CONFIDENTIAL

KAISER WILHELM INSTITUT FUR KOHLENFORSCHUNG
MULHEIM, RUHR.

Date of Visit: April 17-18 and 21, 1945.
Target Number: 30/6.01

Personnel Interrogation:

Dr. Helmut Pichler, Acting Director.
Dr. Herbert Koch, Department Head.
Prof. Karl Ziegler, Director.*

Personnel of Team:

April 17 & 18	(Capt. C.C.Hall, Br. (Dr. Vladimir Haensel,U.S.
April 21	(Mr.E.L.Baldeschwieler,U.S (Dr. G.von Elbe, U.S. (Dr. W.C.Schroeder, U.S.

Object of Visit:

- To obtain information on the work done at the Institute.

Introduction:

See next page.

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* Prof. Ziegler was interrogated on April 25 at Halle.

TARGET No. 30/6.01.

Introduction.

The Institute had completely escaped damage and was carrying on with its normal work when visited. Prof. Karl Ziegler, Director of the Institute, had evacuated to Halle with some of the staff, but Dr. Pichler (Acting Director) and Dr. Koch (a Department Head) were present and were subjected to a thorough interrogation, reported below.

The Institute comprises a number of normal chemical laboratories with the usual offices, library and workshop and a technical or chemical engineering laboratory. The experiments on the Fischer-Tropsch synthesis were carried out partly in small glass or steel reactor tubes erected in an inclined position on normal laboratory benches and partly in rather larger semi-technical steel apparatus in the technical laboratory. A small hand-operated water-gas plant and 2 or 3 gas holders (ca.500 ft^3 capacity) were available for production and storage of synthesis gas. A 1000 atms. compressor formed part of the equipment of the technical laboratory.

Dr. Koch's laboratory contained a large number of spinning band fractionating columns of various lengths and capacities, some designed for handling C_3 and C_4 mixtures.

The Institute was notably lacking in specialized equipment such as X-ray and infra-red absorption spectre apparatus.

Interrogation of Dr. Pichler, April 17 and 18.

Fischer-Tropsch catalysts.

a) Ruthenium Catalyst.

The ruthenium catalyst can be utilized at high pressures, the operation resulting in high wax yields. With increasing pressure, the yield and molecular weight of the paraffins formed are increased. Some experiments have been made at 1000 atms. pressure, but no life test has been made under these conditions. A two year life test has been carried out using this catalyst at 100 atms.

Ruthenium does give carbonyls but these seem to decompose readily with H_2 without loss of metal. The catalyst is more susceptible to sulfur poisoning. Thus, with 1.0 g. S/100 cu.m. of synthesis gas poisoning is produced in a few weeks. (Contraction is reduced by 1/2 in 3 weeks). 0.3 g. S/100 cu.m. of gas gives poisoning in a few months, while no poisoning is obtained when the S concentration is less than 0.01 g. S/100 cu.m. of synthesis gas. This tendency to undergo poisoning by such small amounts of S is not exhibited by iron, nickel or cobalt catalysts. The last three catalysts are different in the respect that sulfides are actually formed throughout the catalyst, and 20-30% of the metal has to be converted to the sulfide in order to show poisoning.

b) Comparison of catalysts for Fischer-Tropsch.

The best normal pressure catalyst is still the one containing cobalt, and when a good F.T. catalyst is required for some new work, the 100 Co : 18 ThO_2 : 100 kieselguhr catalyst is usually selected. The iron group catalysts are, in general, less susceptible to S poisoning than the noble metal catalysts. In the iron group, the least susceptible is iron itself. In comparing the three iron group catalysts, nickel appears to be the worst, since even at atmospheric pressure, there is a loss to carbonyls. Ni-Co mixtures have been used, but that was done to spare cobalt, and cobalt is a better catalyst.

c) Preparation of the Cobalt Catalyst.

For the 100:18:100 catalyst preparation, the precipitation is best carried out by a very rapid addition of sodium carbonate to the nitrate mixture. The reverse addition can also be used, since the observed differences are small. All precipitations are made using hot solutions. The kieselguhr, which is added after the precipitation, has been provided by commercial houses. In the early work, iron and other impurities were removed by an acid wash, but later on it was found that the iron content was not of great importance, and the technical kieselguhr was used directly.

The reduction of the catalyst is carried out at 365°C. at as high a gas rate as possible to keep the water vapor above the catalyst to a minimum. Nickel will be reduced almost completely but with cobalt the reduction is not complete at 365°C. A temperature of 400°C. is too high for a catalyst having a Co:kieselguhr ratio of 1:1, while with higher kieselguhr contents a temperature of 400°C. and even higher can be employed. A reduction time of 4-5 hours is suitable for a hydrogen rate of 2 l.per g. of Co in the catalyst. When longer reduction times are employed, the formation of methane during the synthesis will increase.

d) Medium Pressure Catalysts.

Earlier experiments with cobalt catalysts containing no kieselguhr indicated that at 20 atms. the catalyst becomes inactive after a few hours. Later on, when kieselguhr containing catalysts were used, a good activity was maintained. In the medium pressure synthesis, catalysts can be used which contain more kieselgühr, but the differences are small, and essentially the same preparation is used for both normal and medium pressure synthesis.

In the case of the iron catalysts, their main application is in the middle pressure field since, although they can be used at normal pressure, the life of the catalyst at normal pressure is short. The presence of copper, in amounts raging from 0.5 to 20% (based on iron) is definitely desirable. Iron catalysts containing no copper will work also, but reproducible catalysts are difficult to obtain. The presence of alkali is not essential for activity, but it is necessary for the preparation of a catalyst that can be reproduced. The amount of alkali added is reflected in the product distribution. Thus, 1/8 to 1/4 per cent alkali will give more C_3-C_4 hydrocarbons; with higher alkali contents, the concentration of higher hydrocarbons in the product is increased until at 1% alkali a maximum concentration of higher compounds is attained. However, the catalyst life when 1% alkali is present is definitely shortened. Still higher alkali contents result in the formation of oxygen containing compounds. A suitable catalyst has the following composition:

1/2 to 1% alkali, 2-3% copper, rest iron.

It has been found that the effect of catalyst pretreatment is much greater than that of adding other materials to the catalyst. The pretreatment has little effect upon the product distribution, but primarily upon activity and life. The catalyst pretreatment must be carried out at low pressure, either normal or subatmospheric, the pretreating gas varying in composition from CO alone to water gas or even synthesis gas. When pretreating with CO alone, a typical example would be to use 1/10 atms. absolute pressure at 320 C. and passing 4 liters of CO (NTP) per hour over 10 gms. of Fe for 25 hours. A rate of 25 l. of gas can be employed in conjunction with a total reduction time of 4 hours. With water gas a temperature of 240-250°C. is employed during the reduction. The more hydrogen is present in the reduction gas, the less is the tendency to build up carbon during the reduction and the synthesis that follows. The reduction with CO alone does result in the formation of specially active catalysts; however, the highly active catalysts tend to give carbon deposition. In the preparation of the iron catalyst, it was found that the use of pure ferrous or pure ferric compounds is not desirable, while a mixture of the two produces good results. The ratio of ferrous to ferric compounds in the mixture is not important, and wide limits can be tolerated. Ferrous chloride in dilute solution (50 g. Fe per liter of solution) and ferric nitrate are precipitated very rapidly at the boiling point. The precipitate is quickly filtered, washed free of alkali, then mixed with water and potassium carbonate is added in the required amount. Actually, all sorts of potassium salts can be used to provide the alkali. The catalyst is dried in air, since the oxidation that takes place does not matter and then subjected to the pretreatment.

e) Magnetic-chemical investigation of the Iron catalyst.

The magnetic-chemical investigation of the iron catalyst was undertaken by Pichler in connection with the mechanism of the reaction and changes in the catalyst during its lifetime. The work was started in 1944 and is being continued at the present time. The earlier theories on the carbides of iron were that higher carbides are formed during the synthesis and are necessary for its reaction. By higher carbides are meant Fe_2C and possibly even more carbon-rich iron compounds. The present study showed that, although higher carbides can be formed at 220°C., these decompose at higher temperatures (such as 300-400°C.), leaving Fe_3C as the only stable component. It was found that the most active catalysts were those containing the most Fe_3C. When the catalyst is pretreated at vacuum, that is at about 1/10 atms absolute pressure, more Fe_3C is obtained than when the pretreatment is carried out at atmospheric pressure. During the synthesis, the amount of Fe_3C decreases as the catalyst loses activity, while the concentration of Fe_3O_4 increases. An equilibrium, or possibly a pseudo-equilibrium mixture, of Fe_3C and Fe_3O_4 appears to exist in the catalyst. Thus, when a catalyst containing this apparent equilibrium mixture is used in the synthesis, there is no rapid drop in activity, while with a higher concentration of Fe_3C an initial decrease in activity is observed.

In previous work, attempts were made to prepare Fe_2C. This was done by passing hydrogen over iron oxide to get reduction and then passing CO over it. The amount of CO_2 formed was measured. Then H_2 was again passed over the catalyst at higher temperatures and the amount of methane formed was determined. From the data it was concluded that Fe_2C has been formed under these conditions. However, later magnetic (Curie point) measurements showed that Fe_3C is also present. This indicates that, along with Fe_2C and Fe_3C, a third carbide must be present, and this compound must be still richer in carbon than Fe_2C. In other words, the Fe_3C cristallites must therefore be embedded in a phase the C = Fe ratio of which exceeds 2 = 1, and indeed, additional Curie points were observed but not identified.

At higher temperatures, Fe_3C becomes sintered, and care has to be taken to maintain the temperature low enough to prevent it. The formation of Fe_3C does not take place if you charge the fresh untreated catalyst with water gas under pressure at 220°C. Some Fe_3C can be obtained at 280°C under such conditions, but the catalyst produced is not good.

f) Synthesis with Iron Catalysts.

1) Effect of Pressure.

The preferred operating pressure is 20 atms. since a higher conversion is attained and the paraffins produced have a higher molecular weight. At 10 atms. essentially the same catalyst life is attained, but below 10 atms., the life of the catalyst decreases. Above 20 atms., the tendency is to produce oxygen containing compounds, and at 50 atms, the catalyst life is decreased. In actual operation, taking apparatus costs into consideration, an operating pressure of 10 atms has been favored.

2) Effect of synthesis gas composition.

An equimolar mixture of CO and H_2 is considered to be a suitable synthesis gas composition. The higher the CO concentration in the synthesis, the higher is the required conversion temperature. A higher conversion is obtained with a gas mixture containing $2H_2$:3CO (cannot use this mixture at 220°C.), but there is danger of carbon formation. With water gas, a temperature of 220°C can be used, and when a gas mixture containing $4H_2$:1CO is employed (no practical significance), the synthesis can be started at 180°C. and continued at 200°C., whereby the products obtained are very similar to those formed using the cobalt catalyst (solid paraffin). The life of the catalyst increases as the concentration of hydrogen in the synthesis gas is increased.

In the beginning of the run, the product from the first few hours is carbon dioxide, which is followed by the formation of hydrocarbons along with both CO_2 and H_2O. 50 per cent of the oxygen from the carbon monoxide goes to CO_2 and 50 per cent to H_2O. In the actual operation with water gas at 20 atms., and starting at 215-220°C., a normal cubic meter of gas produces, exclusive of methane, 130 g. of product. After three months of operation, during which time the temperature is gradually increased to 220-225°C., the yield is 10% lower. A catalyst life of one year with a yield of 120 g. was obtained in one case employing a CO enriched water gas and increasing the temperature to 235°C. In another experiment, using a gas mixture consisting of 3 CO:2 H_2, and employing an inclined reaction tube, the catalyst was in operation for two years. In the last case, a vertical reaction tube could not be employed because the catalyst volume increases due to carbon deposition which would result in plugging.

A typical product from the synthesis using water gas has the following composition:

20% C_3-C_4 hydrocarbons containing 50% olefins
40% gasoline, with an olefin content of 50%
20% of fraction boiling at 200-300°C.
20% of solid paraffin having a melting point close to room temperature.

In the beginning of the run, more solid paraffin is produced. The wax formation is favored by the following factors:

1) Increasing alkali
2) Increasing pressure
3) Decreasing temperature,

while the olefin content of the product increases with the following changes:

1) Decreasing hydrogen in synthesis gas
2) Decreasing pressure
3) Increasing temperature
4) Small effect of changing alkali concentration.

Iso-Synthesis.

The work on iso-synthesis was started in October 1941 and is being continued at the present time. As is known, the normal and middle pressure synthesis produce only small amounts of branched chain hydrocarbons. Thus, with the cobalt catalyst of about 10% of the C_4 fraction is isobutane-isobutylene, with the iron catalyst it rises to about 15%. In the C_8 fraction, obtained with either cobalt or iron catalyst, the concentration of iso-compounds rises to 20%, while in the C_{16} fraction, only branched compounds are encountered. Usually the branching does not exceed the presence of one methyl group on a long chain, and no quaternary carbon atom compounds have been found. An examination of products from different Fischer-Tropsch plants gave similar results as far as the extent of branching is concerned, and no difference was found between normal and middle pressure products. When high temperatures and pressures were used with the iron catalyst, formation of carbon, carbonyls, and carbonyl-hydrogen compounds was encountered, but there was no increase in the concentration of iso-compounds in the liquid product. The formation of large quantities of iso-compounds was believed to be possible by first forming higher alcohols, primarily isobutanol, then dehydrating the alcohols, and then hydrogenating the olefins formed to the corresponding iso-paraffins. The combination of all three reactions in one stage makes it possible to achieve a synthesis of iso-paraffins from carbon monoxide and hydrogen in one step.

A number of catalysts have been found which are suitable for this reaction. These are:

1) $ZnO - Al_2O_3$
2) ThO_2
3) $ThO_2-Al_2O_3$
4) Al_2O_3
5) Zno with ThO_2, or CeO_2, or ZrO_2

The reaction is carried out at 450°C. and 300 atms. pressure. The reaction does not take place at atmospheric pressure, but as the pressure is increased, the yields are improved. Above 300 atmospheres, oxygen-containing compounds begin to be formed and in increasing quantities. The throughput used in this process is 5-10 times higher than that used in the regular Fischer-Tropsch process. An example would be the processing of 20 liters of gas (NTP) over 30 gms. of ThO_2 per hour.

The preferred composition of the synthesis gas for this reaction is 1.2 CO : 1 H_2. The yield of product varies from as low as 60 gms. of C_4 and higher to 110 gms. of the same fraction depending upon the catalyst employed for the reaction. With the $ZnO-Al_2O_3$ catalyst, the yield of the C_4 and higher fraction is 80 gms. per cu.m. of gas. The yield of propane under these conditions is 10 gms. The higher compounds are produced in the following proportions:

C_4H_{10} (90% isobutane)	60-70% by weight.
C_5H_{12} (96-98% isopentane)	20-30% by weight.
C_6, C_7 and C_8 compounds	small amounts.

The C_6 fraction contains no neohexane, but primarily 2-and 3-methylpentanes and no normal hexane. Some naphthenes have been found in the higher boiling fraction. The yield of the C_6-C_8 fraction is higher at the lower temperature. Aside from the hydrocarbons produced, some alcohols, amounting to less than 10% of the hydrocarbon production, are also formed. This lower layer of alcohols consists of a small amount of methyl alcohol and a large amount of isobutanol. The exit gas from the iso-synthesis consists of 30% CO_2, 20% N_2, 10% CH_4 (Max.), the rest being CO and H_2.

In the case of the $ZnO-Al_2O_3$ catalyst, an equimolar mixture of the two components is used. When more Al_2O_3 is employed, more C_3-C_4 is obtained, while when more ZnO is present, the proportion of higher compounds is increased. The catalyst is prepared from the nitrates, the dilution being such that about 2-3 liters of water are used to dissolve the required quantity of the nitrates to give 100 gms. of final catalyst. The solution is heated to boiling and a solution of sodium carbonate is added rapidly. The precipitate is washed free of alkali, dried at 110°C for overnight and then heated in air for 2-3 hours at 300°C. A better catalyst is prepared by individual precipitation of $ZnCO_3$ and $Al(OH)_3$ and mixing the two fresh slurries. The aluminum hydroxide is best prepared by reacting a solution of sodium aluminate with carbon dioxide or sulfuric acid.

The thoria catalyst is of interest because this catalyst is capable of performing all the functions required in the reaction. This catalyst is prepared by dissolving thorium nitrate in water (5 lit. for 100 g. of ThO_2) heating to 100°C. and rapidly precipitating with sodium carbonate (no excess of sodium carbonate should be used) while stirring. This is followed by washing until free of alkali, drying at 110°C. and further drying in air at 300°C. for 2-3 hours. The cake is broken up in 2-3 mm. granules before the final drying and used as such in the synthesis. With this catalyst, using a throughput of 20 l. of synthesis gas (NTP) per 30 g. of ThO_2, the yield of butane and higher hydrocarbons per cu.m. of synthesis gas is 60-80 g. In addition, a small amount of water and water soluble alcohols, such as methanol, is obtained.

A better catalyst than thoria alone is the thoria-alumina catalyst, used in equimolar quantities. The preparation consists in mixing fresh slurries which have been previously washed free of alkali and then boiling off the water from the slurry mixture. Filtration apparently requires too long a time. The yield of C_4 and higher hydrocarbons using this catalyst is 100-110 gms. per cu.m. of gas.

The use of alumina alone as a catalyst is not recommended since this catalyst produces too much carbon, although the reaction does take place to give iso-compounds. The zinc oxide-aluminum oxide catalyst produces slightly more alcohols than the thoria-alumina catalyst. The carbon formation with the zinc oxide-alumina is lower than with the thoria-alumina catalyst, the former catalyst remaining white for long periods of time. The life of the catalyst depends upon the severity of the treatment, the regeneration with air does not produce a catalyst activity decrease. The frequency of regeneration is again dependent upon the temperature used during the synthesis; with the zinc oxide-alumina catalyst, three regenerations are required in 4-5 months.

Temperature has a very profound effect upon the reaction. At 400°C., a considerable quantity of alcohols is produced, somewhat higher temperatures result in the formation of dimethyl ether, while at 450°C., isobutane is formed.

At still higher temperatures, the carbon deposition becomes excessive and the catalyst has to be regenerated every few days. The size of the reaction tube is claimed to have an effect upon carbon deposition. 12 to 15 mm. tubes can be used satisfactorily, while the use of larger diameter tubes entails the danger of excessive carbon formation.

Aromatization.

The formation of aromatics from carbon monoxide and hydrogen is effected at 475-500°C., 30 atms. pressure and in the presence of a chromia or molybdena catalyst. The yield of liquid products is extremely small, usually below 10 gms. per cu.m. of synthesis gas. This liquid product contains xylenes and toluene. Most of the gas is converted to methane and carbon. It has been pointed out that, in general, alcohols are produced in the range of 300-400°C., isoparaffins in the range of 400-475°C., while aromatics are obtained at 475-500°C. In view of limited time, no further information on aromatization was obtained.

Interrogation of Dr. Koch, April 17-18, 1945.

The major topics which have been investigated by Dr. Koch and his associates since 1940 are as follows:

1. Alkylation in the presence of hydrogen fluoride.
2. Super-fractionation of alkylates, synthesis and isomerization products.
3. Aromatization of pure hydrocarbons from the standpoint of:
   a) reaction mechanism, effect of structure,
   b) catalysts for aromatization.
4. Isomerization of C_4-C_8 paraffins in the presence of aluminum chloride and hydrogen chloride.
5. Polymerization of alpha-olefins to lube oils.
6. Isomerization of olefins in the presence of catalysts such as cobalt, alumina and phosphoric acid.
7. Cracking and isomerization of pure hydrocarbons in the presence of aluminum chloride.
8. Analytical procedures - mostly by superfractionation.

9. Isomerization of paraffins - determination of equilibrium in the C_4 fraction.

10. Methylation.

11. Synthesis of alpha-olefins.

12. Study of mechanism of decomposition of paraffins in the presence of aluminum chloride, hydrogen chloride and hydrogen.

Most of the reports on this work are contained in a box which has been removed by Dr. Ziegler, director of the Institute. Upon questioning Ziegler in Halle, it was found that this box was not taken by him to Halle, but was shipped to Ringelheim, from where it was taken to a mine at "Hermann Göring Werke" in Salzgitter, and either Dr. Weinrotter or Dr. Gilfert know where it is located. *

Olefins in Fischer-Tropsch Products.

According to Dr. Koch, the Fischer-Tropsch synthesis does give alpha-olefins as the most likely primary products. The beta-olefins are formed from the alpha-olefins through an isomerization reaction, the degree of this isomerization being dependent upon the ratio of hydrogen to carbon monoxide, pressure and catalyst. An investigation of the C_4 cut for alpha and beta olefins showed that by increasing the ratio of hydrogen to carbon monoxide, a greater concentration of beta-olefins is obtained, presumably by means of atomic hydrogen. A higher operating pressure gives more alpha-olefins. The use of the iron catalyst produces a higher concentration of alpha-olefins. This is shown in the following table:

Catalyst	Butene-1/butene-2
Cobalt at normal pressure	0.25
Iron at 10 atms.	0.67-1

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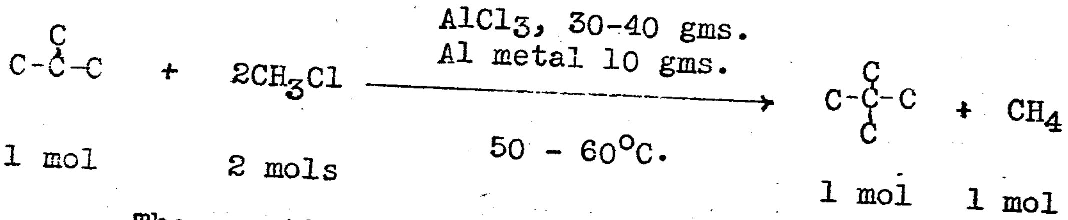
* Upon locating Dr. Gilfert at Steinlah (near Salzgitter) it was found that these documents had been removed by Lt. Aldrich, of the U.S.Navy. So far, the documents have not reached CIOS, London.

It is realized that the comparison is not strictly accurate because the two catalysts have been used at different pressures, and higher pressures do give a higher concentration of alpha-olefins. No information on the ratio of butene-1 to butene-2 produced by the cobalt catalyst at medium pressure is available. No information is available on the effect of temperature used in the synthesis.

Two methods have been used for the separation of alpha and beta olefins. The first one involves the use of peracetic acid oxidation according to the method of Böseken and Sturman, Rec. Trav. chim. Pays Bas 56, 1034 (1937); this method has been used without modification. A better and quicker method involves the use of mercuric acetate in glacial acid. The alpha-olefins form a compound and give a lower layer, while the beta-olefins remain in the upper layer. In the second step of the treatment with mercuric acetate, the upper layer is contacted and a new lower layer is obtained; this time, it contains the beta-olefins. The treatment is carried out at room temperature. A complete description of the method is contained in the few documents that were picked up on the spot.

Methylation.

The methylation reaction has been developed at the Institute for the conversion of lower paraffins into more highly branched paraffins containing one more carbon atom in the molecule. The reaction involves the use of methyl chloride, aluminum chloride and aluminum metal along with the paraffin which is to be methylated. The reaction works best in the case of isobutane which can be converted quantitatively into neopentane, as shown by the equation:



$$\underset{1\ \text{mol}}{\mathrm{C{-}\overset{C}{C}{-}C}} + \underset{2\ \text{mols}}{2CH_3Cl} \xrightarrow[50 - 60^{\circ}C.]{\substack{AlCl_3,\ 30\text{-}40\ \text{gms.} \\ Al\ \text{metal}\ 10\ \text{gms.}}} \underset{1\ \text{mol}}{\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}} + \underset{1\ \text{mol}}{CH_4}$$

The reaction is carried out in an autoclave (400 cc. capacity for the amount of charge shown above) for a period of 24 hours. The pressure rises from an initial pressure of 15 atms. to a final pressure of 60 atms. The aluminum metal is converted to $AlCl_3$ during the reaction. The aluminum metal used is in the form of powder.

The same reaction was tried with isopentane, di-isopropyl and normal butane. With the first two compounds, the expected formation of neohexane and triptane did not take place, since apparently, under the experimental conditions, the tendency of both the reactant and the product is to decompose into isobutane. Thus, neopentane was again formed. With normal butane, the product obtained is also neopentane since the starting material undergoes isomerization to isobutane during the reaction.

The reaction was also investigated by using $CHCl_3$ and CCl_4 as the "methylating" agents. Reaction did take place but a variety of products was formed.

Miscellaneous Reactions Employing Aluminum Chloride.

The reaction of carbon tetrachloride with normal hexane proceeded according to the following equation:

$$CCl_4 + n\text{-}C_6H_{14} \xrightarrow[30\text{-}40^\circ C.]{AlCl_3} CHCl_3 + iso\text{-}C_4H_{10} + n\text{-}C_4H_{10} + \text{sludge.}$$

The reaction was carried out at atmospheric pressure using a glass flask with a stirring mechanism. The iso- and n-butane were formed in proportions equivalent to the equilibrium amounts for that temperature.

In the case of the reaction of normal butyl chloride with normal heptane, as shown in the following equation:

$$n\text{-}C_4H_9Cl + n\text{-}C_7H_{16} \xrightarrow[30\text{-}40^\circ C.]{AlCl_3} n\text{-}C_4H_{10} + iso\text{-}C_4H_{10} + \text{higher compounds.}$$

the butane fraction was allowed to evaporate from the reaction zone as soon as it was formed and the ratio of iso- to n-butane did not correspond to that given by the equilibrium.

A number of paraffins were decomposed in the presence of aluminum chloride, hydrogen chloride and hydrogen. Usually, for one mol of the paraffin, the amount of $AlCl_3$ employed was 1/5 mols, the amount of HCl varied from at least one mol to as high as three mols. The reactor was pressured up with hydrogen after introducing the hydrogen chloride. It was found that clean products of hydrocracking were obtained from starting materials such as normal pentane up to normal dodecane. At least 50-100 atms. was required to keep the aluminum chloride clean, that is, there was no sludge formation. The temperature required for the hydrocracking reaction varied from 50 C. for dodecane to 80-100°C. for normal hexane. Even higher temperatures were necessary when decalin (decahydronaphthalene) was reacted in a similar manner.

Of particular interest was the fact that with normal heptane no propane was formed when no hydrogen was used, while in the presence of hydrogen a clean split into isobutane and propane was obtained. Normal octane decomposed into two molecules of isobutane.

Preparation of alpha-olefins.

No new ways of preparing alpha-olefins by cracking have been found.

The method developed by Ziegler produces "perfectly pure" alpha-olefins, and consists of contacting $n\text{-}C_4H\,Cl$ with lithium metal in benzene solution to give $n\text{-}C_4H_7Li$ and lithium chloride. The lithium alkyl is heated to 100°C. to give the pure alpha-olefins and lithium hydride. The reaction is believed to be general for all sorts of compounds, but has not been tried with very many higher chlorides.

Miscellaneous Studies.

The following topics have been investigated at the Institute and some of them reported in the literature:

1. Formic Acid Synthesis - Brennstoff Chemie p.73 (1942)
2. Acetic Acid Synthesis from carbon monoxide and methanol was not successful because of numerous side reactions which prevented a good yield of acetic acid. Work discontinued.
3. City gas manufacture - Brennstoff Chemie p.244 (1941)
4. The resistance of steel to CO (up to 1000 atms. and 200°C.) also data on carbonyl formation and equilibrium determinations. Brennstoff Chemie p.133(1940)

5. Determination of the isobutane concentration in the butane cut from low temperature carbonization gas. Very little isobutane was found.

6. Polymerization of ethylene with $AlCl_3$ and $AlBr_3$ Work done before the war but the results have not been reported in the literature. Conclusion reached was that iron and oxygen had to be kept out of the reaction zone for successful operation.

7. Comparison of HF and H_2SO_4 alkylates, composition was found to be very similar. Some work has been done on the effect of temperature upon the composition.

Interrogation of Dr. Ziegler at Halle.

The work of Dr. Ziegler at Halle and at Mülheim concerned itself with the metallo-organic compounds and preparation of pure hydrocarbons using metallo-organic compounds as intermediates. New olefins were synthetized from butadiene, lithium alkyls and alkyl halides.

No successful method of preparing hexamethylethane in good yields has been found. Have tried the following:

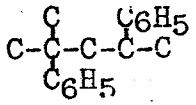
$$(CH_3)\,2C{=}N \;--\; N{=}C(CH_3)2 \quad \text{plus} \quad 2\ CH_3Li$$

to give (after hydrolysis ?)

$$(CH_3)_3C-NH-NH-C\ (CH_3)_3$$

followed by elimination of nitrogen to give the hexamethylethane, but the reaction failed.

Sym. Tetramethyldiphenylethane has been prepared and tested out as an antiknock agent in 1-2% concentration in gasoline. The result was that the octane number went down by 2-3 points. However, the use of 2,4-diphenyl-2-methylpentane :



$$C-\overset{C}{\underset{C_6H_5}{C}}-C-\overset{C_6H_5}{C}-C$$

resulted in an increase in octane number by 2-3 points.

Some work has been done on the analysis of dinitrotoluene in TNT, but no practical analytical methods have been developed.

The purpose of the visit to Dr. Ziegler was to find the box of documents relating to the Institute. As pointed out above, the box has been shipped elsewhere.

VLADIMIR HAENSEL.