than in aromatics of similar molecular weight (35). Whatever the cause, highly polar intermediates are probably not involved in the hydroformylation reaction.

### Effect of Bases

Basic solvents retard reactions occurring under hydroformylation conditions (159). Thus, benzhydrol is not reduced to diphenylmethane when pyridine is the solvent, and hydroformylation of a mixture of 2,3-dimethylbutenes at 135° C. and 233 atm. of synthesis

gas can be completely inhibited by triethylamine. To obtain a more quantitative picture of the effect of bases, workers at the Bureau of Mines (50) studied the hydroformylation of cyclohexene in the presence of varying amounts of amines. Their results are summarized in table 26.

TABLE 26.—Effect of bases on the rate of hydroformylation of cyclohexene<sup>1</sup>

Base	Volume of base, ml.	Base: Co <sub>2</sub> (CO) <sub>8</sub> , mole ratio	Specific reaction rate constant, <i>k</i> 10 <sup>-3</sup> min <sup>-1</sup>
Pyridine	0	—	25.8
	.1	.15	6.6
	.3	.45	6.3
	.8	1.2	6.3
	2	3.1	5.3
	5	7.6	1.6
	11	17	(3)
Triethylamine	0	—	25.8
	.05	.044	6.2
	.1	.087	5.8
	.5	.44	4.8
	1	.87	3.1
	2	1.7	2.1
Piperidine	3	2.6	(4)
	1	1.2	2.6
	2	2.5	(4)

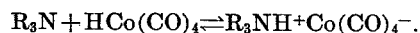
<sup>1</sup> Conditions: 0.50 mole cyclohexene, 2.8 g. (8.2×10<sup>-3</sup> mole) dicobalt octacarbonyl, initial pressure 233 atm. 1H<sub>2</sub>+1CO, 110° C., sufficient methylcyclohexane to make 65 ml. of solution, including the added base.

<sup>2</sup> Rate in the absence of added base.

<sup>3</sup> Very slow.

<sup>4</sup> No reaction.

The reaction rate was increased by the addition of very small amounts of organic bases and was decreased by larger amounts. The amount of base needed to accelerate and to completely inhibit the reaction evidently depends on the strength of the added base. Piperidine and triethylamine are strong bases, but triethylamine is a base with high steric requirements (20); one may surmise that the mechanism of inhibition does not involve interaction of the base with an intermediate with exceedingly high steric requirements. It is likely that the reaction is inhibited because cobalt is tied up as the amine salt of cobalt hydrocarbonyl:



When dicobalt octacarbonyl is synthesized in the presence of hydrogen and excess pyridine, the amine salt of the hydrocarbonyl is the only product (157).

### Kinetics at Low Pressures (Under 100 Atm.)

Natta, Ercoli, and Castellano (94) have extended their studies of the kinetics of the hydroformylation reaction to pressures below 100 atm. Under these conditions the pressure drop is difficult to follow. These workers therefore made discontinuous isochronic (equal reaction

period) measurements at various partial pressures of carbon monoxide and hydrogen under otherwise equal conditions. In each run the partial pressures of carbon monoxide and hydrogen were kept constant; at the end of each run the amounts of unreacted olefin and aldehyde formed were determined. The conversion values

$$R = \frac{\text{moles of aldehyde recovered}}{\text{moles of olefin introduced}}$$

were linear functions of time, showing that the reaction was first order with respect to olefin even at low pressures.

The hydroformylation of cyclohexene was independent of the total pressure of 1H<sub>2</sub>+1CO pressures of 63 to 68 atm., but with at least 15 atm. of carbon monoxide, the rate again was increased by an increase in hydrogen pressure and by a decrease in carbon monoxide pressure.

Three series of runs were made at constant hydrogen pressures but different carbon monoxide pressures at 110° C. with 100 g. of a 33 to 34 percent solution of cyclohexene in toluene and 1.4 g. of dicobalt octacarbonyl. The conversion values for these runs were plotted as a function of the partial pressure of carbon monoxide (fig. 13). A similar family of curves was obtained at 120° C. These curves have a maximum for carbon monoxide partial pressures of about 8 to 9 atm. at 110° to 120° C. Thus, increased partial pressures of carbon monoxide beyond the optimum greatly decrease the reaction rate. For equal carbon monoxide pressures, the increase in rate is approximately

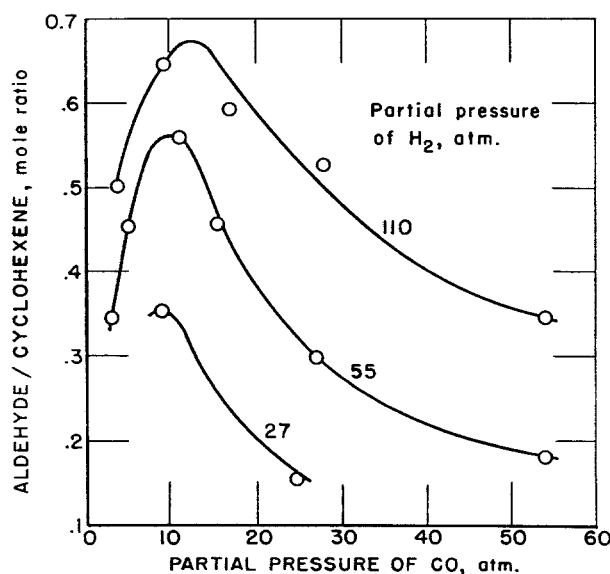


FIGURE 13.—Rates of Hydroformylation of Cyclohexene as a Function of CO and H<sub>2</sub> Pressures. Isochronic experiments at constant pressure, 110° C. (94).