

INFORMATION DIVISION TRANSLATION T46-12

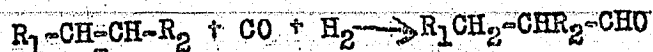
Synthesis of Aldehydes and Other Oxygen  
Containing Compounds Starting with Carbon  
Monoxide and Hydrogen (Communication From  
The Research Laboratory of Ruhrbenzin A.-G.)

1)

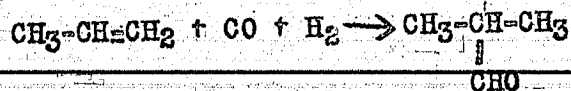
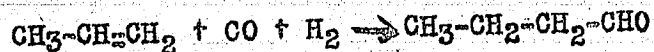
It is already known that aldehydes and other oxygen containing compounds can be produced from hydrocarbons and carbon monoxide by means of aluminum chloride. Where the carbon monoxide is attached to form a carbon-hydrogen bond according to the equation  $R-H + CO \rightarrow RCHO$ . This reaction, however, produces an individual aldehyde only in definite cases, for example, the conversion of benzene to benzaldehyde. In the aliphatic series on the contrary other types of by-products occur predominantly.

2)

It has now been found that olefinic double bonds at elevated temperature and in the presence of catalysts will attach carbon monoxide and hydrogen. Here each double bond takes up one mol. of carbon monoxide and a mol. of hydrogen and from the olefin there is produced the next higher aldehyde according to the equation:



The carbon monoxide attaches itself partly to one and partly to the other carbon atom of the double bond. From unsymmetric paraffins, therefore, both isomers are obtained. For example, from propylene there is formed n-butyraldehyde and isobutyraldehyde.



The proportional amount of the two isomers is influenced by reaction conditions.

It has further been found that carbon monoxide and hydrogen, instead of engaging with one mol each, can also attach to two mols of olefin and thereby instead of aldehydes form the

pertinent ketone according to the equation



For example, in the attachment of carbon monoxide and hydrogen to ethylene, diethylketone is obtained, in addition to propyl aldehyde. Here also the proportional amount of the two reaction products is dependent upon reaction conditions.

In the manner described, olefins of the most varied nature can be converted into the next higher aldehydes. Thus, for example, we were able to produce aldehydes from the following olefinic substances: ethylene, acetylene, propylene, butylene, higher primary olefins from carbon monoxide hydrogenation, olefins obtained from cracking, olefins resulting through polymerization, isooctene, olefinic lubricating oils, oleic alcohols, oleic acid, linseed oil, oil of turpentine, caoutchouc, styrol, cyclohexene, etc.

It may therefore be assumed that this is a generally applicable reaction which leads from olefins to OXO compounds.

3.)

As catalysts for the new reaction, metals of the iron group (iron-cobalt-nickel) have shown themselves to be suitable particularly in the finely divided or activated form. Non-specific catalysts, such as active charcoal, are completely ineffective.

To a very slight degree, the reaction proceeds even at normal pressure. However, reaction velocity increases very rapidly with rising pressure. At pressures of 100 atm. and over, for example, at 400 atm., we obtained space-time-yields which can be technically valuable.

The temperature range within which the conversions take place is notably low. The lowest temperature at which we could attach water gas to ethylene was around 40°. As is generally true, in this case also the reaction velocity is dependent not only upon temperature but also upon the activity of the catalyst. With highly active catalyst we obtained satisfactory conversions at 80-120°. With other catalysts the reaction temperatures are somewhat higher, for example, at 140-160°.

The synthesis of aldehydes from olefin, carbon monoxide and hydrogen proceeds in general as in the hydrocarbon synthesis from carbon monoxide and hydrogen most favorably within a very

definite temperature range. If the temperature is too low, conversion is too slight. If the temperature is too high, side reactions take place. In the case of hydrocarbon synthesis, methane results from hydrogenation of carbon monoxide. In the aldehyde synthesis, saturated compounds occur through olefin hydrogenation, and alcohols through aldehyde hydrogenation. In contrast to hydrocarbon synthesis in which the most favorable temperature range is very narrow, for example, amounting to around  $5^{\circ}$ , the permissible temperature range in the aldehyde synthesis is greater and amounts to from  $30-50^{\circ}$ .

Aldehyde synthesis from olefin, carbon monoxide and hydrogen is highly exothermic. Since the reaction temperature must be maintained within definite limits, provision must be made for removal of heat in carrying out the reaction. Since the reaction is carried out under high pressure and at relatively low temperatures, control of the reaction temperature offers no difficulties.

The reaction may be carried out in varied ways so far as apparatus is concerned. Ethylene and water gas can be readily converted by charging the gas mixture over a rigidly disposed catalyst which is placed, for the purpose of heat transfer, in suitable reaction chambers, for example, in narrow tubes. Olefins which are liquid under reaction conditions can be advantageously converted, in that the catalyst is sludged in these olefins and the suspension is then treated with water gas. The liquid olefins can also be allowed to trickle over a fixed layer of catalyst, which, is treated at the same time with carbon monoxide and hydrogen. All three methods of operation were accomplished without difficulty.

The absorption of carbon monoxide and hydrogen, when reaction conditions are correctly selected, takes place exactly in the stoichiometric proportion of 1:1. Gaseous by-products such as methane or the like do not occur. Therefore, the water gas used in the reaction can be recycled until the enrichment of inert gases becomes too great.

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4)

In the attachment of carbon monoxide and hydrogen to olefins various side reactions may occur. For example, the reaction products may contain, according to reaction conditions, more or less dissolved metal, originating from the catalyst,

for example, in the form of carbonyl compounds. Freeing the reaction products from dissolved metal is easily possible, as we have found by treatment of the same with dilute acids, acid salts, sulfides or the like. Under certain conditions the aldehydes, according to our experience, were not altered by such treatment. As already mentioned, hydrogenation of the olefins to form saturated compounds can also occur as side reaction, as well as the conversion of aldehydes to alcohols. It has been found experimentally, however, that this is only the case when the reaction temperature is too high. Of special interest in this connection is the fact that pure hydrogen, under conditions of the OXO synthesis (that is, 100°, 15 atm. and with cobalt catalyst) is capable of hydrogenating olefin hydrocarbons at appreciably lower temperatures than those at which the OXO synthesis takes place in the presence of carbon monoxide. It must, therefore, be assumed that carbon monoxide blankets the catalyst and makes it inactive for olefin hydrogenation.

Finally, the aldehydes have a tendency, even during the synthesis, to form high molecular substances such as polymers, aldols, esters and the like. By suitable choice of reaction conditions, however, the formation of such by-products can be avoided to any appreciable amount.

5)

It is known that aldehydes can be reduced to alcohols with great ease. Accordingly, it is readily possible, by way of aldehyde synthesis, to prepare the next higher primary alcohols from olefins, carbon monoxide and hydrogen. As already mentioned, this alcohol formation at times takes place even during aldehyde synthesis as a side reaction. For conversion of olefins into alcohols, therefore, one may proceed so that aldehydes are prepared from olefin and water gas in a first stage and then are hydrogenated with hydrogen in a second stage. However, alcohols can also be produced in one operation from olefins, carbon monoxide and hydrogen for which such high temperatures are required that an appreciable hydrogenation of olefin to the saturated compound is unavoidable. The best yields of alcohol are obtained, therefore, with the two stage operation. Here the yields are excellent.

With suitable catalysts the first and second stage of alcohol production can be carried out with the same catalyst and naturally also in the same container. In the hydrogenation of the aldehydic reaction products, the previously mentioned dissolved metal compounds are destroyed whereby the metal

precipitates again as such. Accordingly, if one starts from any pure olefin, then after attachment of carbon monoxide and hydrogen with subsequent hydrogenation, the catalyst can be easily filtered out and the pure alcohol is obtained directly merely mixed with small amounts of higher boiling by-products.

The production of primary alcohols from olefins was possible very simply in this manner.

6)

It is known that aldehydes can very readily be oxidized to fatty acids. Accordingly, we were able to prepare fatty acids from our synthetic aldehydes by blowing in air or oxygen in a simple manner. It is known that aldehydes absorb oxygen spontaneously at ordinary temperature. Therefore, the oxidation to fatty acids can be carried out at very low temperatures, for example temperatures below 40° and without catalysts with sufficient speed. These mild reaction conditions make it possible to carry out aldehyde oxidation in the presence of hydrocarbons without attacking the latter, which facilitates the preparation and purification of the fatty acids.

7)

Of special interest is the application of aldehyde synthesis to those olefinic hydrocarbons which are obtained from the catalytic hydrogenation of carbon monoxide. Here the olefin hydrocarbons occur exclusively in mixtures with saturated hydrocarbons. Now it is a fact that up to now there has been no simple method of operation aside from extraction with SO<sub>2</sub> to separate the pure olefins from this mixture. It is therefore necessary, for the production of aldehydes, alcohols or fatty acids, to start with a mixture of olefinic and gaseous hydrocarbons.

We have found that the separation of reaction products from paraffin hydrocarbons can be accomplished relatively simply by the following method of operation. In the synthesis, the olefin hydrocarbon is first converted into the next higher homologous oxygen-containing compound. This is combined with such an appreciable increase in boiling point, that a smoother separation through distillation becomes possible. For this purpose the initial hydrocarbon mixture is so broken down by fractional distillation that after the reaction the highest boiling hydrocarbon fraction still boils lower than the lowest boiling reaction product. The initial hydrocarbon mixture is best broken down so that each fraction contains only one molecular magnitude. Then gaps in boiling between the paraffin hydrocarbons

and, for example, the alcohols and the fatty acids are obtained which are so high (40-60°) that reaction products, free of neutral oil, are easily produced with moderate fractionation.

By the new synthesis not only aldehydes in general, but also numerous compounds of different types produceable from the same are made relatively accessible. We have already prepared several of them. Among others, starting with carbon monoxide and hydrogen--where the carbon monoxide was first hydrogenated catalytically to olefins which were then converted into aldehydes and then into alcohols--we were able to produce a complete series of aliphatic primary alcohols from C<sub>3</sub>-C<sub>20</sub>.

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Requested by B.H. Shoemaker - R.F. Baldaste

Reported by - I.B. Wallace

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