TABLE 1. - <u>Experiments showing migration of double bond with higher olefins</u>

(Table shown on page 05647, T.O.M. Reel 14)

Autoclave charged with-

Dode-cene-1 cc.	Catalyst vol. or wt.	Reaction Temp., °C.	Gas used	Press., atmos.	Position of = in chains from end carbon					
					1	2	3	4	5	6
395	Fischer Kt. 100 cc.	200	N_2	200	100					
395	Fischer Kt. 100 cc.	300	N_2	200	7	45.5	30.1	8.3	5.8	3.0
265	Fischer Kt. 200 cc.	250	CO	100	3	15.0	20.0	22.0	21.0	18.5
265	20 gm. cobalt metal	150	CO	100	3	24.0	25.0	18.0	16.0	13.5
265	Fischer Kt. 200 cc.	150	CO	100	8.1	27.2	23.0	18.1	13.3	10.3
265	65 gm. iron pentacarbonyl	150	CO	100	58.2	17.8	8.9	5.7	3.1	4.2
265	20 gm. nickel metal	150	CO	75	100					

Preheating time in all experiments, 1 hour.
Time at reaction temperature in all experiments, 1 hour.

4. Even when the starting material is a pure olefin, mixtures of isomeric aldehydes, alcohols, and corresponding acids are obtained. If a terminal olefin is used, about 60 percent of the branched compound is obtained in the oxo process. Not only are α-methyl compounds formed from a terminal olefin; but, in general, double-bond isomerization causes production of α-alkyl branched products. The amount of isomeric α-alkyl branched alcohols decreases with increasing size of the alkyl radical.

5. It has been stated that the oxo reaction and the isomerization proceed simultaneously, the former with the greater velocity. For this reason, when terminal olefins are used, the formation of branched products in the reaction is not as great as would be predicted from laboratory experiments on the isomerization of olefins in the presence of CO but in the absence of H_2.

MECHANISM OF OXO REACTION

Cyclopropanone Ring Intermediate

The chemistry of the oxo reaction can be perceived more clearly after consideration of other reactions involving carbon monoxide. Dr. Reppe and his coworkers have developed new reactions and processes that involve novel reactions of the acetylenes, olefins, and metallic carbonyls and hydrocarbonyls. Reppe has also made important contributions to the chemistry of carbon monoxide. For many years, carbon monoxide has been a substance of

extraordinary interest to the chemical industry. Some examples of the large-scale utilization of carbon monoxide are the synthesis of CH_3OH from CO and H_2, of formic acid, of acetic acid from CH_3OH and CO, and the Fischer-Tropsch synthesis.

The great reactivity of carbon monoxide can be attributed to its free electron pair, and it was considered that CO should be capable of participating in many more reactions than had been reported. It was discovered that acetylene and all acetylenic compounds reacted with CO in the presence of a compound containing an active hydrogen atom.

These reactions could be carried out at atmospheric pressure, using $Ni(CO)_4$ in stoichiometric quantities, or catalytically at elevated pressures using CO and metals capable of forming carbonyls. Under the same conditions, however, Reppe was unable to add hydrogen itself to acetylene.
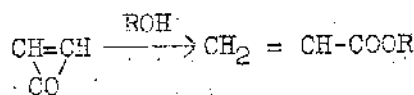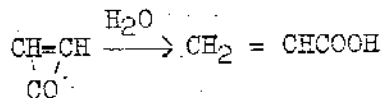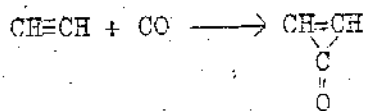
Using metal carbonyls at atmospheric pressure, the so-called stoichiometric method, it was necessary to use an acid to remove the metal. The equation for the reaction is as follows:

$$4H_2O + 4C_2H_2 + Ni(CO)_4 + 2HCl(aq.) \longrightarrow 4CH_2=CH-COOH + NiCl_2(aq.) + H_2.$$
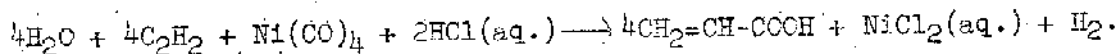
In the catalytic process, nickel halides were found to be the most favorable catalysts. The reaction must be carried out under pressure so that nickel carbonyl will be formed from the nickel salts. In the synthesis of ethyl acrylate, the alcohol is passed over the catalyst at 120°-180° C. in a pressure tower with a countercurrent stream of acetylene and carbon monoxide. The crude liquor containing a high percentage of ethyl acrylate is continuously removed from the foot of the tower. The formation of ethyl acrylate from acetylene, carbon monoxide, and alcohol is an exothermic reaction, and the general reaction may be formulated in this way:

$$C_2H_2 + CO + ROH \longrightarrow CH_2=CHCOOR + 50.7 \text{ kcal./mol.} \quad (R=CH_3)$$
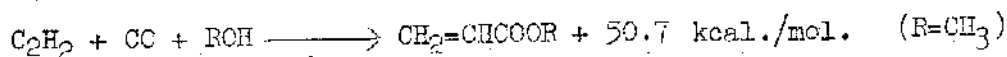
It was postulated that the intermediate product in this type of reaction is cyclopropenone and that acrylic acid derivatives are formed by fission of this hypothetical unstable ring system, as follows:

$$CH\equiv CH + CO \longrightarrow \begin{array}{c} CH=CH \\ \diagdown \diagup \\ C \\ \parallel \\ O \end{array}$$

$$\begin{array}{c} CH=CH \\ \diagdown \diagup \\ CO \end{array} \xrightarrow{H_2O} CH_2 = CHCOOH$$

$$\begin{array}{c} CH=CH \\ \diagdown \diagup \\ CO \end{array} \xrightarrow{ROH} CH_2 = CH-COOR$$

In the same manner, esters, thioesters, amides, and other compounds could be produced.

Similarly, using phenyl acetylene, phenylcyclopropenone was postulated, and this might be expected to open in two ways.

$$C_6H_5C \equiv CH + CO \longrightarrow C_6H_5C = CH$$
$$\underset{CO}{\diagdown\diagup}$$

I $\quad C_6H_5C=CH \xrightarrow{H_2O} C_6H_5C=CH_2 \quad \alpha\text{- phenylacrylic acid}$
$\qquad \underset{CO}{\diagdown\diagup} \qquad\qquad \underset{COOH}{|}$

II $\quad C_6H_5C=CH \xrightarrow{H_2O} C_6H_5C = CH-COOH \quad \text{cinnamic acid}$
$\qquad \underset{CO}{\diagdown\diagup} \qquad\qquad \underset{H}{|}$
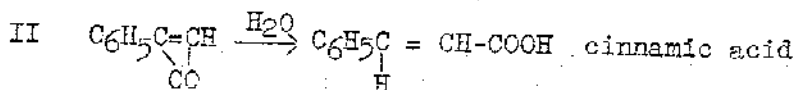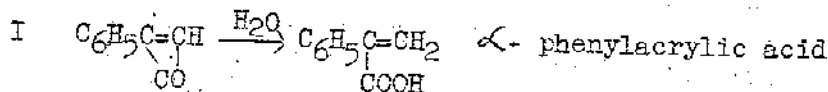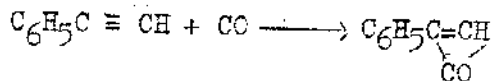
For some reason, only α-phenylacrylic acid was formed. With phenylmethyl-acetylene, however, fission of the hypothetical phenylmethylcyclopropenone occurred in both direction, and both α-phenylcrotonic acid and α-methyl cinnamic acid were obtained.

If the process using acetylene could be applied to olefins, it was thought that the cyclopropanone ring would be formed as an intermediate product. This should, in a similar manner, undergo hydrolytic fission with compounds containing active hydrogen atoms, thus:

$$RCH=CH_2 \xrightarrow{CO} R-CH-CH_2$$
$$\underset{O}{\overset{\diagdown C \diagup}{|}}$$

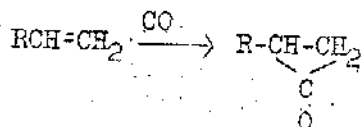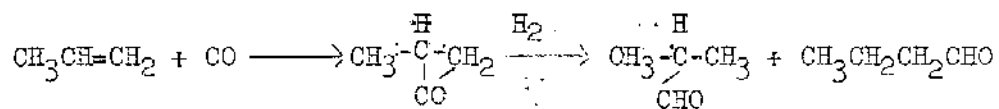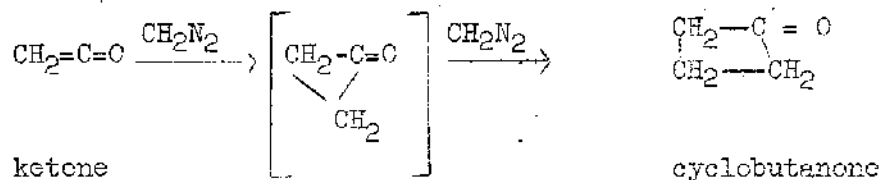$$R-CH-CH_2 + H \longrightarrow \underset{COOH}{\overset{RCHCH_3}{|}} \quad \text{or} \quad RCH_2CH_2COOH$$
$$\underset{O}{\overset{\diagdown C \diagup}{}} \quad \underset{OH}{\overset{|}{}}$$

It was found, in fact, that, by interaction of olefins, $CO + H_2O$ at 200°-300° C., and 150-300 atmospheres, both straight-chain and α-methylated carboxylic acids were formed. During the early part of this work, information on the oxo process as carried out by Ruhrchemie became generally available in Germany. This firm discovered the oxo process in following up observations made on the Fischer-Tropsch process. It is quite interesting to note that the manufacture of aldehydes and alcohols by the interaction of an olefin with water gas over a catalyst containing cobalt was reported by Smith, Hawk, and Golden of the Federal Bureau of Mines in 1930 (Jour. Am. Chem. Soc., vol. 52, 1930, p. 3221). These workers passed CO and ethylene over a cobalt-copper-manganese oxide catalyst at 204° C. but recovered the ethylene unchanged. No reaction occurred when ethylene and H_2 were passed over the same catalyst; but when C_2H_4, CO, and H_2 were passed over the catalyst at 204° C., up to 35 percent of water-soluble compounds containing oxygen were formed, and the presence of both aldehydes and alcohols was established. It remained for Roelen, in a country hard-pressed for chemicals, fats, and detergents, to develop the oxo process.

Carbonylation is the name given to reactions wherein CO is added to another compound, for example, to C_2H_2, olefins, cyclic oxides, etc., along with such an H-containing compound as H_2, H_2O, ROH, NH_3, RSH, etc. Reppe includes the oxo reaction in the above as a special case. Using propylene, the proposed reaction mechanism for the oxo reaction includes formation of the cyclopropanone ring.

$$CH_3CH=CH_2 + CO \longrightarrow CH_3-\overset{H}{\underset{CO}{\overset{|}{C}}}-CH_2 \xrightarrow{H_2} CH_3-\overset{H}{\underset{CHO}{C}}-CH_3 + CH_3CH_2CH_2CHO$$

Although postulation of a 3-membered ring intermediate in the addition of CO to acetylenes and olefins in the above synthesis is convenient, existence of the intermediate cyclopropenone and cyclopropanone rings is open to question. The idea of 3-membered ring compounds as intermediates has generally lost favor in the last few years. Experiments performed to test the postulate, especially for molecular rearrangements, have consistently shown that the ring intermediate did not exist. Cyclopropanone itself has not been prepared.

A cyclic ketone, when treated with diazomethane, yields the next higher cycloalkanone. An attempt to make cyclopropanone by treating ketene with CH_2N_2 yielded cyclobutanone as the chief product. Although cyclopropanone was a presumed intermediate, none was isolated:

$$CH_2=C=O \xrightarrow{CH_2N_2} \left[\overset{CH_2-C=O}{\underset{CH_2}{\diagdown\diagup}} \right] \xrightarrow{CH_2N_2} \overset{CH_2-C=O}{\underset{CH_2-CH_2}{|\qquad|}}$$

ketene   cyclobutanone

It would be interesting to note if a derivative of cyclobutanone could be isolated from an oxo reaction run in the presence of diazomethane.

Although cyclopropanone has not as yet been isolated, the possibility that it may be stable at room temperature is not denied, but the compound must be highly reactive at room temperature. At the temperature of the oxo reaction (150°C.), the compound should be more reactive and this may be construed as a point in favor of the ring intermediate.

Carbonium-Ion Mechanism

During recent years, it has been quite definitely established that many reactions proceed by a carbonium-ion mechanism. The carbonium ion is generally formed in the presence of a strong acid or electrophillic reagent. The latest development in carbonylation chemistry is the use of metallic hydrocarbonyls, which are acids and react differently from simple carbonyls. Nickel carbonyl, $Ni(CO)_4$, is not an acid and does not catalyze the oxo reaction. It boils at 43° C., melts at -25° C., and has a density of 1.32 at 17° C. It is extremely poisonous and must always be kept under water. There are 28 extra-nuclear electrons in the nickel atom; if 2 electrons are contributed by each

of 4 CO groups, the carbonyl has an inert gas structure (krypton). In a sense, the nickel exhibits zero valence. It has been shown that the chief contributing structure for $Ni(CO)_4$ is

$$\overset{\displaystyle ..}{\underset{\displaystyle ..}{O:}}\;\;\; :\!O::C::Ni::C::O: \;\;\;$$
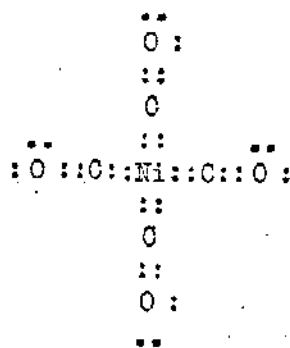
with the CO bond having partly triple-bond character.

Cobalt has 27 extranuclear electrons; and, if 2 electrons are contributed by each of 4 CO groups, 35 electrons surround the cobalt nucleus. Cobalt carbonyl $\left[Co(CO)_4\right]_2$ melts at 51° C. and decomposes at 52° C. If 1 electron is contributed by a hydrogen atom, giving the cobalt hydrocarbonyl $H^+\left[Co(CO)_4\right]^-$, a shell of 36 electrons exists about the cobalt nucleus, and the inert gas form has been attained. The structure for this acid is probably:

$$\left[\; :O::C::Co::C::O: \; \right]^{-} \quad H^{(+)}$$
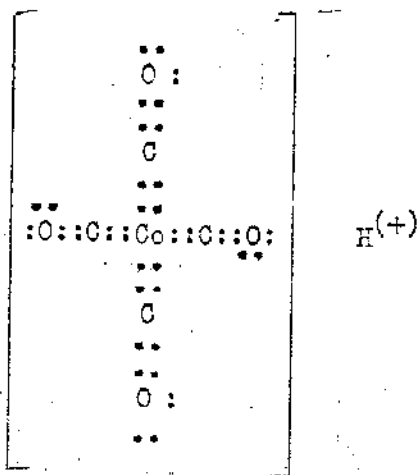
This acid decomposes at high temperatures, in accordance with the following equation:

$$2H\,Co(CO)_4 \rightleftharpoons H_2 + \left[Co(CO)_4\right]_2$$
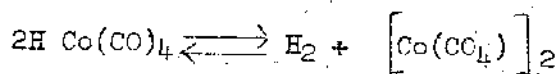
It is possible that high-pressure hydrogen is essential in the oxo reaction to suppress this decomposition.

Reppe has developed new methods of preparing the compounds $H\,Co(CO)_4$ and $H_2\,Fe(CC)_4$ in large quantities and has studied their physical constants and

chemical behavior. Cobalt hydrocarbonyl is a stable compound, which, according to Hecht, melts at about $-33°$ C. and boils with decomposition at about $+10°$ C. Its alkaline solution can be heated to $200°$ C. for long periods without decomposition. On the other hand, iron hydrocarbonyl can be obtained pure only with difficulty and is decomposed rapidly by alkali at $100°$ C. Cobalt hydrocarbonyl is a strong acid (about like HCl) and $H_2Fe(CO)_4$ behaves like an average monobasic acid. It can be titrated with caustic soda, using methyl orange, and the end point can be approached from either the acid or alkaline side. Cobalt hydrocarbonyl can be formed from a solution of ammoniacal cobalt chloride by treatment with H_3PO_4 in the presence of CO. The reaction stops with formation of $H Co(CO)_4$, which, in contrast to the iron compound, is stable to carbon monoxide. The reaction can be represented as follows:
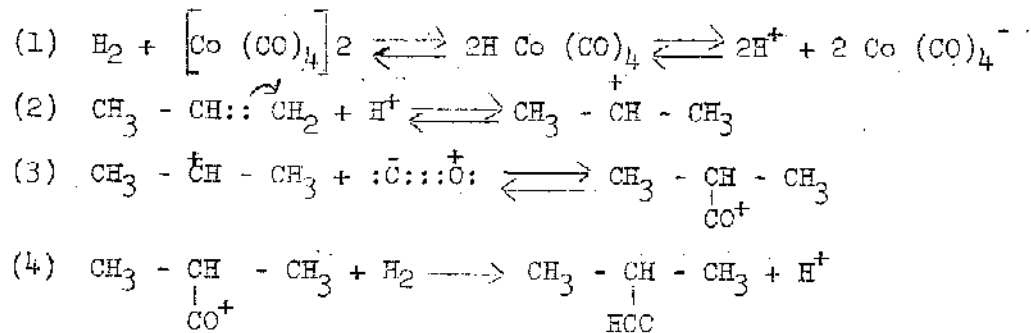
$$2CoCl_2 + 4NH_3 + 3H_2O + 11CO \longrightarrow 2H Co(CO)_4 + 4NH_4Cl + 3CO_2,$$

or, including excess ammonia to interact with the CO_2, the following reaction may be written:

$$2\left[Co(NH_3)_6\right]Cl_2 + 11CO + 6H_2O \longrightarrow 2H Co(CO)_4 + 4NH_4Cl + 3 (NH_4)_2CO_3 + 2NH_3.$$
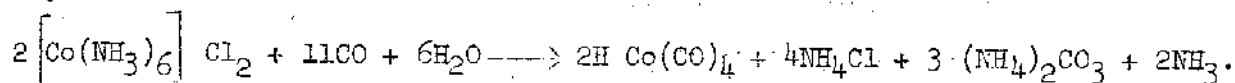
It may be noted, at this point, that the metallic hydrocarbonyls are not new chemical compounds. They have been studied by W. Hieber and his colleagues (Ztschr. anorg. allgem. Chemie, vol. 204, 1932, p. 145). Methods of preparation and properties of the metal carbonyls and hydrocarbonyls have been reviewed by Arthur A. Blanchard (Chem. Reviews, vol. 21, 1937, p. 3) and by W. Conard Fernelius (Inorganic Syntheses, vol. II, p. 229).

Carbon monoxide is a colorless, odorless gas with well-known poisonous properties. It may be condensed to a colorless liquid at $-190°$ C., and solidifies $9°$ C. lower. For many years, there have been discussions as to which of the structures, :C::O: and :C:::O:, is the better one. Pauling showed that three resonating structures contribute to the molecule: (a) :C:O: (b) :C::O: and (c) :C:::O:. Evidence from the parachor, heat of formation, dipole moment, the force constant, and the interatomic distance indicates that all three forms are probable, with :C:::O: perhaps making the chief contribution. The resonance energy of carbon monoxide is 58 k.-cal./mole (that for benzene is only 39 k.-cal./mole) and it is this very large resonance energy which stabilizes CO despite its lack of saturation of the carbon valences.

Using propylene as an example, the following mechanism is proposed:

(1) $H_2 + \left[Co (CO)_4\right]2 \rightleftarrows 2H Co (CO)_4 \rightleftarrows 2H^+ + 2 Co (CO)_4^-$

(2) $CH_3 - CH::CH_2 + H^+ \rightleftarrows CH_3 - CH^+ - CH_3$

(3) $CH_3 - CH^+ - CH_3 + :C:::O: \rightleftarrows CH_3 - CH - CH_3$ with CO^+ below

(4) $CH_3 - CH - CH_3 + H_2 \longrightarrow CH_3 - CH - CH_3 + H^+$ with CO^+ below the first, HCO below the product
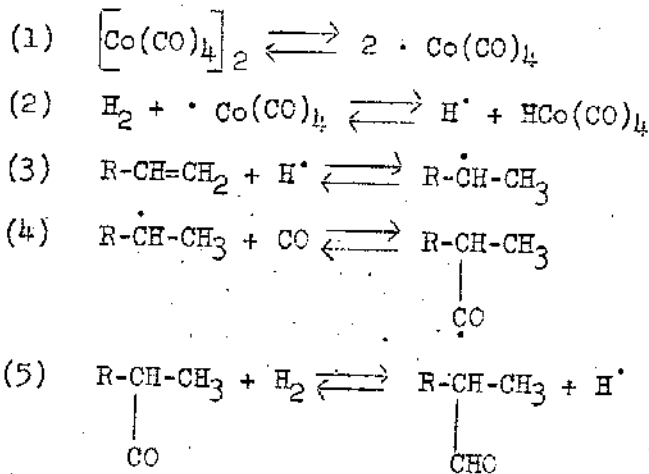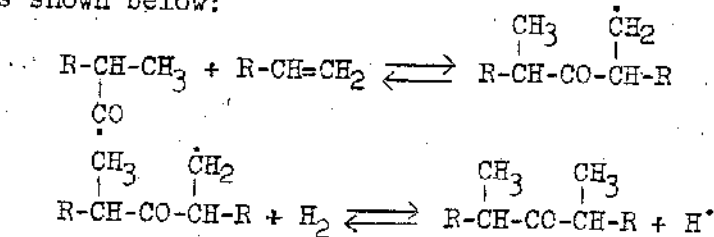
The possibility for an electron shift in the opposite direction also exists; that is: $CH_3 - \overset{H}{\underset{C}{\cdot}} \overset{H}{\underset{}{\cdot} CH} \xleftrightarrow{} CH_3 - \overset{H}{\underset{C}{\underset{..}{\cdot}}} : CH_2 \underset{+}{}$. The direction and extent of this shift will depend on the substituent on either carbon.
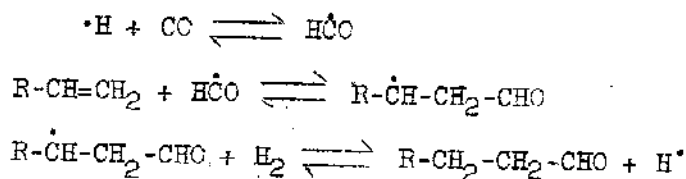
Free-Radical Mechanism

Professor M. S. Newman, in a discussion of the mechanism of the oxo reaction with the authors, suggested the possibility of a free-radical type of mechanism. In such a mechanism, the cobalt carbonyl may function as the chain initiator and the hydrogen atom as the chain carrier. One way in which such a free-radical mechanism can be formulated is as follows:

(1) $\left[Co(CO)_4 \right]_2 \rightleftharpoons 2 \cdot Co(CO)_4$

(2) $H_2 + \cdot Co(CO)_4 \rightleftharpoons H^\cdot + HCo(CO)_4$

(3) $R\text{-}CH{=}CH_2 + H^\cdot \rightleftharpoons R\text{-}\overset{\cdot}{C}H\text{-}CH_3$

(4) $R\text{-}\overset{\cdot}{C}H\text{-}CH_3 + CO \rightleftharpoons R\text{-}\underset{\underset{\overset{|}{\overset{\cdot}{C}O}}{|}}{C}H\text{-}CH_3$

(5) $R\text{-}\underset{\underset{\overset{|}{CO}}{|}}{C}H\text{-}CH_3 + H_2 \rightleftharpoons R\text{-}\underset{\underset{\overset{|}{CHO}}{|}}{C}H\text{-}CH_3 + H^\cdot$

The variety of reaction products obtained during the oxo reaction can be satisfactorily accounted for by suitable combinations of free radicals. Thus, the ketones obtained may be explained by the combination of a keto radical produced in the fourth step with a molecule of olefin to give a new free radical, which could then react with hydrogen to give a ketone plus a hydrogen atom, as shown below:

$$R\text{-}\underset{\underset{\overset{|}{CO}}{|}}{C}H\text{-}CH_3 + R\text{-}CH{=}CH_2 \rightleftharpoons R\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}CO\text{-}\overset{\overset{\overset{\cdot}{C}H_2}{|}}{C}H\text{-}R$$

$$R\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}CO\text{-}\overset{\overset{\overset{\cdot}{C}H_2}{|}}{C}H\text{-}R + H_2 \rightleftharpoons R\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}CO\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}R + H^\cdot$$

Another suggested scheme for writing a free-radical mechanism is one in which the carbon monoxide reacts with a hydrogen atom:

$$\cdot H + CO \rightleftharpoons H\overset{\cdot}{C}O$$

$$R\text{-}CH{=}CH_2 + H\overset{\cdot}{C}O \rightleftharpoons R\text{-}\overset{\cdot}{C}H\text{-}CH_2\text{-}CHO$$

$$R\text{-}\overset{\cdot}{C}H\text{-}CH_2\text{-}CHO + H_2 \rightleftharpoons R\text{-}CH_2\text{-}CH_2\text{-}CHO + H^\cdot$$

It must be emphasized that all the mechanisms suggested are purely speculative, for a systematic investigation of the oxo reaction, with carefully controlled experimental conditions, is yet to be published. The suggested mechanisms can, however, provide the bases for such investigations, some of which are now under study at the Bureau of Mines.

OXO REACTIONS WITH PURE COMPOUNDS

Gaseous Olefins

The chemistry of the oxo reaction can be elucidated further by a study of the behavior of pure compounds. Ethylene has been used extensively.

Roelen stated that the oxo reaction had to be done in the liquid phase. With ethylene, a liquid medium must be used - for instance, water or toluene - as otherwise, the concentrated aldehydic product tends to polymerize and the polymers act as an effective solvent for the cobalt catalyst. The optimum temperature of the reaction for ethylene is quite low (115° C.). A reaction temperature lower than the optimum favors production of byproducts.

With ethylene, of course, only one aldehyde can be formed. It is interesting to note that the chief product in this case (propionaldehyde) can be isolated. One experiment with ethylene gave the following products:

	Percent
Propionaldehyde	59
Propyl alcohol and diethyl ketone	18
Methyl ethyl acrolein	8
Higher-molecular weight products	10
Unidentified	5
	100

The opinion is expressed that the higher-molecular-weight products probably are produced by condensation of methyl ethyl acrolein during distillation and probably are recoverable as the monomer by careful vacuum distillation.

I. B. Farben. carried out the synthesis of propionaldehyde with a fixed-bed catalyst in an aqueous system. The gas used contained equal volumes of C_2H_4, CO and H_2. The rate of water circulation was adjusted so that the issuing solution contained 2-3 percent of propyl aldehyde, which was removed by distillation and the water recirculated. Roelen has stated that 20 - 25 percent ethane was found in this reaction; this large amount of saturated hydrocarbon is unusual. In the usual oxo reaction, very little, if any, products of straight hydrogenation of the olefins occur. The presence of CO hinders this hydrogenation. The cobalt concentration of the catalyst was maintained in this process by adding cobalt salts of fatty acids to the ingoing water. The yield of propionaldehyde derived from the reaction with ethylene in the presence of H_2O was later raised to over 90 percent.

Ruhrchemie prepared propionaldehyde in the presence of toluene as solvent because toluene was easy to separate from the reaction products. Yields were good (80 percent). A much smaller amount of ethane was reported.

Diolefins - Conjugated Systems

When 2,5-dimethylhexadiene-1,5 ($CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - (CH_2)_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$) was sub-
jected to the oxo reaction in the absence of a solvent, strong resin formation
owing to polymerization of the dimethyl-hexadiene took place. If the diolefin
was dissolved in about four times its volume of solvent, (generally cyclohex-
ane), the reaction went smoothly, and the products were distillable after hy-
drogenation. After the catalyst was removed by filtration, the solvent was
evaporated and the alcohols fractionally distilled at 5 mm. Hg pressure.
Fractions at 70°-75° C. and 148°-153° C., were obtained; the higher-boiling
fraction (36 percent of the product) was a pure decane-diol, whereas the
lower-boiling fraction was a nonyl alcohol.

The oxo reaction, therefore, occurred only to a small extent at both
double bonds. The greater portion of water gas combined only with one double
bond, the other double bond being simply hydrogenated. The nonyl alcohol thus
formed was entirely saturated and had an agreeable odor similar to citronel-
lal - a substance to which it is structurally very similar. The decane-diol
was a colorless, odorless, thick liquid.

An attempt was made to repress formation of the C-9 alcohol as much as
possible and to increase the diol yield. For this purpose, the carbon monox-
ide content of the water gas was increased to repress the hydrogenation. For
the same reason, the oxo reaction was carried out at the lowest possible tem-
perature. The diol yield, however, was not increased by these measures. Car-
bon disulfide, which represses hydrogenation in the first stage, was added to
the catalyst; subsequently, the aldehyde groups formed were hydrogenated to
alcohols with a different catalyst. Even this did not increase the yield be-
yond 35 percent of the theoretical. A further attempt to prevent hydrogena-
tion by using paraformaldehyde instead of water gas failed; no reaction oc-
curred.

To stabilize the dialdehyde initially formed, an attempt was made to
prepare the acetal in situ. For this purpose, methanol was used as a solvent,
but no increase in the yield of diol was achieved. Unsuccessful experiments
also were performed with the purpose of modifying the oxo reaction by using,
instead of water gas, CO and H_2O or CO and alcohol on the diene, in the hope
of obtaining a good yield of dimethyl suberic acid or of its ester, respec-
tively. No conversion at all occurred in these attempts.

Tetramethylbutadiene (3,4-dimethylhexadiene-2,4) gives an almost quanti-
tative yield of C-9 alcohol under the usual oxo conditions; no diol at all is
formed. This was assumed to be due to the fact that the conjugated double-
bond system is hydrogenated first, even in the presence of carbon monoxide,
and the resulting mono-olefin then undergoes the usual oxo reaction. Experi-
ment verified this assumption; at 100° C. in the presence of water gas and the
usual cobalt catalyst, 1 mole of hydrogen was absorbed.

It was suspected that the reason that 2,5-dimethylhexadiene-1,5 formed
only 40 percent diol was that it was contaminated with the conjugated isomer.
Careful physical measurements, however, showed that this was not the case.

Isomerization of the isolated diolefin to the conjugated diolefin under conditions of the reaction was also investigated, but it was found that a temperature of over 200° in the presence of the catalyst was required to isomerize the compound to the conjugated isomer. It was possible that local overheating produced such high temperatures during the oxo reaction; however, dilution with solvent did not increase the diol yield. Replacement of the kieselguhr with aluminum oxide (to minimize isomerization) did not increase the diol yield.

Dimethallyl sulfide and dimethallyl ether were prepared and subjected to an oxo treatment. It was expected that a higher yield of a diol would be formed, since the sulfur atom or the oxygen atom should prevent the double-bond migration to form a conjugated system. Both substances, however, react, when dissolved in cyclohexane under the usual oxo conditions, in a yet inexplicable way. The boiling point of the reaction products increased gradually from 100° to 400°, and each fraction had only a very small hydroxyl number.

Additional work was done on the question of isomerization of diolefins under oxo-reaction conditions, but the diol yield was not improved. In this sense, results were negative, but the work with diolefins is of much interest because methods of attack upon the oxo reaction are illustrated.

Miscellaneous Pure Olefins

2-Methyl-Pentene-1: The following products were identified in the oxo reaction of 2-methyl-pentene-1: 3-methyl-hexaldehyde (mostly), 3-methyl-hexanol-1, 3 methyl-caproic acid, and 2,8-dimethyl-undecanone-6.

Cyclohexene: A scheme for preparing cyclohexyl ethylene to be used as the starting material in plastic manufacture was outlined as follows:

cyclohexene   75 percent   methylene-cyclohexene

β-cyclohexylethyl alcohol   cyclohexyl-ethylene
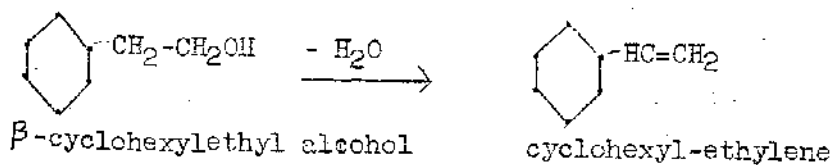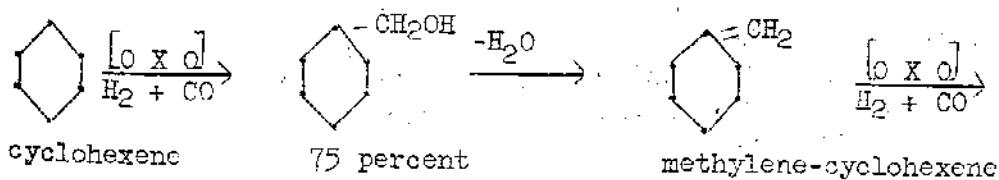
Partly reduced aromatic rings undergo the oxo reaction. However, attempts to further build up the higher alcohols in a series of oxo reactions and dehydrations were not successful probably because of extensive formation of branched chain olefins.

Dipentene: This compound absorbed only enough water gas to react with 1 double bond.

Dicyclopentadiene: The oxo reaction with this compound produced a brown-black, viscous, resinlike mass.

Ethyl Oleate: This compound gave an 87 percent yield of hydroxymethyl ethyl stearate.

Allyl Alcohol: Only 40 percent of the expected volume of water gas was absorbed with this compound. However, 100 percent conversion took place, as indicated by the complete absence of allyl alcohol in the reaction product. The expected 1,4 butane diol could not be found with certainty in the reaction products. Aldehydes, alcohols, and esters were present in the product.

Styrene: Aromatic compounds containing an olefinic link in the side chain reacted in the side chain, although difficulties sometimes were experienced due to polymerization of the olefin, for example, with styrene. The aromatic ring did not react.

Halogenated Compounds: An oxo reaction occurred with this type of compound, but the nature of the products was not clear.

ANALYSIS OF OXO PRODUCTS

An olefin in the $C_{10} - C_{20}$ range when subjected to the oxo reaction forms a primary alcohol which boils some 30° above the original olefin. If the boiling range of the oxo charge does not exceed 30° C., the alcohols may be separated from the hydrocarbons by distillation.

For raw materials of a wider boiling range, the alcohols may be separated by the boric acid ester method. The crude product is fractionated into 50°-60° boiling range cuts, and these are worked up separately. The product is esterified with a slight excess of boric acid at 95°-120° C. and atmospheric pressure. The water formed and the lower-boiling hydrocarbons are continuously removed as overhead. The reaction products are then distilled at atmospheric pressure, or under vacuum, if this is necessary to avoid decomposition of the boric acid ester. These esters are stable up to about 300° C. at atmospheric pressure. The separation of alcohols and hydrocarbons is not difficult, as the esterification increases the boiling point of the alcohol about 120° C. above the rest of the cut.

The separated esters are now mixed with recycle boric acid solution and hydrolyzed by heating to 95°-120° C. The hot mixture of alcohols and 16-17 percent H_3BO_3 solution separates into two layers, and the upper alcohol layer is washed with water and redistilled. The boric acid solution is cooled to 5° C., the boric acid crystals are filtered off for recirculation to the esterification stage, and the filtrate is recycled to the hydrolysis stage.

In a patent application by Dr. Herald and Dr. Brüde at Ludwigshafen it was claimed that the boric acid ester of all known types of alcohols could be made. This includes aliphatic, mono or polynuclear aromatic, alicyclic, and polyhydroxy compounds. The alcohol group may be in one of the nuclei or attached to a side chain.

A complete account of this method of separating oxo alcohols is given in T.O.M. Reel 134, Section II, Document 22, Frames 1047-1059.

In most of the oxo work, the products were not fully identified. This was especially true for oxo charges that were olefin mixtures. The olefin content of the charge was first determined; usually the iodine number was used. A general idea of what had transpired during the oxo reaction was then obtained by making the following determinations:

1. The OH number using acetic anhydride.

2. The CO number using $H_2NOH.HCl$ and bromophenol blue indicator.

3. A molecular weight by the conventional freezing point depression.

4. A saponification number.

5. A density determination - in the conventional manner with a pycnometer.

The degree of branching in the oxo alcohols could be determined by dehydration, ozonization, and subsequent cleavage of the olefin. Two new ideas were claimed in this determination by the Germans.

1. The end point in ozone addition could be determined by working at low temperatures. At low temperatures the excess of ozone is dissolved in the hydrocarbon, giving a blue color which thus indicates the end point of the ozone addition.

2. Silver oxide is used for the oxidative cleavage of the olefins. Only acids are thus formed as final products, and good yields are obtained.

OPERATING CONDITIONS

Effect of Temperature

The temperature employed in the oxo reaction covers a wide range (115°-190° C.) and, in general, depends upon the activity of the catalyst and the particular charge stock. With fresh catalyst, the optimum temperature varies from 115° C. for ethylene to about 160° C., depending on the molecular weight of the olefin; higher temperatures sometimes are used for olefin mixtures. The reaction velocity is low at low temperatures. If the temperature is too high, however, side reactions occur, and some CH_4 usually is formed.

Using a C-16 olefin, if the oxo reaction is started and maintained at a high temperature (170°-190° C.), the resulting oxo alcohols will have a low melting point. If the oxo reaction is started at low temperatures (100°-130° C.) and the temperature slowly raised while the reaction is going to completion, the resulting oxo alcohols will have an appreciably higher melting point. It appears that displacement of the double bond induced by cobalt carbonyl is much more temperature-dependent than the oxo reaction itself and occurs at a faster rate at higher temperatures.

Effect of Pressure

The oxo reaction, especially under continuous conditions, is markedly pressure-dependent. Pressure dependence, it is true, is not very marked when a fresh catalyst is used, but a once-used catalyst showed the following behavior:

Pressure (atm.)	Approximate conversion (%)
50	10
100	50
150	70-80
225	95

These values hold for a reaction time of 1 hour. It was concluded that continuous plant operation under 150 atmospheres was not feasible.

Process Conditions

It is important to note that both the oxo reaction and the hydrogenation are exothermic, and some means of temperature control must be incorporated into the oxo process. Another factor essential to any scheme for operating the oxo process is that the synthesis-gas rate in both stages must be high enough to insure efficient stirring and complete suspension of the catalyst.

1. Batch Production of Oxo Alcohols

In the full-scale oxo plant at Holten, the reactors were 12 meters long and had an external diameter of 570 mm. and an internal diameter of 400 mm.; the volume of a reactor was 1.2 cubic meters. Inside the reactor was a bundle of 31 cooling tubes connected to a steam chest; the tubes were 8 meters long and 38 mm. in outside diameter, with a total area of 30 square meters. 1,250 kg. of olefins per hour were mixed with 3 to 5 percent of finely ground catalyst in a tank and then transferred in batches of 700-720 liters to the charging vessel. Here, the pressure of the mixture (150 atmospheres) was equalized with that of the reactor. It was then mixed batchwise in the reactor with water gas at the rate of 750 cubic meters an hour; each batch of 700 liters filled the reactor about three-quarters full.

From a temperature of about 125° C. at the start, the temperature rose to approximately 135° C. after 10-15 minutes and to approximately 145° C. after 20-30 minutes. The oxo reaction was then complete. The waste gas was partly vented and the rest recycled, being continuously made up to the correct proportions of CO and H_2. The whole oxo reaction, including charging and discharging, took about an hour. About 50-100 cycles exhausted the catalyst.

The same type of reactor was used to hydrogenate the crude aldehydes. At 150 atmospheres and 180° C., hydrogen of 90-92 percent purity was used as the gas feed at the rate of 400 cubic meters per hour. Hollow ceramic filter elements were used to separate the catalyst from the products, and the alcohols were then distilled under vacuum. One kilogram of olefins usually yields about 1 kilogram of distilled alcohol.

2. Continuous Operation

Work at Leuna showed that considerably higher throughputs were obtained from continuous operation. A description of the latest method of operation of the Leuna plant was obtained by W. A. Horne from Dr. Gemassmer, the chemist directly in charge of the plant. This description, including a flow sheet of the continuous oxo plant, is given in Information Circular 7370, Report on the Investigation by Fuels and Lubricants Teams at the I. G. Farbenindustrie A. G. Leuna Works, Merseburg, Germany, pages 89-91, edited by R. Holroyd.

USES OF OXO PRODUCTS

Detergents

Germany's main interest in the oxo process from a commercial standpoint from 1940 onward was apparently for the production of washing and wetting agents, obtainable by sulfonating alcohols. It was concluded that the mixture of oxo alcohols was better than any of the individual alcohols when converted to washing and wetting agents. Test proved that oxo alcohols were better for this purpose than the small fraction of similar number carbon-atom alcohols that could be obtained from the Synol process. A typical procedure for obtaining oxo detergents is given below.

Low-temperature thermal cracking of gatsch (soft paraffin wax) produced olefins having the following boiling ranges:

Boiling range, °C.	Olefins, %
190-305	56.0
210-305	53.0
230-305	49.0

The "oxierung" of these cuts was carried out at 130° C. and 200 atmospheres of water gas, using the usual Fischer-Tropsch catalyst. Reduction of the resulting aldehydes was carried out at 180° C. and 200 atmospheres of H_2. The oxo alcohols were then sulfonated with chlorosulphonic acid in the usual way:

$$R\text{-}CH_2\text{-}CH_2OH + ClSO_3H \longrightarrow RCH_2CH_2CSO_3H + HCl$$

Alcohol Sulfate

The resulting "soaps" were fine white powders forming clear colorless solutions when 5 percent was dissolved in water at room temperature. These products met requirements of storage stability, wetting power, and foam propensity. They were excellent for washing both wool and cotton, including "fine washing."

Plasticizers

In addition to use in making washing powders, the oxo process was used or was planned for use by the Germans to make phthalic acid esters of 7-10 carbon-atom alcohols. The products were alleged to make excellent plasticizers. Beginning in April 1943, Ruhrbenzin planned to deliver, at a regular yearly rate, 6,000 tons of a Kogasin fraction, cut to include 7-10 carbon-atom molecules (80-175°C.) and containing at least 35 percent olefin.

This cut was to be sent through the oxo process at Leuna, and the crude alcohols were to be shipped to Schkapou (site of an I. G. Farben. rubber-manufacturing plant). It was planned to esterify the alcohols in the presence of the neutral oils. It was found that the neutral oil could be used advantageously as a water-transporting medium (the azeotropic removal of water in continuous esterification).

Fatty Acids

With the shortage of fats, it was natural that the Germans should have turned to oxo alcohols as a source of fatty acids. It was found possible to convert 90 percent of high-molecular-weight oxo alcohols into fatty acids by heating with an alkali amalgam. Attempts to oxidize oxo alcohols to fatty acids by blowing air through the liquid alcohols in the presence of a catalyst - that is, 0.5 percent manganese stearate - were not successful. To obtain fair yields of fatty acids, temperatures above 200° C. were necessary; at these temperatures, dehydrogenation conditions were reached. The C_{12}-C_{16} fatty acids prepared from the oxo alcohols had remarkably low melting points. Soaps prepared from C_{15} and C_{16} fatty acids were satisfactory; soaps from C_{12}, C_{13}, and C_{14} fatty acids had peculiar odors. Soaps prepared from fatty acids of a lower carbon content were hygroscopic. An almost negligible amount of fatty acids was derived from oxo alcohols by Germany.

Other Uses

Some of the pilot-scale products from the further processing of oxo alcohols included cutting oils, lubricating oils, Diesel oils, and hydraulic fluids. Very good lubricating oils, with pour points of -70° C. and below, were made by preparing acids and alcohols from suitable olefins and uniting the two to form esters. This technique, applied to olefins of lower molecular weight, gave good hydraulic fluids. Diesel oil with the astonishing cetene number of 280 was made by converting a range of oxo alcohols to their nitric acid esters; this oil was under consideration during the war as a cold-starting aircraft fuel. Roelen had used propionaldehyde, prepared by subjecting ethylene to the oxo reaction, in making a synthetic drying oil. I. G. Farben. prepared a nC_9-C_{10} alcohol mixture from a dimethyl-hexadiene that could be substituted for rose essence in perfumes. The oxo process has almost unlimited synthetic possibilities.