PREFACE

The chemistry of the addition of carbon monoxide and hydrogen to unsaturated carbon compounds to form the corresponding aldehydes is the subject of the review and critical discussion presented in this paper. It is important not only because of the expanding horizons of possible industrial synthesis of aliphatic organic compounds but also because the discussion of reaction mechanisms contains ideas that are of value also in the analysis of probable mechanisms for the Fischer-Tropsch synthesis.

Although olefinic and saturated paraffin hydrocarbons constitute the bulk of the Fischer-Tropsch product, some alcohols and aldehydes usually are obtained under normal operating conditions. However, the product of the synthesis at low temperatures (185°-190° C.) and with short contact times obtained by recycling 25 to 100 volumes of end-gas per volume of fresh synthesis gas contains large amounts of alcohols. It is possible that these alcohols are formed by a mechanism similar to that described in this paper for the oxo process.

The oxo reaction appears to be a case of homogenous catalysis with cobalt hydrocarbonyl as the catalyst. There are several outstanding characteristics of the Fischer-Tropsch process that cannot be explained on the basis of the carbidic carbon - methylene polymerization hypothesis proposed by F. Fischer, but are necessary consequences of a mechanism similar to that of the oxo synthesis. Thus the 50 to 70 percent of alcohols obtained under conditions cited above could be formed by way of addition of carbon monoxide and hydrogen to an olefin, as in the oxo synthesis. The higher proportion of aldehydes in the oxo product is due largely to the absence of dissociatively adsorbed hydrogen, as most of the surfaces are poisoned by cobalt carbonyl. In the Fischer-Tropsch synthesis the hydrogenating activity of the catalyst surface is only partly poisoned, so that, although methane formation is retarded, the hydrogenation of aldehydes to alcohols occurs at a suitable rate. Upon longer contact time, the alcohols are dehydrated to form olefins.

The concentration of ethylene in Fischer-Tropsch products - relatively very low - and the results of experiments in which ethylene is added to the synthesis gas indicate that some mechanism consumes this olefin rapidly. The unique position of ethylene in the synthesis may be due to the fact that it is the first member of the olefin series and probably reacts rapidly in the adsorbed phase on the catalyst surface with carbon monoxide and hydrogen to form propyl alcohol by a mechanism similar to that of the oxo synthesis. The initial production of the steady-state concentration of ethylene in the adsorbed phase may proceed by way of conversion of an adsorption complex of hydrogen and carbon monoxide to ethylene and water.

The carbidic carbon intermediate postulated by F. Fischer and others in discussions of the mechanism of the Fischer-Tropsch synthesis should permit multiple branching and growth of single branches to include several carbon atoms. In fact, however, Fischer-Tropsch products contain virtually no multiply-branched hydrocarbons, and the branching is largely confined to a single methyl group. If a mechanism similar to that of the oxo synthesis occurs on the surface of Fischer-Tropsch catalysts, the analysis of the products obtained is easily explained. All branching according to this mechanism results from the addition of carbon monoxide to a nonterminal carbon atom of the olefin; branches larger than a methyl group are improbable because the oxo reaction is retarded owing to steric hindrances imposed by the first branched carbon. More than one branch is impossible in the oxo reaction when the reactant is a mono-olefin.

In addition to the scientific importance of discussions of the mechanism of the oxo synthesis, the practical importance of this reaction is clearly outlined in this paper. The industrial production of long-chain alcohols, aldehydes, and fatty acids from olefin fractions of Fischer-Tropsch products or of petroleum products appears now to be a matter of careful cost estimating and engineering design. A substantial portion of the basic chemistry has been disclosed.

H. H. Storch

INTRODUCTION

The oxo reaction consists of catalytic conversion of olefins by reacting the olefins with CO and H_2 (water gas) to aldehydes that contain one more carbon atom than the starting olefin. The aldehydes are then generally reduced with hydrogen to primary alcohols in a second stage. The two-stage process is called the oxo process. The word "oxo" is derived from the German "oxierung" (ketonization); thus the exact English equivalent of "oxo" is "keto". The oxo process may be applied to nearly all olefins.

A wide range of pressures and temperatures may be used in both stages. The pressure range usually employed is 150 to 200 atmospheres. The temperature in the first stage is usually about 140° C. and in the second or hydrogenation stage about 180° C. Although a standard Fischer-Tropsch catalyst may be used for both steps, cheaper catalysts have been utilized to effect hydrogenation of the aldehydes.

Most of the information for this report on the oxo process was gathered from Technical Oil Mission microfilms. T.O.M. Reels 14, 55, and 134 were especially valuable. T.O.M. Report 6 by H. M. Weir was very helpful. Information on the oxo process is scattered throughout documents captured in enemy territory, and the present report does not include all the available data. Some of the information was procured by personal interview. Where, in the body of this report, certain investigators are quoted, the source of the statement is either personal interview or the T.O.M. reports.

ACKNOWLEDGMENTS

We wish to thank Morris Pollchik for valuable assistance in preparing the manuscript.

DEVELOPMENT OF OXO PROCESS

Dr. Otto Roelen, who is probably the discoverer of the modern oxo process, has stated that he first predicted the possibility of the oxo synthesis in 1938 but that realization of the reaction had to await development of a suitable plant. A patent application relating to the oxo reaction itself was filed by Dr. Roelen in Germany September 19, 1938, and was assigned to Ruhrchemie. This probably corresponds to U. S. Patent 2,327,066, August 17, 1943, Otto Roelen, inventor, unassigned but seized by U. S. Alien Property Custodian - application date, April 15, 1939.

Ruhrchemie A. G. and I. G. Farbenindustrie cooperated in the development of the oxo process. Stock in the operating company, the Oxo Gesellschaft, was held by these two companies, with some participation by Henkel & Cie. Offices of the Oxo Gesellschaft were at Oberhausen-Holten. Ruhrchemie conducted the oxo process batchwise on a semiplant scale, but I. G. Farben developed a continuous process and installed a pilot plant for its operation at Leuna. It was generally agreed that the I. G. Farben continuous process was more efficient than the Ruhrchemie intermittent operation. Although the capacity of the Leuna plant was about 100 tons a month, it never produced more than 40 to 50 tons a month in its 2 years of operation. In May 1944, only 7 tons were produced, and production then ceased. Ruhrchemie's batchwise plant at Holten had an annual capacity of some 8,000 to 10,000 metric tons of product, but the plant was never operated at full capacity. From a chemical standpoint, there seems to have been no lack of confidence in the oxo process in Germany. Progress was held up only by war conditions.

RAW MATERIALS

Olefins

Practical application of the oxo process in Germany was directed mostly toward processing olefins derived from Fischer-Tropsch oils in the boiling range 180°-320° (C_{11}-C_{17} carbon atoms) and to the processing of straight-chain olefins with a terminal double bond. The latter were obtained by cracking Fischer-Tropsch paraffin gatsch (soft wax) under mild conditions. Oxo alcohols were also prepared from cracked gas oils and cracked gasolines of German, Swedish, and Rumanian petroleum. Oxo alcohols also were obtained from Estonian, Swedish, and German shale oils and from brown-coal low-temperature carbonization products. Although the oxo reaction was found to be feasible with most of these oils without previous refining, low-temperature carbonization products required pretreatment with lye and dilute acid or a refining process with liquid SO_2 and butane to prevent the formation of strongly colored products.

The following are some of the unsaturated substances subjected to the oxo reaction:

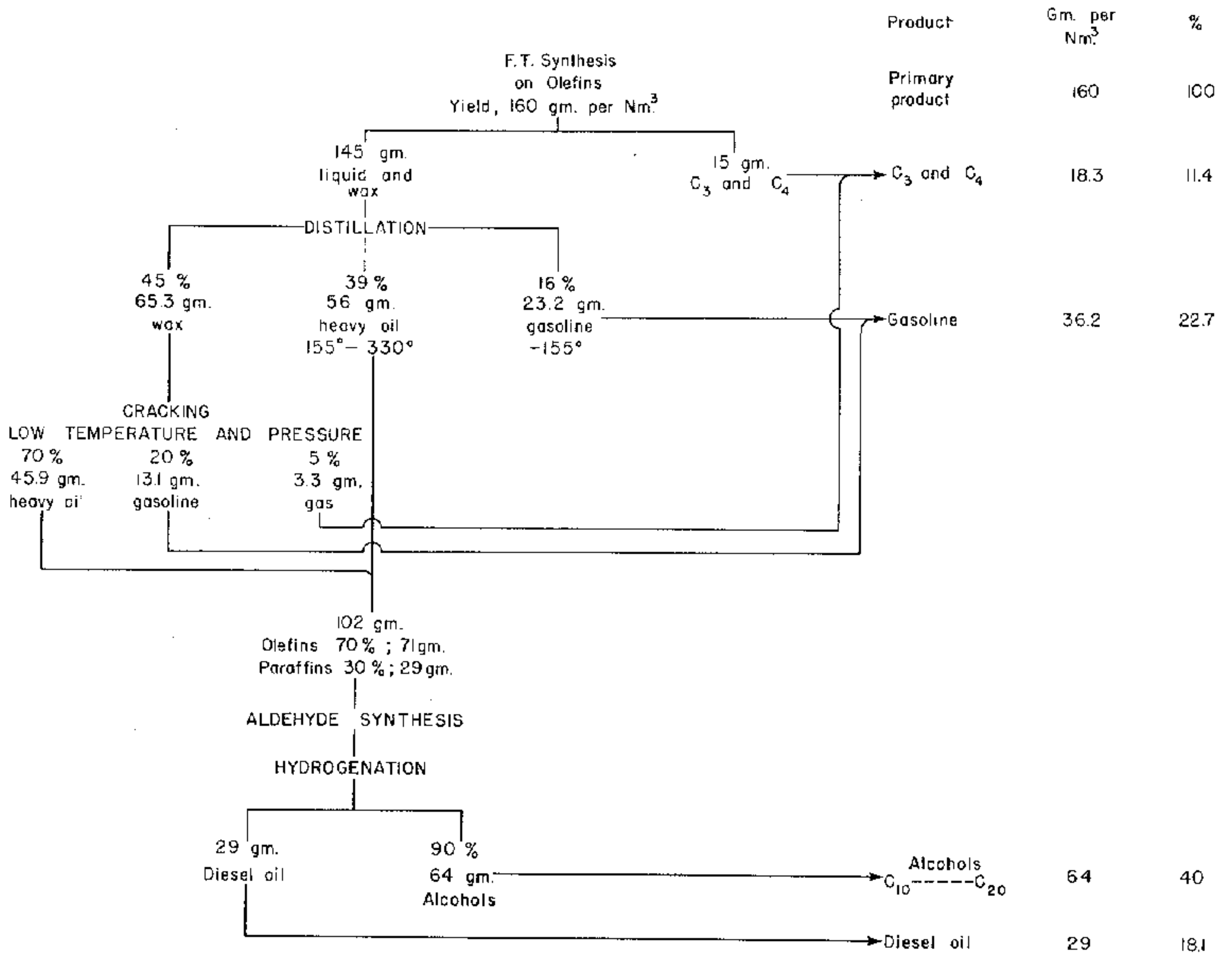


Figure 1. - Scheme for Fischer process with oxo. (Using iron catalyst at 20 atm. and 280°-300° C. Yields based on 1 cubic meter of ideal synthesis gas.) Prepared by Ruhrchemie February 7, 1940.

acetylene
ethylene
propylene
butene
cetene
cyclohexene
n-octene
i-nonene
styrene
allyl alcohol
dicyclopentadiene
dipentene
2,5-dimethylhexadiene-1,5
butadiene
n-decene
n-dodecene-1
olefinic lubricating oil
diisobutylene
octalin
oleic alcohol
oleic acid
linseed oil
rubber
vinyl ether
tetrahydrofuran
ethyl acrylate
tetramethylbutadiene

Although it has been claimed that all of these substances were treated successfully in the laboratory, careful reading of some of the experimental work indicates that difficulties were encountered in many cases, and it remains to be demonstrated that all olefins will undergo the reaction. Most hydrocarbon mono-olefins and many oxygen containing olefins were processed with excellent (over 90 percent) yields of the expected primary alcohols.

In 1940, the production of 40,000 tons per year of alcohols in the C_{10}-C_{20} range from Fischer-Tropsch olefins was visualized by Dr. Martin of Ruhrchemie. The scheme for this process is outlined in figure 1. The heavy oil (155°-330° C. boiling range) from the Fischer-Tropsch process at 20 atmospheres (using an Fe catalyst) was to furnish slightly more than half the raw materials, and low-temperature and low-pressure cracking of the Fischer-Tropsch wax was to supply the rest of the oxo charge. The total charge consisted of about 70 percent olefins and 30 percent paraffins.

Dr. Martin stated that an 85-percent yield of olefins could be made by the thermal cracking of Fischer-Tropsch wax at 250° C. with only 5-percent loss. At 250° C., mostly terminal double bonds were produced. As the temperature of cracking was raised, the double bonds tended to wander toward the middle of the carbon chain and were almost entirely in the middle of the chain at a temperature of 350° C.

Water Gas

The presence of sulfur does not hinder the oxo reaction but definitely inhibits the hydrogenation of the aldehydes. While a ratio of 1 volume of CO to 1 volume of H_2 is usually employed in the oxo reaction, this ratio need not be maintained closely, because a large excess of gas is always used.

Catalysts

Standard Fischer-Tropsch catalysts were used in most of the experiments on the oxo process. These catalysts were used for both steps mainly because they were readily available. It was well known that nickel and other cheaper catalysts could be used for the hydrogenation. A standard Fischer-Tropsch catalyst was reported to have the following composition:

	Percent
Cobalt	30
Thorium oxide	2
Magnesium oxide	2
Kieselguhr	66

Because cobalt was scarce, the cobalt content of the catalyst was decreased from 30 percent to 25 percent with no deleterious effect on the oxo reaction. Iron carbonyl also catalyzed the reaction, but its activity was much lower than that of the cobalt catalyst.

Although the cobalt catalyst was sensitive to sulfur in the gases used in the Fischer-Tropsch synthesis, the oxo reaction did not appear to be affected by sulfur. Sulfur, however, definitely hindered hydrogenation of the aldehyde in the second stage when cobalt catalyst was used. When olefins or oils containing sulfur were used in the oxo reaction, the catalyst was filtered from the products of the first-stage reaction and the hydrogenation carried out over a catalyst not affected by sulfur as fixed nickel-tungsten sulfide. It is preferable to perform a partial hydrogenation of the crude first-stage product before filtering to convert any cobalt carbonyl to cobalt.

Both Dr. Roelen and Dr. Reppe believed that the reaction mechanism involved formation of cobalt hydrocarbonyl as the active catalyst. Both cobalt and iron form hydrocarbonyls, and both catalyze the oxo reaction. Nickel, on the other hand, does not form a hydrocarbonyl and does not catalyze the oxo reaction. Roelen has stated that cobalt could be introduced in several forms and that reduced cobalt metal was not essential. Cobalt carbonyl, prepared separately, and fatty acid salts of cobalt were good catalysts for all olefins. According to Dr. Hecht, assistant to Dr. Reppe, cobalt naphthenate was an excellent oxo catalyst. It was even found possible to employ basic cobalt carbonate without preliminary reduction.

A proportion of the cobalt goes into solution as cobalt carbonyl in the first stage. Some of this cobalt carbonyl is carried away in the gas stream, from which it can be recovered by scrubbing with hydrocarbons or oxo-process alcohols. The loss of cobalt due to its solution in the reaction products, and particularly in their polymers, is much more serious. However, upon hydrogenation, the cobalt is precipitated and regenerated by treatment with hydrogen at 250°-270° C. In the intermittent process, the release of pressure after the first stage would result in considerable volatilization of cobalt carbonyl. In the continuous process, however, the cobalt carbonyl that dissolved in the reaction mixture is completely destroyed in the hydrogenation step, and the catalyst is then restored to the active condition. The continuous process is, therefore, particularly advantageous in respect to conservation of catalyst.

During the reaction with Co catalyst, some iron carbonyl is formed from the walls of the reaction vessel. This contaminates the Co catalyst, and it is probable that a complete recovery of the cobalt might be necessary at some stage to free it from iron.

Some small-scale catalytic experiments were carried out to poison the catalyst in such a manner as would still allow the oxo reaction but would prevent the hydrogenation of aldehydes to alcohols that occurs to some extent in the first step. It was found that such a result could be achieved by adding a small amount of an organic sulfur compound (carbon disulfide) to the catalyst mixture. The hydrogenation-inhibiting effect of the sulfur was sharp.

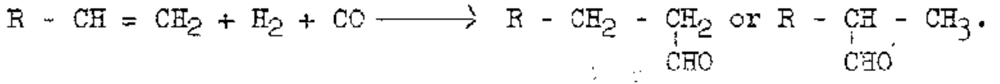
Experiments to poison the catalyst by adding exactly measured amounts of H_2S during precipitation of the catalyst were unsuccessful. It is interesting to note that, when an experiment was performed in which bismuth was the poisoning agent, this metal exerted no poisoning action whatsoever on the hydrogenation; on the contrary, it strongly increased hydrogenation of the olefins.

It would be of theoretical interest to learn if rhodium (atomic number 45) and iridium (atomic number 77) could catalyze the oxo reaction. The carbonyls of these metals are known and are quite stable, and there is some evidence that they both form hydrocarbonyls. If these hydrocarbonyls are more stable than cobalt hydrocarbonyl, it may be possible to conduct the oxo reaction with smaller partial pressures of carbon monoxide in their presence.

CHEMISTRY OF PROCESS

Basic Oxo Equation

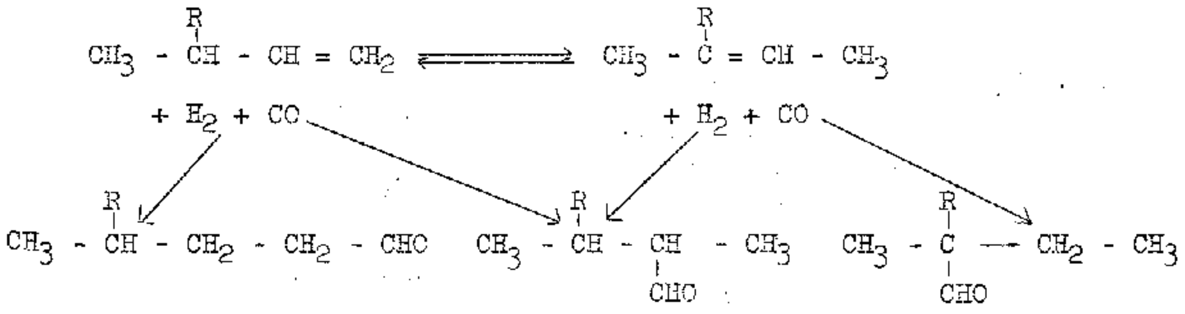
Using a pure olefin, a mixture of aldehyes is obtained as the product of the oxo reaction. The aldehydic group adds to either carbon of the double bond:



$$R - CH = CH_2 + H_2 + CO \longrightarrow R - CH_2 - \underset{CHO}{\underset{|}{CH_2}} \text{ or } R - \underset{CHO}{\underset{|}{CH}} - CH_3.$$

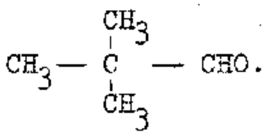
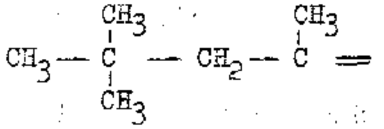
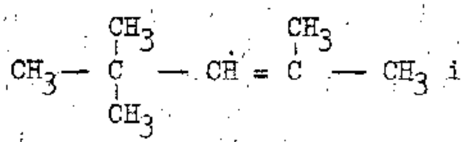
As a general rule, about 60 percent branched- and 40 percent straight-chain aldehydes are obtained.

This tendency toward a mixed product is increased further by isomeriza-of the olefin in the presence of cobalt carbonyl, thus:



Steric Effects

The reaction that predominates is the one involving the least steric hindrance. Using isobutylene, more $CH_3 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - CHO$ is obtained than

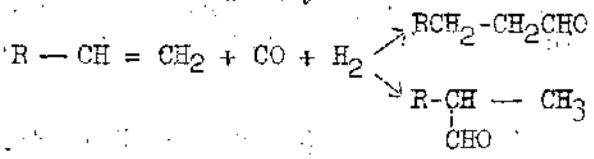
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CHO$. In a similar manner, if the trimethylpentenes obtained from polymerization of isobutylene are used as the oxo charge, the chief products will be those derived from  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH_2$ isomer, as distinct from  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3$ isomer. The only olefins completely unreactive with water gas are those in which the double bond is located between two tertiary carbon atoms. Such olefins also resist hydrogenation.

Nature of Products

The aldehydes are completely reduced to primary alcohols in the hydrogenation stage. As is to be expected, there are other products of the oxo reaction besides aldehydes. The reactions occurring may be listed in the following manner:

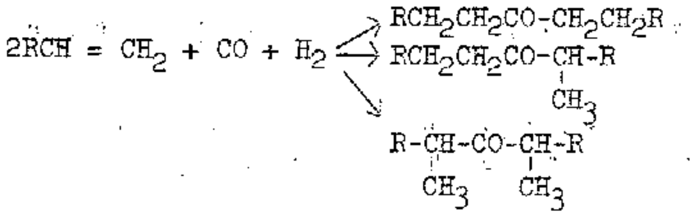
1. Primary reactions

   a. Formation of aldehydes



$$R-CH=CH_2+CO+H_2 \begin{cases} \to RCH_2-CH_2CHO \\ \to R-\underset{CHO}{CH}-CH_3 \end{cases}$$

   b. Formation of ketones



$$2RCH=CH_2+CO+H_2 \begin{cases} \to RCH_2CH_2CO-CH_2CH_2R \\ \to RCH_2CH_2CO-\underset{CH_3}{CH}-R \\ \to R-\underset{CH_3}{CH}-CO-\underset{CH_3}{CH}-R \end{cases}$$

2. Secondary reactions

   a. Formation of alcohols. Under the drastic conditions of the oxo reaction, some aldehydes are reduced to alcohols in the first stage. Alcohols may also occur as the result of a Cannizzaro-type reaction.

   b. Formation of acids - acids may result from a Cannizzaro-type reaction.

   c. Formation of esters - acids are esterified by the alcohols present in the mixture.

d. Formation of acetals - aldehydes and alcohols present in the mixture give acetals.

e. High-molecular-weight compounds are formed by polymerization and condensation reactions.

f. Formation of saturated hydrocarbons - these are produced by hydrogenation of the double bond with no oxo reaction taking place. Practically no saturated hydrocarbons are formed in the presence of carbon monoxide.

The oxo process must be looked upon primarily as a source of alcohols rather than aldehydes. Much work was done in an effort to use the reaction as a source of aldehydes, but the attempts were abandoned for the following reasons:

1. In order to react the olefins completely, a sufficiently drastic treatment with water gas must be used so that much conversion of aldehyde to alcohol takes place in the first stage.

2. The aldehydes are very reactive and tend to polymerize, condense, form acetals, etc., during the oxo reaction.

3. Attempts to separate the aldehydes (especially by distillation) result in great losses and formation of much residue.

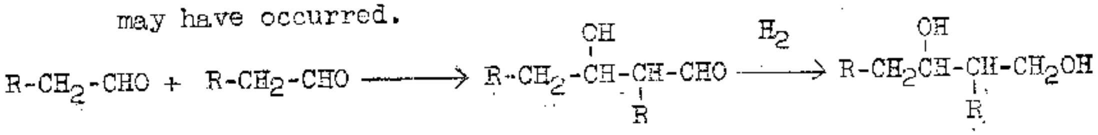
If aldehydes were desired, it probably would be better to produce the alcohol by the oxo reaction, isolate it, and then use known methods to oxidize the alcohol to the desired aldehyde.

When distilling crude oxo alcohols prepared from a sharp olefin cut, there always remains a high-boiling residue ("Dicköl"), which can account for as much as 20 percent of the total crude product. Dicköl has a high hydroxyl number and therefore contains high-molecular-weight alcohols, perhaps polyhydric in character. These high-molecular-weight alcohols may be formed in either or both of the following ways:

a. Two olefin molecules react with 1 CO and 1 H_2 molecule, thus forming a ketone, which subsequently is reduced to a secondary alcohol.

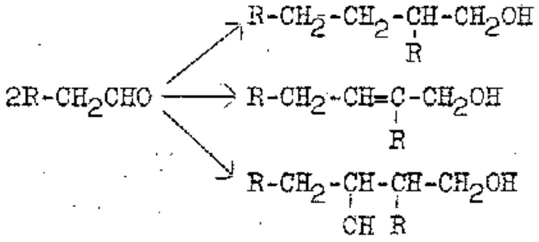
$$2\ R\text{-}CH{=}CH_2 + CO + H_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}R \xrightarrow{H_2} R\text{-}CH_2\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}CH_2R$$

b. An aldol condensation of two monomeric aldehyde molecules may have occurred.



$$R\text{-}CH_2\text{-}CHO + R\text{-}CH_2\text{-}CHO \longrightarrow R\text{-}CH_2\text{-}\overset{OH}{\overset{|}{CH}}\text{-}\underset{\underset{R}{|}}{CH}\text{-}CHO \xrightarrow{H_2} R\text{-}CH_2\overset{OH}{\overset{|}{CH}}\text{-}\underset{\underset{R}{|}}{CH}\text{-}CH_2OH$$

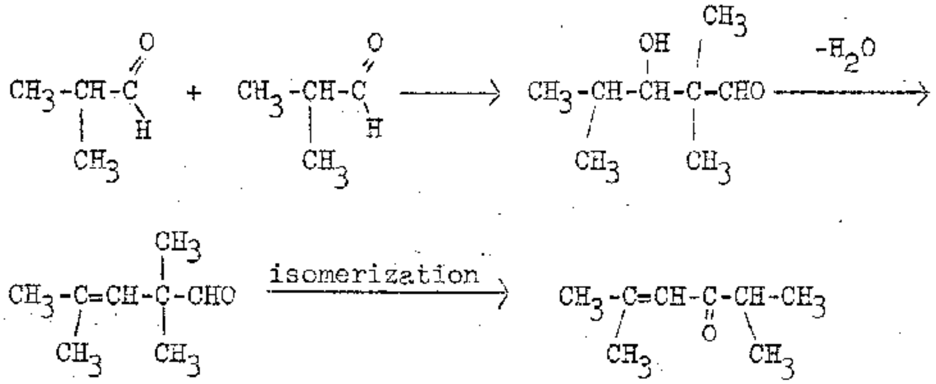
Such aldol condensations are known to occur during hydrogenation. For example, v. Braun (Ber., vol. 67, 1896) obtained the following byproducts from the hydrogenation of aldehydes:



In a modification of the usual oxo process, it was endeavored to obtain aldol condensation of oxo aldehydes at the moment of formation by adding alkaline substances and by varying pressure and temperature. Upon hydrogenation, compounds with double the number of original carbon atoms should result. These products may be diols, unsaturated primary alcohols, or saturated primary alcohols in case secondary OH groups are split off as H_2O, and the double bond formed is then hydrogenated.

The following agents were tried: Aqueous sodium hydroxide, methyl alcoholic sodium hydroxide, sodium ethylate, solid sodium hydroxide, calcium oxide, sodium carbonate, and aqueous ammonia. However, no major effect in the desired direction could be established. Varying the temperature and pressure rather than the media had a much greater effect on the quantity of high-boiling material. Increasing both variables resulted in the production of significantly larger amounts of higher-boiling material. The high-boiling residue so obtained, however, contained few OH groups, and it is quite possible that the actual reaction did not take place via the aldol condensation.

It is possible for an aldol condensation to occur in such a way that the final product need not contain an hydroxyl group. Such a mechanism involves isomerization of the aldol initially formed to a ketone. Thus, H. Pines and V. N. Ipatieff (Jour. Am. Chem. Soc., vol. 69, 1947, p. 1337) have proposed the isomerization of an aldol in the presence of $AlCl_3$-HCl at 80° C. and a carbon monoxide pressure of 125 atmospheres as follows:



The isomerization of an aldehyde of the 2,2,4 trimethyl-3-pentene-1-al type to a ketone as above by the use of sulfuric acid (S. Danilow and E. Venus-Danilowa, Ber., vol. 59B, 1926, p. 377) and $AlCl_3$ (H. Hopff, C. D. Nenitzescu, D. A. Isacescu, and I. P. Cantuniari, Ber., vol. 69B, 1936, p. 2244) as catalysts has been reported. The catalyst - cobalt hydrocarbonyl - is a strong acid, and the absence of many OH groups after hydrogenation may perhaps be explained by the dehydration and subsequent isomerization of the aldol. The pressures and temperatures used in the oxo reaction are higher than those used by Pines and Ipatieff, and it is probable that the isomerization is favored under these conditions.

As a result of the aldol experiments with different materials in the oxo reactor, two quite interesting observations were made:

1. The oxo-reaction is almost completely inhibited in the presence of aqueous ammonia; 85 percent of the original olefins were recovered unchanged. This may be explained by assuming that the cobalt-ammine complex thus formed is more stable than the cobalt-carbonyl complex. The content of cobalt carbonyl in the catalyst required for the oxo reaction is thus decreased and the reaction inhibited. This might well be proof, thus far lacking, that cobalt carbonyl is required and essential for the oxo reaction.

2. In the presence of sodium methylate, the hydrogenation that occurs to some extent in the oxo reaction is completely inhibited while the oxo reaction itself is not all affected. As little as 0.2 percent sodium methylate inhibits hydrogenation. Although a strong base, such as methylate ion, tends to promote condensation of aldehydes, appreciable quantities of aldehyde could be found in the reaction products. It may be that the hydrogenation poisoning agent is formic acid or sodium formate.

Double-Bond Isomerization

The rearrangement or isomerization of the double bond is an important feature of the oxo reaction. Table 1, taken from T.O.M. Reel 14, Frame 05647, effectively summarizes the experiments showing migration of the double bond with higher olefins. Pure dodecene-1 was the olefin used. Examination of the table and of oxo products reveal these facts:

1. Cobalt catalyst in the presence of an inert gas does not cause isomerization at 200°, the upper limit of the usual oxo temperature. If conditions are maintained the same while the temperature is raised to 300° C., isomerization occurs, and all of the isomeric dodecenes are formed.

2. At temperatures below 250° C., cobalt carbonyl is responsible for isomerization. In the presence of either Fischer-Tropsch catalyst or cobalt metal at temperatures between 150°-250° C. and 100 atmospheres of CO, all dodecene isomers in almost equal ratios are formed.

3. Using iron pentacarbonyl as the catalyst at 150° C. and 100 atmospheres CO, all dodecene isomers are formed, but only 40-45 percent of the original dodecene-1 is isomerized. Under the same conditions, using nickel metal, no isomerization occurred. It may therefore be concluded that the three metals, Co, Fe, and Ni, catalyze the oxo reaction in about the same order as their effectiveness in isomerizing the double bond.