T.A.C. REPORT S: MC-6

(T.O.M. REPORT No. 12)

REPORT ON INTERVIEW WITH DR. J. W. REPPE
I.G. FARBENINDUSTRIE, A.G. AT GENDORF, GERMANY

Interviewed May 19 & 20, 1945

Reported by

E. B. Peck,   U.S.A.
Irvin H. Jones, U.S.A.

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of the

PETROLEUM INDUSTRY WAR COUNCIL

REPORT ON INTERVIEW ITH
Dr. J. W. Reppe
I.G. Farbenindustrie,A.G.
at
Gendorf, Germany
on
May 19-20, 1945

Reported by

Dr. L. B. Peck,
Irvin H. Jones.

on behalf of

U.S. Technical Industrial Intelligence Committee

CIOS TARGET No. 30/Opportunity

Fuels and Lubricants.

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear), APO 413.

R E S T R I C T E D

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T.I.C. REPORT SnMC-6

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REPORT ON INTERVIEW WITH DR. J. W. REPPE
I.G. FARBENINDUSTRIE, A.G. AT GENDORF, GERMANY

Dr. J. W. Reppe, director of I.G. Farbenindustrie and
head of the Hauptlaboratorium at Ludwigshafen, was interviewed
with respect to his contribution to the German war effort. He
played an important part in the last war (1914-1918) in develop-
ing the German process for making mustard gas but has had nothing
to do with war gases in this war.

His principal contributions to this war were stated
to be:

    a.   Synthesis of a substitute for blood plasma
          called Periston;
    b.   An adhesive that makes Buna adhere to fabric
          and is called Korosin - it formed an essential
          part of the German synthetic rubber program;
    c.   New reactions in the synthesis of butadiene.

Dr. Reppe and his co-workers have developed new processes
that involve novel reactions of the acetylenes, olefines and re-
actions of metallic carbonyls; these developments will probably
be of future industrial importance and are discussed below along
with other reactions described by Dr. Reppe.

The industrial success of the above acetylene chemistry
depended first on the development of safe method and means of
handling acetylene (C_2H_2) under pressure, and for some of its
reactions, and the safe use of large quantities of metallic
acetylides - more especially that of copper. Reppe's laboratory
has C_2H_2 piped at 30 atm. pressure and plans are made to use it
at pressures of 150 atm. Basic investigations of explosions in
compressed acetylene in the absence of oxygen in small bombs showed
that the pressures developed to 10 times its initial partial
pressure in a mixture and that the large scale application depended

(1) on the provision of equipment to withstand such possible pressure increases and (2) restricting possible explosions to rather small volumes. This latter requirement was met in small-scale apparatus by using for a required delivery of acetylene instead of a single pipe a plurality of smaller pipes about one inch in diameter through which more than a given output of acetylene was continuously circulated by looping the lines back to the suction-side of the large capacity compressor and by using one-way bicycle-tire valves at spaced intervals in the lines. In larger installations, the 4-6 inch pipelines were completely filled throughout their length with pipes of small diameter (about 5-10 mm.) to form a sort of honeycomb structure throughout their extent. The latter has worked so well that, in the large plant for manufacturing about 4500 tons per month of butindiol from acetylene and formaldehyde at Ludwigshafen, of the three explosions experienced, only the lines were burnt through in a very small area without further trouble. After these explosions, the tubes were carefully cleaned and re-assembled.

Explosions are prevented in large masses of metal-acetylide catalysts by keeping them wet. They are formed in situ by depositing a salt of the required metal, for example the nitrate, on silica-gel pellets and heating the same for conversion of the nitrate to the oxide and thereafter treating them with acetylene under pressure. The only acetylide catalyst in commercial plants is made by reacting copper oxide with acetylene in situ (see butindiol process).

Acetylene Chemistry.

Reactions of Alcohols and Acetylenes.

Dr. Reppe discussed the well-known reaction between acetylene and alcohols and stated that the reaction was quite general for both aliphatic and aromatic alcohols including primary and secondary alcohols, mercaptans and phenols. Potassium hydroxide is employed as the catalyst. Ethers and esters and secondary amines also react with acetylene under pressure. For example, the reaction between methyl alcohol and acetylene goes very smoothly at about 200°C. to give methyl vinyl ether in the presence of KOH:

$$CH_3OH + HC \equiv CH \longrightarrow CH_3O - \overset{H}{C} = CH_2$$
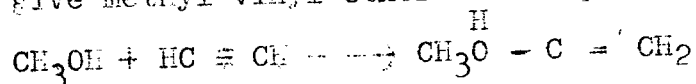
Methyl vinyl ether is hydrolyzable at 180°C. with water to give acetaldehyde and methyl alcohol and the latter can be returned to the process.

This production of acetaldehyde without a mercury catalyst
was considered important for German industry because 2 kgs of mer-
cury are lost in the production of a ton of Buna; however, a plant
was never built.

Another important reaction of acetylene and an alcohol
is that with phenol, also employing KOH as the catalyst, which
gives first phenyl vinyl ether that can convert to vinyl phenol.
Depending upon the amount of acetyle substituted on the benzene
nucleus, will depend the characteristics of the polymer made from
the resultant oxystyrenes wherein the vinyl groups are normally
in the ortho and para position to the hydroxy group. To make a
resin of the Bakelite type, phenol is reacted with acetylene at
a pressure of 10 atm.

Organic zinc salts, for example the naphthenate, are
good catalysts for the phenol-acetylene reaction and they can
give substituted oxy-styrenes that are solids.

Although the mercaptans, as above mentioned, react with
acetylene to give products analogous to those derived from the
oxygen alcohols, the products are malodorous and are not of par-
ticularly practical value.

Korosin, the adhesive for synthetic rubber, is made by
reacting isobutylphenol with acetylene. This was considered an
indispensable development in the German synthetic rubber program
as this material bound the synthetic rubber to the fabric. It
also assists in producing a tire that does not get hot in use.
In this case, the acetylene does not form an ether but substitutes
for hydrogen on the benzene ring under the influence of zinc naph-
thenate as the catalyst. The reaction takes place in the liquid
phase (Rieselverfahren) forming the hypothetical monomer shown
below which, however, polymerizes as formed:

$$OH$$

$$H-C=CH_2$$

$$H_2C$$

$$H_3C-C-CH_3$$
$$H$$
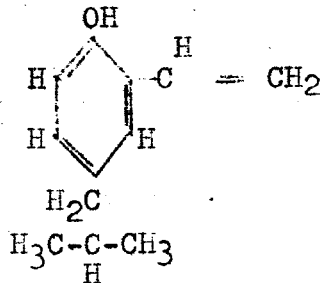
At Ludwigshafen, the I.G. Farbenindustrie has a small
plant for the production of vinyl ether especially from methyl
alcohol and acetylene. The reaction was carried on in liquid
phase at 15 to 20 atm. pressure of acetylene which was delivered
to the reaction vessel as a 50-50 mixture with nitrogen; the total
pressure in the system was thus about 30-40 atm. The compressors
were of the vertically-reciprocating piston type and the connecting
rods were enclosed in a transparent case to prevent ingress of
dust as a precaution against friction and possible explosion that
the presence of dust in the cylinder would cause. The compressors
were of the usual type and were capable of delivering 100 and 180
m^3 per hour.

Reactions of Aldehydes with Acetylene.

Such aldehydes as formaldehydes, acetaldehyde, propion-
aldehyde etc. can be reacted with acetylene under pressure in the
presence of metallic acetylides to form unsaturated alcohols.
Either one or two molecules of the employed aldehyde can react
with the acetylene and the so-formed alcohols have as many carbon
atoms as are present in the reacted reagents, for example with
acetylene and formaldehyde, there can be prepared both

(1) Propargyl Alcohol $HC = C-CH_2OH$
(2) Butine 3 diol 1,4
                 $HOCH_2 - C = C - CH_2OH$

The reaction is one of the most promising developments
of Mr. Reppe and his co-workers. The above alcohols are made by
introducing a mixutre of reaction products with sufficient of a
35% aqueous solution of formaldehyde to provide a 10% solution
of the latter in concurrent flow into a tower that is packed with
copper acetylide (10-12%) deposited on baked silica gel pellets.
The catalyst is prepared by depositing CuO $(Cu(NO_3)_2$ and roasting -
it may contain some Bismuth also - and treating with acetylene
in situ in the contact vessels in the presence of water at 60-70°C.
The reaction may be controlled to make up to 70-80% of the product
as propargyl alcohol, but the usual procedure makes 92% of said
butinediol and 4% propargyl alcohol. The latter is recycled when
only the diol is wanted. The reaction conditions employed are 5
atm. pressure and 100°C. The acetylene is employed in excess
and is dry upon entering the process; it therefore evaporates
water sufficiantly to remove the exothermic heat of reaction. The
outlet gaseous mixture from the reactor should be water-vapor and
acetylene in the ratio of respectively about 4 to 1.

A plant has been running at Ludwigshafen for two years at a capacity of 4500 metric tons per month of butinediol. In this plant the acetylene is compressed in 2 stages to 5-6 atm. with ring-water centrifugal compressors and the compressed gas (without dilution by N_2) is piped to the honeycomb pipes described above. There are 6 reactors (1.5x18 m.) designed for 50 atm. pressure which however operate at the above 5 atm. only. They are lined with stainless steel (V_4A) and have each a volumetric capacity of 20 m³ of catalyst containing 2000kg. of copper acetylide. The inlet solution of formaldehyde is dripped (Riesel verfahren) through the tower at the rate of 10 m³ per hour concurrent to a stream of acetylene of 1 m³ per hour. The reaction being highly exothermic, the only heating employed is heat exchange in the formaldehyde feed lines. The Leistung is 1 ton of butinediol per cubic meter catalyst per day. The outlet solution from the reactor is distilled to recover 10% unreacted formaldehyde and produced propargyl alcohol which are recycled. Based on formaldehyde, the yield of butinediol is about 90%. There were some difficulties at the beginning of the top of the reactor which were overcome by diluting the formaldehyde solutions, as above described. There have been acetylene explosions in the pipes near the control valve to the reactor, but the only damage was to burn a small hole in the pipe.

The reaction solution contains about 30% butindiol. By evaporation and crystallization from ethyl acetate, the butindiol can be recovered in crystalline form; the butindiol as prepared above in aqueous solution can be hydrogenated while still in such solution to butenediol 1,4 and also to butanediol 1,4 by means of a nickel or copper catalyst at 200-300 atm. by means of circulated hydrogen. The conversion of butindiol 1,4 to Butanediol 1,4 by hydrogenation is 96%.

The butanediol 1,4 (n-butylene glycol) can be recovered from the aqueous solution and be dehydrated in one step to butadiene over a phosphate catalyst as developed by I. G. Farben in 1926. The butanediol is now made at Ludwigshafen for 60 pfg. per kilo and it is expected to reduce this to 40-50 pfg. per kilo.

However, it is preferable because of higher yields and for other reasons according to Dr. Reppe, to dehydrate the butanediol to butadiene in two steps: that is, first to tetrahydrofurane and then the latter to butadiene.
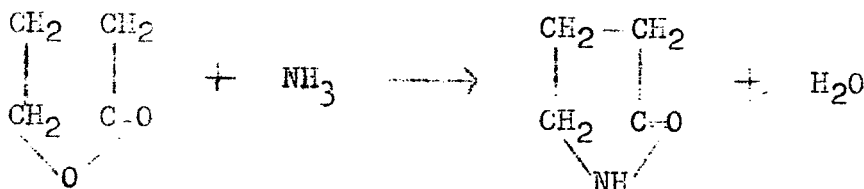
Tetrahydrofuran appears to be an important new building block in synthetic chemistry. It is a good solvent for many types of compounds including also such high polymers as polyvinylchloride, polyvinyl carbazol, natural rubber and Buna. It enters many
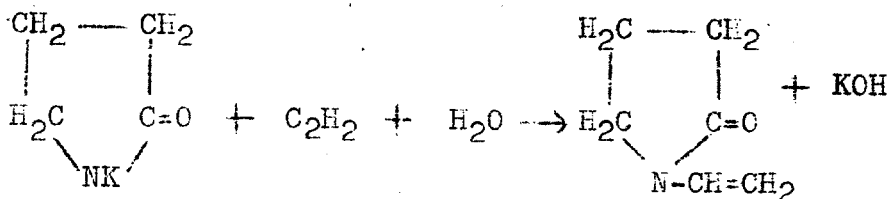
reactions. Adipic acid can be made therefrom (see below). In the above aqueous solution of 30-35% butanediol 1,4, obtained by hydrogenation of the reaction product of formaldehyde and acetylene, the former can be dehydrated to tetrahydrofuran in said solution by the addition of a small amount of H_3PO_4 and maintaining the pH at at least 2 and distilling the mixture at a temperature of about 260-300°C. and a pressure of 60-100 atm; the THF (tetrahydrofuran) is easily volatilized under these conditions and is quantitatively produced. The Na and Ca ions in the solution added for control of the pH value are substituted by H ions and by ion-exchange media (Wolfatite).

The THF can then be converted at 260-280°C. to butadiene by means of a phosphate catalyst; it can also be treated with metallic carbonyls and converted to adipic acid.

Butanediol 1,4 is also the starting product for the new blood plasma substitute. By oxidation of its hydroxy-groups to aldehydes by simple spraying over a Cu catalyst at 200°C. by the well-known Cannizzaro reaction, there is produced gamma hydroxybutyric acid and butyrolactone which is the end-product of the reaction, and gamma butyrolactone by reaction with liquid ammonia at 250°C. gives alpha pyrrolidon, as described by Prof. Späth of Vienna, and in accordance with the following equation:

$$
\begin{array}{c}
CH_2 \quad CH_2 \\
| \qquad | \\
CH_2 \quad C{-}O \\
\diagdown \quad \diagup \\
O
\end{array}
\;+\; NH_3 \;\longrightarrow\;
\begin{array}{c}
CH_2 - CH_2 \\
| \qquad | \\
CH_2 \quad C{-}O \\
\diagdown \quad \diagup \\
NH
\end{array}
\;+\; H_2O
$$

Conversion of pyrrolidon to its potassium salt and the latter's reaction with acetylene, similarly to the known preparation of vinyl carbazole, gives a N-vinyl-pyrrolidon which is the monomer of Periston.

$$
\begin{array}{c}
CH_2 - CH_2 \\
| \qquad | \\
H_2C \quad C{=}O \\
\diagdown \quad \diagup \\
NK
\end{array}
\;+\; C_2H_2 \;+\; H_2O \;\longrightarrow\;
\begin{array}{c}
H_2C - CH_2 \\
| \qquad | \\
H_2C \quad C{=}O \\
\diagdown \quad \diagup \\
N{-}CH{=}CH_2
\end{array}
\;+\; KOH
$$

Vinyl Pyrrolidone can be polymerized to Periston by aqueous solution of $NaHSO_3$ or by oxidation with H_2O_2 at a temperature of 70-80°C.; the H_2O_2 is the catalyst and is employed in amounts of 0.05 to 1% plus NH_3 to the extent of $\frac{1}{4}$ to $\frac{1}{2}$ of the employed H_2O_2 which determines the degree of polymerization. Periston is neutral, has a high viscosity and is broken down in and eliminated by the human body. It has been used in thousands of German soldiers, but the Allied medical experts have not accepted its use.

By reaction of NH_3 or amines with THF, it is converted to Pyrrolidine and its N- substituted products; these products are valuable in insecticides and in vulcanization acceleration. The dehydrogenation of pyrrolidine gives pyrrol. The reaction between THF and NH_3 is:

$$
\begin{array}{ccc}
CH_2 - CH_2 & & CH_2 - CH_2 \\
| \quad \quad | & + \ NH_3 \ \longrightarrow & | \quad \quad | \quad + \ H_2O \\
CH_2 \quad CH_2 & & CH_2 \quad CH_2 \\
\quad \diagdown O \diagup & & \quad \diagdown NH \diagup
\end{array}
$$

Propargyl alcohol which is made when one mole of formaldehyde adds to acetylene has promising uses. When oxidized with air at 30°C. in the presence of copper chloride, it forms the following:

$$ HO-H_2C-C \equiv C - \begin{array}{|cc|} \hline H & H \\ & \\ \hline \end{array} - C \equiv C-CH_2OH $$

$$ \downarrow O $$

$$ HOH_2-C \equiv C - C \equiv C-CH_2OH $$

Hexadiindiol, 2,4 diin, - 1,6 diol.

This latter compound, on incomplete hydrogenation, yields two isomers of hexdienol -

a) Hexadienediol, 2,4 diene, 1,5 diol -

$$ CH_3-C \overset{OH}{} \quad \overset{H \ H \ \ H \ H}{C-C = C-COH} \ \underset{H}{} $$

b) Hexadienediol, 2.4 diene, 1,6 diol -

$$HOH_2C-C \overset{H}{=} \overset{H}{C}-\overset{H}{C}=\overset{H}{C}-C_2HOH$$
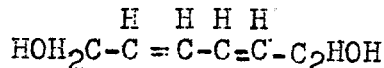
No use is known for the compound (a), but the compound
(b) can be converted to either of two Nylon building blocks. It
is hydrogenated to hexanediol 1,6 and it then can be oxidized with
nitric acid to adipic acid on the one hand, or said diol can be
partially oxidized to give epsilon hydroxy caproic acid that easily
dehydrates to caprolactone; reaction of the latter with NH_3 gives
epsilon caprolactam which has the following structural formula:

$$
\begin{array}{c}
CH_2 \\
CH_2 \quad\quad CH_2 \\
CH_2 \quad\quad C=0 \\
\quad\quad NH \\
CH_2
\end{array}
$$
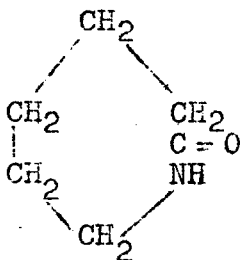
Propargyl alcohol can be partially hydrogenated to give
allyl alcohol and further n-propyl alcohol in neutral or alkaline
solution; in acid solution by hydrogenation the propargyl alcohol
converts to propionaldehyde. Allyl alcohol can be converted to
glycerine either by treatment with hydrogen peroxide (or persalts)
or by conventional method with chlorine and water. For the
hydrogenation step Fe can serve as the catalyst and for the H_2O_2
oxidation to glycerine selenic acid is employed.

Carbonylation.

Carbonylation is the name given to reactions wherein
carbon monoxide is added to another compound, for example to
acetylene, olefine, cyclic oxide, and the like, along with such
a hydrogen-containing compound as H_2, H_2O, ROH, NH_3, RSH, etc.
These reactions include the OXO reaction (olefines - CO - H_2) as
a special case. In this reaction, olefines in liquid phase are
reacted with CO - H_2 in the presence of the Fischer-Tropsch cobalt
catalyst to give a mixture of aldehydes, having more carbon atoms
than the employed olefines; the aldehydes are thereafter hydro-
genated to alcohols for separation by distillation. A character-
istic of this process resides in the fact that, due to the shift

of olefinic double bond along the hydrocarbon chain during the
reaction (isomerization), a multiplicity of isomers of the produced
branched and normal alcohols is formed. Separation of a single
compound in pure form is difficult if not impossible even when
a single olefine is that starting material. This result seems
to be a property of the cobalt catalyst.

Dr. Reppe prefers to use as the catalysts Nickel Carbonyl
($Ni(CO)_4$) or Iron Carbonyl ($Fe(CO)_5$) and H_2O instead of H_2 when
the desired end-product is alcohols; by means of this advance,
Reppe produces from a given olefine, or the like, a mixture of
two isomeric carboxy acids having each one more carbon atom then
the employed starting material, the acids can then be reduced to
corresponding alcohols or aldehydes if they are the desired pro-
ducts. The said acid isomers are usually straight chain and
alpha substituted acids if the employed olefine is a straight-
chained compound.

The nickel carbonyl can be formed outside the reaction
vessel and be added to this reaction mixture or it can be formed
in situ from a nickel salt, for example $NiCl_2$, that forms $Ni(CO)_4$
but in any event it must be present in a stoichiometric relation-
ship to the product formed. $NiCl_2$ in the presence of excess NH_3,
reacts readily with CO at 150-180°C. to give the Nickel Carbonyl,
as follows:

$$NiCl_2 + 2 NH_3 + H_2O + 5CO \longrightarrow$$
$$Ni(CO)_4 + 2NH_4Cl + CO_2$$
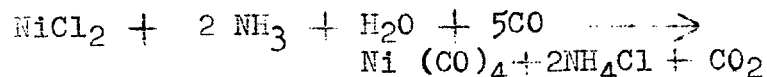
The NH_4Cl is regenerated with CaO.

As an example of the above reaction, the following
synthesis of acrylic acid from acetylene was given, the reaction
taking place at 40-42°C;

$$Ni(CO)_4 + 4 C_2H_2 + 4 H_2O + 2 HCl \longrightarrow H_2 +$$
$$NiCl_2 + 4 CH_2 = \underset{H}{C}-COOH$$
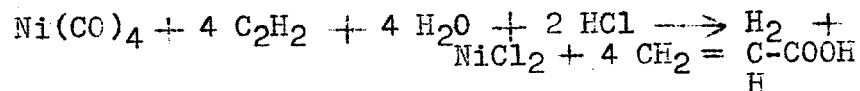
Cobalt and iron catalysts do not react as well in the
above reaction.

Similarly also to acetylene, the olefines react with
CO and H_2O and form saturated acids in the presence of $Ni(CO)_4$;
for instance, ethylene yields propionic acid at 270°C. and 200

atm. pressure, as follows:

$$C_2H_4 + CO + H_2O \longrightarrow CH_3-CH_2-COOH$$
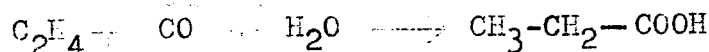
and if an acid is used instead of water in the above reaction, it is possible to go directly from ethylene to propionic anhydride in the reaction -

$$C_2H_4 + CO + CH_3CH_2COOH \longrightarrow (CH_3CH_2CO)_2O$$
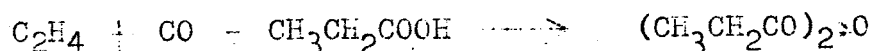
If alcohol, ammonia, or amine is used instead of water, the corresponding ester or amide of the corresponding acid is obtained.

If the employed acetylene or olefine lacks symmetry in respect of the unsaturated bond, two isomers of the formed acid, or the like, are fomed; this is consonant with Dr. Reppe's theory that during the reaction CO unites at the unsaturated bond of the hydrocarbon to form the propenons ring because there thus exists the possibility of severing the ring at either carbon valence of its CO-group; for example, when reacting phenyl acetylene with CO - H_2O, the reaction may progress as follows:

Cinnamic Acid   Atropic Acid
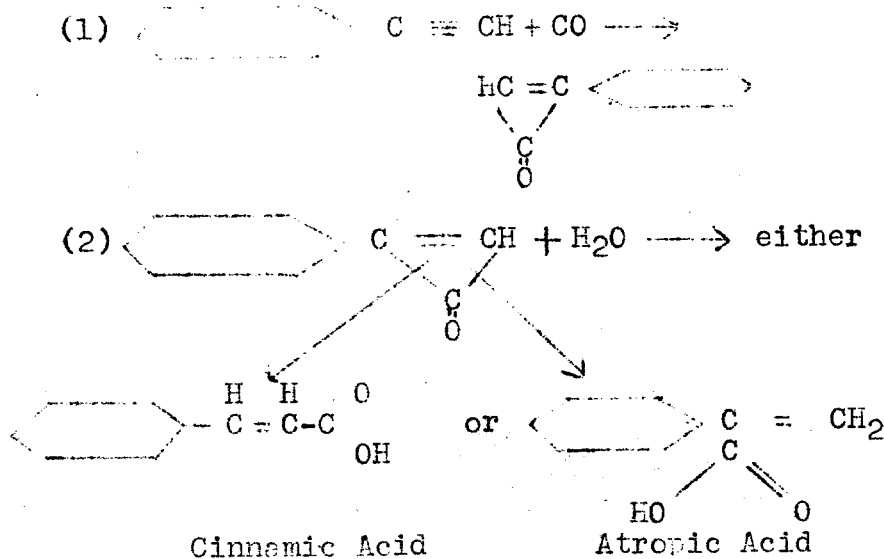
Oleic olefine reacts as above to give corresponding fatty acids.

As aforementioned, these carbonylations can be carried out with $Ni(CO)_4$ added to the reactor or it may be formed in situ

from such soluble nickel salt as nickel chloride activated with
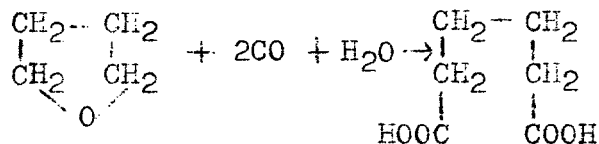sodium iodid - said carbonyl being formed under the pressure con-
ditions of reaction.

In the preparation of propionic acid from C_2H_4, CO and
H_2O, said acid is formed as follows: into a reactor maintained
at about 235°C.-280°C. and at a pressure of 250-300 atm., CO,
C_2H_4 and H_2O are introduced at the bottom thereof, said reactor
also containing elemental nickel or nickel acetate. $Ni(CO)_4$ is
formed from said nickel or its compound by reactions with the in-
flowing CO. In the case of ethylene, as the unsaturated hydro-
carbon, no solvent or liquid phase is necessarily present in the
reactor although it is of advantage. The reactor can be made
with a lining of absolutely pure copper; iodine or other halogens
are not necessary but they have an advantage if apparatus resistant
to them are developed - which copper is not. The use of the hal-
ogens has the disadvantage that they must be eliminated from the
product.

The propionic acid formed in the reactor upon removal
therefore contains some $Ni(CO)_4$ which can be removed therefrom
by volatilization - it is very poisonous and boils at 45°C. and
decomposes in the air. Fractional condensation has been found
effective in performing the separation - the separated $Ni(CO)_4$
can be returned to the process.

When the employed unsaturated hydrocarbon is propylene
or butylene, it is necessary to employ a solvent, such as the
formed acid in the reactor; in the case of the higher olefines
(such as produce fatty acids) the use of a solvent is not necessary
probably because of their high boiling points.

From ethylene up to 95 yield of propionic acid is
obtained.

Not only can monocarboxylic acids be made from olefines
but also from alcohols, and polycarboxylic acids are preparable
from CO and the glycols as well as from cyclic ethers of the latter.
For example, Hexandiol 1,6 smoothly reacts to Suberic acid; and
Tetrahydrofuran with CO - H_2O converts to Adipic acid in the
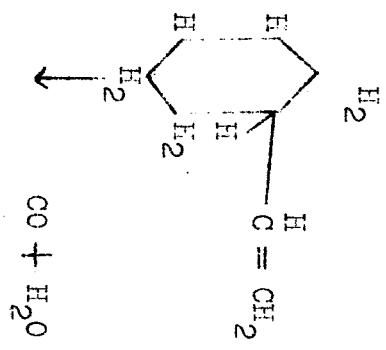presence of the above metal carbonyls as follows:

$$\begin{array}{ccc} CH_2 - CH_2 & & CH_2 - CH_2 \\ | \quad | & + 2CO + H_2O \rightarrow & | \quad | \\ CH_2 \quad CH_2 & & CH_2 \quad CH_2 \\ \diagdown_O\diagup & & | \quad | \\ & & HOOC \quad COOH \end{array}$$

Although not specifically so-stated by Dr. Reppe, it may be assumed, from his above statement, that methyl acetate can be formed from methyl ether -
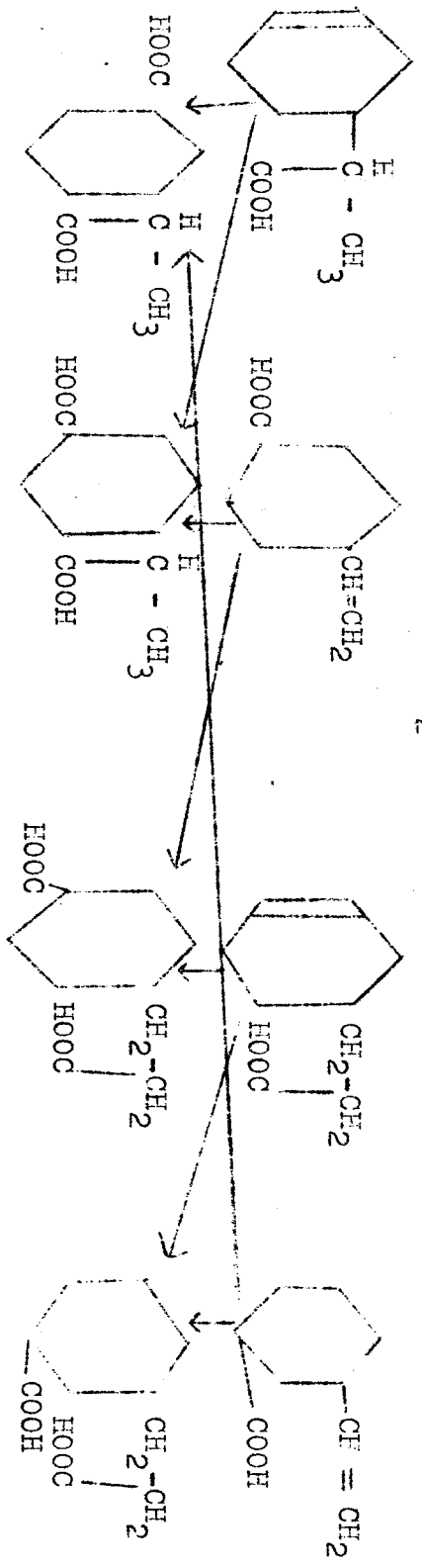
$$(CH_3)_2 {>} O \ + \ CO \ \xrightarrow{\quad NiCl_2 \ + \ NaI \quad} \ CH_3\overset{O}{C} - OCH_3$$
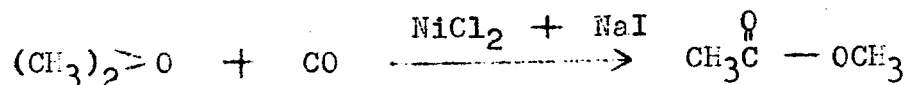
The above carbonylation of the THF is carried out in continuous operation in the liquid phase with $NiCl_2$ and NaI as catalyst at 200 atm. and 270°C. In an 8 liter reactor, 40 liters/hour of CO, measured at 200 ats. is passed counter-current to a downward flow of 300-600 cc/hour of a 10% aqueous solution of THF containing 1% of NaI, the CO being recycled; the conversion of THF to adipic acid is better than 90%.

The diolefin, butadiene, reacts with CO and H_2O in the presence of $Ni(CO)_4$, giving a 70%-90% yield of fatty acids at 200 atm. pressure and about 270°C. The reaction is good for the manufacture of poly-amides to make high polymers of the Nylon-type. The reaction proceeds along rather complicated courses giving a multiplicity of closely-related products. Firstly, under the conditions of reaction, butadiene condenses with itself to form vinyl cyclohexene which then carbonylates at the unsaturated bonds to give carboxy-acids, as shown on the next page.

$$2\ CH_2= CH - CH = CH_2$$

Vinyl cyclohexene

$$CO + H_2O$$

$$H_2$$

$$H_2$$

$$CH=CH_2$$

$$CH_2-CH_2$$

$$CH = CH_2$$

$$CH_2-CH_2$$

HOOC — C — CH$_3$ — COOH

HOOC — COOH

The commercial development of these carbonylations was held up for lack of acid-resisting materials of construction that were not available in Germany during the war.

## Synthesis of Alcohols from Water and Olefines.

At a pressure from 200-300 atm. and a temperature of 300°C. for ethylene and about 250°C. for propylene, these unsaturateds can be converted directly to alcohols by reaction with water in the presence of tungsten oxide supported on silica gel. The tungsten oxide forms about 20% of the catalyst by weight. The higher the pressure employed, the better. Tungsten Trioxide (WO_3) is inoperative but must be reduced at 600°C. to W_2C_5 before starting; about 5% ZnO in methylamine solution promotes the catalyst.

In practising the above process, C_2H_4, for example, and H_2O are introduced at the above pressure into the top of a reactor tower containing the catalyst which is maintained at the above required temperature. From the bottom of the reactor tower, there is withdrawn into an expansion vessel, about a 20% aqueous solution of the formed alcohol. Molybdenum is also operative for the same purpose, but is not as good as the tungsten.

When propylene or butylene are used in the above reactions, the secondary alcohols are produced.

Cyclopolyolefines.

Dr. Reppe discussed his recent developments in the field of cyclopolyolefines, a development that may have only scientific interest, but may have wide future application. He has done extensive research to establish the structural formula of especially C_8H_8 - cyclooctatetraen, which is the counterpart of C_6H_6 in the benzene series of compounds. It is now indisputably established that this compound has the structure -

$$
\begin{array}{ccc}
 & HC = CH & \\
HC & & CH \\
\| & & \| \\
HC & & CH \\
 & C = C & \\
 & H \quad H &
\end{array}
$$
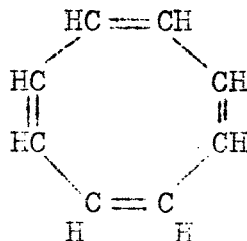
In the preparation of these compounds, acetylene, at a pressure of 10 to 20 atm using nitrogen as a diluent and such

neutral solvent as especially tetrahydrofurane, is coverted at temperature of from 60-70°C. and up to 130-140°C. in the presence of such nickel compounds as its cyanide, thicyanate, or halide into the cyclopolyolefines by condensation with itself. The yield of product from acetylene is about 90%. The formed cyclopolyole- fines are predominently C_8H_8 with minor amounts of $C_{10}H_{10}$, $C_{12}H_{12}$, and some soluble resins, and azulene. The $C_{10}H_{10}$ and $C_{12}H_{12}$ are monocyclic compounds where as the azulene is dicyclic; the latter is an isomer of naphthalene and is formed by the dehydrogenation and rearrangement of cyclododecapentaen.

The inert solvent used is preferably tetrahydrofuran (THF). The actual catalyst is assumed to be a very labile nickel - acetylene compound that is just made from the nickel halide, or the like, by reaction of C_2H_2 under pressure. The formation of nickel acetylide can be promoted by the addition of a cyclic oxide such as ethylene oxide.

The portion of the condensed acetylene that converts to $C_{10}H_{10}$ and $C_{12}H_{12}$ can be considerably increased by variation of the temperature of reaction. At 60-70°C., there is a preponder- ance of cyclooctatetraen formed. The optimum temperature for $C_{10}H_{10}$ is 80-90°C. whereas that for $C_{12}H_{12}$ is 130-140°C. The most azulen (intense blue color) is formed by a by-product of reaction at 120°C. Azulen is a dicyclic hydrocarbon having a C_7 and a C_5 ring with 5 olefine bonds as follows:
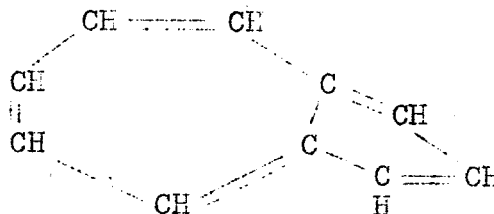
Azulen has a m.p. of 99.5° in the absolutely pure form in which Dr. Reppe has prepared it.

Physical Properties of the Cyclopolyolefines.

	Name	B.P.	Color
1)	Cyclooctatetraen	142-3°C. at 760 mm.	Golden Yellow
2)	Cyclodecapentaen	190-195°C " " at 2 mm. 48-50°C.	Orange
3)	Cycloduodecahexaene	230-235°C. at 760 mm. 60-65°C. at 0.5 mm.	Bright Yellow

The constitution of the latter two compounds has not been definitely established.

These compounds have no practical value; they have been investigated pharmocologically and no essential action established by their use. However, Prof. Kohn at Heidelberg in the case of the $C_{12}H_{12}$ fraction (b.p. 230°C. to 235°C. and colored deep-blue with some azulen - about 3%) determined that the increases of certain pathological bacteria were completely suppressed in dilution of said fraction of 1:100,000.

Dr. Reppe said that the $C_{10}H_{10}$ fraction called cyclodecapentaene did not yield an oxidation sebacic acid and he believes that the compound may be instead vinyl cyclooctatetraene.

Samples of the above three fractions and of the refined azulen prepared by Dr. Reppe were obtained by members of CIOS Trip No. 215 - Ministry of Supply.

In consequence of its olefinic character, cyclooctatetraene is very reactive in the presence of various reagents. It is -

1. Easily oxidized even in the air.

2. Halogens are quickly absorbed.

3. Polymerizes to a dimer and hard resins even upon standing.

4. Forms crystalline addition products with aqueous $AgNO_3$ and cupric-ammonia, chloride solution.

5. Hydrogenatable to cyclooctane.

In certain of its reactions, cyclooctatetraene:-

1. Retains its 8-carbon ring structure.

2. Converts to aromatic series forming derivatives of ethylbenzene and p-xylene; phenylacetaldehyde is formed by water suspension of C_8H_8 with, for example, $HgSO_4$; dehydrogenation of C_8H_8 with Se yields p-xylene.

3. Converts to compounds having both a 6-carbon and a 4-ring; for example, upon halogenation (complete) the highest chlorinated compound is formed in $C_8H_8Cl_6$, m.p. 126°C., and thus shows

there has been an extensive change in structure
to a derivative of C_8H_{14}. Dr. Reppe showed
C_8H_{14} to be -
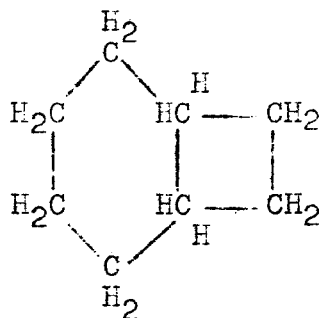
Bicyclo - [0.2.4] - octane m.p. - 136°C.

4. By treatment of C_8H_8 with hypochlorite there is
produced terephthalic aldehyde which must
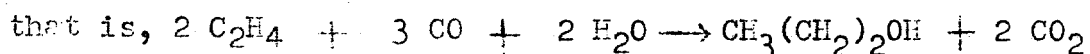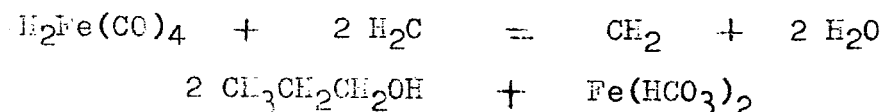be derived from a compound having the basic
structure -
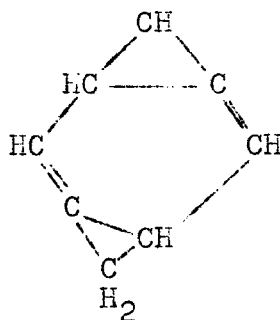
## Recent Advances in Carbonylation Chemistry.

The latest development in the carbonylation chemistry
is the use of the metallic hydro carbonyls which are strong acids
and react quite differently than do the above simple carbonyls.
Dr. Reppe has worked with both the nickel and cobalt hydrocarbonyls.

Dr. Reppe developed new methods of preparing the above
compounds, $H Co(CO)_4$ and $H_2FE(CO)_4$, in large quantities and
studied their physical constants and chemical behavior. This
work showed that $H Co(CO)_4$ belonged to the group of strongest

acids (about like HCl) and that H_2 Fe(CO)$_4$ behaved like an average mono basic acid. These compounds were reacted with acetylene and olefine in the presence of water and the reaction products in the case of the olefines proved to be aliphatic alcohol, and in the case of the acetylene to be hydroquinone, or the like. The empirical equation for the reaction with the iron compound can be the following:

$$H_2Fe(CO)_4 \quad + \quad 2 H_2C \quad = \quad CH_2 \quad + \quad 2 H_2O$$

$$2 CH_3CH_2CH_2OH \quad + \quad Fe(HCO_3)_2$$

that is, $2 C_2H_4 + 3 CO + 2 H_2O \longrightarrow CH_3(CH_2)_2OH + 2 CO_2$

The reaction progresses at about 100-110°C. and needs no Iodine, but there should be present an organic base that does not react with CO (amines), to form the $H_2Fe(CO)_4$, as follows:
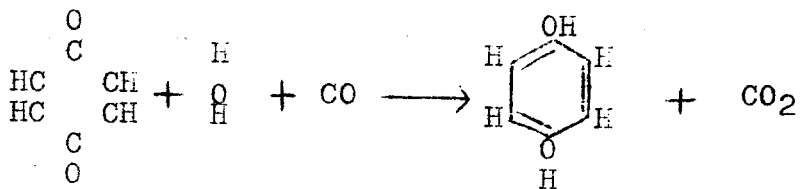
$$2 Fe(CO)_5 + base + 2 H_2O \quad \longrightarrow$$

$$2 H_2Fe(CO)_4 + base + 2CO_2$$
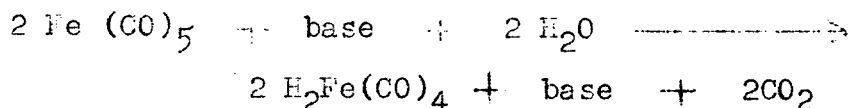
In contrast to $Ni(CO)_4$, the iron hydrocarbonyl can react at ordinary pressure but has the disadvantage that for each CO taken up to form product, two CO_2 molecules are lost. The relation between this reaction and that with $Ni(CO)_4$ as catalyst in the reaction between ethylene, carbon monoxide, and water to give ether propionic acid or its anhydride is recognizable.

If a portion of the water in the above empirical equation is substituted by NH_3, propylamine is produced, as well as the di- and tri- propylamine.

$$CH_2 = CH_2 + 3CO + H_2O + NH_3 \longrightarrow$$

$$H_2N - CH_2 - CH_2 - CH_3 + 2CO_2$$
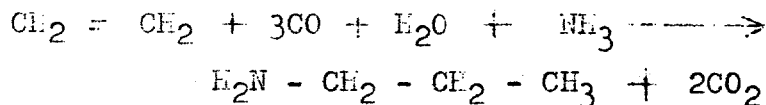
By extension of this olefinic reaction with metallic hydrocarbonyls, Dr. Reppe thought to arrive at unsaturated alcohols but, instead, with substituted acetylene arrived at hydroquinone derivatives in a yield of about 30% as far as his investigations have been conducted; empirically it seems to progress about as follows:

$$HC \begin{smallmatrix} O \\ \| \\ C \end{smallmatrix} CH \quad + \quad \begin{smallmatrix} H \\ O \\ H \end{smallmatrix} \quad + \quad CO \quad \longrightarrow \quad [\text{benzene ring with OH and H substituents}] \quad + \quad CO_2$$

Stoichiometrically, the reagents react in the following ratio:

$$H_2Fe(CO)_4 \quad + \quad 4C_2H_2 \quad + \quad 2H_2O \quad \longrightarrow$$

$$2\ C_6H_6O_2 \quad + \quad Fe(OH)_2$$
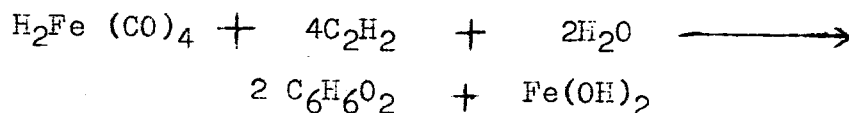
When employed substituted acetylenes and $H_2Fe(CO)_4$, benzene derivatives are formed; for example $CH_3 - C \equiv CH$ yields trimethylbenzene.

The success of this new carbon-monoxide chemistry is attributable to this first use of these hitherto unusable catalysts or their substitution products, i.e. metal carbonyls or metal hydrocarbonyls, as is also the similar situation in the use of the heavy metal acetylides and their first employment as catalysts in the ethylenetion reactions.

(The metallic hydrocarbonyls are not new chemical compounds. They have been extensively investigated by W. Hieber and his colleagues. In 1932, he and others published method of preparation and certain reactions of $Fe(CO_4)H_2$ in the Z. anorg. allgem. chemie, Vol. 204, pages 145-64. Hieber therein describes the preparation of $Fe(CO)_4 H_2$ according to the following reaction:

$$Fe(CO)_5 \quad + \quad CH_3ONa \quad + \quad H_2O \quad \longrightarrow$$

$$Fe(CO)_4 H_2 \quad + \quad CH_3OCO_2Na$$
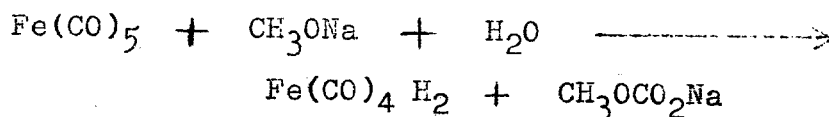
Hieber also states that alkaline solutions of iron hydrocarbonyl have a strongly reducing action on organic substances such as nitrobenzene, quinone and dyes - for example indigo. Although stable in alkaline solution, the hydrocarbonyl easily decomposes in the free state or in the presence of acids because of the initial reaction $2\ Fe(CO)_4H_2 \longrightarrow Fe(CO)_5 + Fe(CO)_3 + H_2$ which proceeds further leading to indefinite results).

APPENDIX A

A LIST OF IMPORTANT PATENTS, BOTH GERMAN AND FOREIGN ISSUED ON INVENTIONS OF DR. REPPE

DRP 489 537	DRP 510 712	DRP 511 517	DRP 550 403
DRP 550 425	DRP 552 987	DRP 566 033	DRP 578 994
DRP 584 840	DRP 588 352	DRP 589 970	DRP 591 774
DRP 591 845	DRP 593 399	DRP 610 371	DRP 617 543
DRP 618 120	DRP 621 963	DRP 624 622	DRP 625 017
DRP 625 660	DRP 631 016	DRP 636 077	DRP 639 843
DRP 624 386	DRP 643 220	DRP 645 112	DRP 646 995
DRP 647 036	DRP 662 156	DRP 662 936	DRP 663 779
DRP 664 231	DRP 679 607	DRP 684 820	DRP 695 218
DRP 695 219	DRP 696 774	DRP 696 779	DRP 687 802
DRP 698 273	DRP 699 430	DRP 699 945	DRP 700 036
DRP 701 825	DRP 703 956	DRP 704 235	DRP 704 237
DRP 705 273	DRP 706 108	DRP 706 694	DRP 708 262
DRP 709 370	DRP 711 709	DRP 713 565	DRP 714 359
DRP 714 490	DRP 715 268	DRP 715 815	DRP 721 004
DRP 724 759	DRP 725 326	DRP 725 532	DRP 726 714
DRP 727 476	DRP 728 466	DRP 730 648	DRP 734 241
DRP 624 845			
AP 1827 285	AP 1998 413	EP 466 316	EP 497 939
EP 504 957	EP 508 543	EP 510 876	EP 510 902
EP 512 182	FP 50208/Zspat.	FP 606 715	FP 814 349
FP 842 577	FP 844 533	FP 845 600	FP 851 178
FP 853 148	FP 853 606	FP 858 185	FP 865 354
PP 865 428	Schweiz. 220 204		Schweiz F 220 208

Anmerkung: Auslandspatente sind nur bei den Anmeldungen
angegeben, die bisher in Deutschland nicht erteilt bzw. nur
in Ausland eingereicht wurden.

D O C U M E N T S

Three type-written and bound documents relating to
to the herein-discussed subject-matters have been deposited
with the MIRS in CIOS Document Bag No. 3518 for safe-keeping.
They have been duplicated in the B Series of microfilms. The
documents consist of:

    (1) Report on Cyclopolvolefines;

          33 Pages and Appendix 24 Pages.

    (2) Dr. J. W. Reppe: Personal History and
          Contributions in the Field of
          Acetylene Chemistry;

          39 Pages and 2 Tables.

    (3) Dr. J. W. Reppe; Further Details of his
          Work including Activities in Divers
          Fields of Organic Chemistry;

          10 Pages