E. Kinetics of the Oxo-reaction in relation to the constitution of the alcohols formed.

During the years 1940-1944 Dr. Nienburg carried out considerable research concerning the constitution of the Oxo-alcohols obtainable from various types

of olefines. A brief survey of the results was drawn up after the war and is attached to this report (vide addendum II).

In the case of n.cetene the C_{17}-alcohols formed were analysed to consist for

50% of n.C_{17}-alcohol,

20% of d-methyl C_{16}-alcohol

and 30% of d-ethyl-, propyl-, etc. alcohols.

This finding is in perfect agreement with the results of Leuna where Asinger and Berg could prove that the formylation is always accompanied by a simultaneous shift of the double bond. This isomerisation is catalysed by Co-carbonyl.

A number of branched-chain olefines (iso-butylene, 2-methyl-butene-2, 2.3-dimethyl-butene-2, 2.4-dimethyl-pentene-2 and di-iso-butylene) were subjected to the Oxo-reaction with the aim of obtaining alcohols with highly branched chains which subsequently might be converted into paraffin hydrocarbons suitable for high octane-number gasoline. These attempts failed completely: in no case a quarternary or adjacent tertiary structure was formed, a shift of the double bond always preceding the formylation proper.

However, Dr. Nienburg had studied another possibility for preparing high octane paraffins which looked very promising: rather than adding CO and H_2 to the di-olefinic double bond, formaldehyde was made to react with the olefine at atmospheric pressure and about 80°C with 1% H_2SO_4 and water as the catalyst to form 1.3-dioxane compounds. By subsequent hydrogenation of these compounds methanol was split off and a primary alcohol was obtained. By this procedure the higher branched structure was always obtained (e.g. 2.3-dimethyl-butene-2 yielded 2.2.3-trimethyl-butanol-1 from which 2.2.3-trimethyl-pentane, triptane, was obtained.

II-14

It was also possible to decompose the dioxane over a phosphoric acid catalyst which resulted in water and formaldehyde being split off and a conjugated di-olefine being formed.

Whereas oxygen containing unsaturated compounds as allyl alcohol and acrylic esters definitely reacted with carbon oxide and hydrogen, no clearcut products were formed possibly due to concomitant polymerization reactions.

It was found possible to carry out the Oxo-synthesis with a mixture of ammonia and CO rather than with synthesis gas. In this case the corresponding amides were obtained.

In connection with the above-reported kinetic results it may be of interest to note that Dr. Nienburg had also experienced great differences in reaction-velocity in some cases: whereas iso-butylene reacted smoothly and at a high rate, the formylation of di-and tri-iso-butylene was rather slow. However, with sufficient contact time any olefine could be converted practically completely.
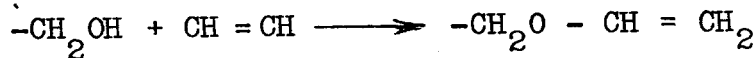
F. Various applications of Oxo-alcohols

1. General information

According to Dr. Schuster Oxo-alcohols have been applied or have been considered as base materials for the following purposes:

a. Higher molecular alcohols from mainly straight chain olefines have been used successfully for the preparation of sulphonate detergents. This type of products was mainly prepared and investigated in connection with the work of Leuna. As stated in Dr. Nienburg's report, Oppau had investigated the possibility of applying the Oxo-alcohol from tri-isobutylene, which was not found suitable for this purpose.

b. Oxo-alcohols from the lower olefines have been found to be suitable as base materials for the preparation of phthalates to be

used as plasticizers. This point was dis-
cussed in some detail with Dr. Kling of the
Plastic Department (vide 2).

c. Various Oxo-alcohols as well as the corres-
ponding aldehydes and acetates (especially
those of terpenes) offer possibilities
for application in the perfume industry.
For this purpose the aldehydes may be re-
covered from the non-hydrogenated Oxo-
product via the bisulphite compound; they
may also be obtained by dehydrogenation of
the alcohols over copper catalysts. Dr.
Schuster had favourable experience with
the Ludwigshafen B.B.E. contact for this
conversion.

d. When reacted with acetylene in the presence
of alkali, the Oxo-alcohols yield vinyl
ethers, which have been applied successfully
as components of polumerization feed stocks:

$$-CH_2OH + CH = CH \longrightarrow -CH_2O - CH = CH_2$$

e. In special cases available olefines may be
converted into alcohols useful in the
pharmaceutic industry (e.g. iso-butylene
as base stock for iso-amyl alcohol).

2. Application of Oxo-alcohols for the preparation of plasticizers

Various batches of Oxo-alcohols prepared at
Ludwigshafen or at Oppau have been converted into
the corresponding di-alkyl phthalates in the depart-
ment of Dr. Hambsch. A detailed description of this
manufacture has been given previously. [1]

[1] B.I.O.S. FR. 753: Manufacture of phthalic anhy-
dride and phthalates at I.G.
Ludwigshafen. ·

F.I.A.T. FR. 861: Plasticizers for polyvinyl-
chloride.

General tests applied to plasticizers

For the plasticizers as such the following properties are usually determined:

1. **Boiling range**

   convertional method.

2. **Colour**

   visual comparison with KJ – J_2 solutions of different concentration, the intensity of the colour being indicated as mg.J_2/litre.

3. **Volatility**

   The plasticizer is placed in an open cup and is kept for 11 days at 90°C under constant slow renewal of the air atmosphere.

The behaviour of the phthalates as plasticizers for P.V.C. was determined by milling a mixture of 60 parts by wt. of P.V.C. and 40 parts by wt. of plasticizer to sheets which were subjected to further tests. In those cases where the plasticizer proved to possess outstanding properties, a mixture of 75 parts by wt. of P.V.C. and 25 parts by wt. of plasticizer was subjected to investigation.

Conventional practice was to determine for those P.V.C.-sheets:

1. Compatibility

2. Tensile strength

3. Elongation strength

4. Volatility index

5. Cold flex resistance

6. Specific electrical resistance

The volatility index was determined in the same way as with the plasticizer as such. Evaporation

loss should be less than 5 % by wt.

The resistance to cold flex was determined by bending a sheet of 6 x 1 cm to a 180° bend and dropping a weight of 200 g from 20 cm height on the bend. The brittle point is then recorded as the temperature at which the sheet cracks.

Dr. Kling has ample experience with phthalate plasticizers prepared from various types of alcohols. In his opinion C_4 and C_5 phthalates of any type of alcohol are too volatile, whereas C_{10} and C_{11} become insufficiently compatible: sheets of 60/40 composition are greasy to the touch and the plasticizer definitely sweats out in 50/50 proportion. However, both C_5 and C_{11} phthalates may be incorporated in small proportions in full range mixtures, C_5-C_{11} having been used at Ludwigshafen.

As to the influence of the specific structure of the alcohols, comparisons have been made between the phthalic esters of:

1. n. C_7 – C_9 alcohol
   (from hydrogenation of corresponding fatty acids);

2. 2-ethyl hexanol;

3. Oxo-alcohols from Michael gasoline (which contains mainly single-branched olefines).

Occasional slight differences were found in the various tests, with the exception of the cold flex resistance. This proved to be influenced unfavourably by branching of the alcohol molecule.

Plasticizers phthalate of:	Brittle point in cold flex test
n.C_7-C_9 alcohol (Palatinol-F)	- 30°C
2-ethyl hexanol	- 25/- 28°C
Oxo-alcohols from Michael olefines (mono and dibranched)	- 20°C
C_6-C_7 alcohols from Leuna synthesis (Palatinol-HS)	Definitely higher than for Palatinol-F. Figure not obtained.

The brittle point may be improved by mixing of the esters: the cold flex resistance of the mixture was found to be better than that calculated proportional to the amounts of the components used.

Brittle point

-20

-30

Di-Oxo-Alcohol   Di-n.C_7-C_9-alcohol
phthalate   phthalate
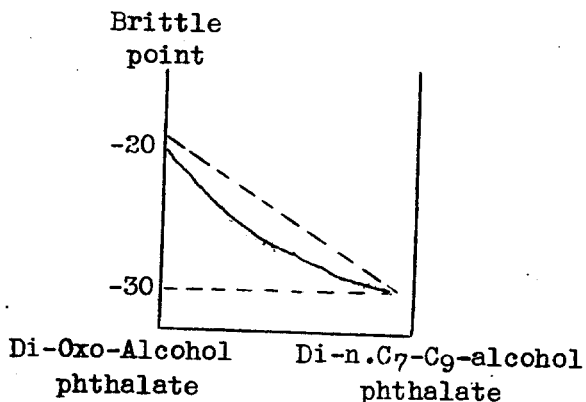
The cold flex resistance was not affected by preparing the plasticizers through concommittant esterification of a range of alcohols instead of by mixing the esters obtained from the separate components of such a range: No differences were found between the mixture of n. C_4-C_6 phthalate plus n. C_7-C_{11} phthalate and the esterification product of the corresponding mixture of n. C_4-C_6 and n. C_7-C_{11} alcohols.

Prof. Dr. Walther Hieber (Techn.Hochschule,
Münchon)

Munich, May 27th, 1947

G. The chemistry of cobalt carbonyls

In view of the extremely important role played
by cobalt carbonyl compounds in the chemistry of the
Oxo-reaction, as opined by Dr. Roelen [1]), Dr. Schuster
and Dr. Nienburg, Germany's expert on the chemistry
of metal carbonyl compounds, Prof. Dr. Walther
Hieber, was visited at his home, Kaulbachstrasse 89,
Munich.

Dr. Hieber and his co-workers have investigated
the formation of carbonyls from various metals and
carbon monoxide under pressure, and have also studied
the formation of carbonyls via the "wet way". A
survey of this work has been published during the
war.   [2])

Prof. Hieber showed that various metal carbonyls
may be obtained by treating the corresponding metal
halides with carbon monoxide under high pressure in
the presence of an acceptor for the halogen. In the
case of CoJ_2, when treated for 15 hours at $250^\circ C$ un-
der 200 ats CO in the presence of Cu, the cobalt
could be completely converted into cobalt tetra-
carbonyl dimer, $[Co(CO)_4]_2$. The same preparation can
be applied to iron carbonyl and nickel carbonyl and
it has also been proved to hold for the noble metals.

Whereas Blanchard [3]) has effected the synthesis
of cobalt hydrocarbonyl via reaction in liquid phase
and at low pressure, Hieber and co-workers have shown
that the hydrocarbonyl may also be obtained by direct
synthesis from cobalt compounds, hydrogen or
hydrogen-containing substances and carbon monoxide

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[1]) B.I.O.S. FR No. 447
    "Interrogation of Dr. Otto Roelen of Ruhrchemie
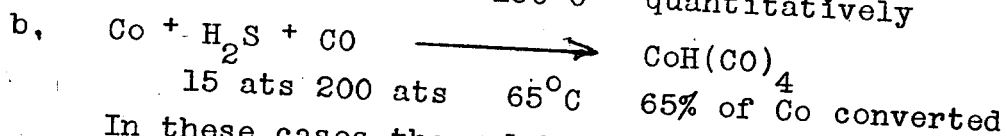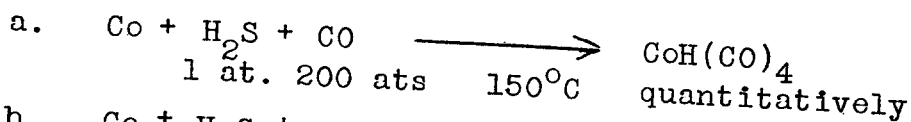   A.G."(p.40)

[2]) W. Hieber – Die Chemie 55, 7, 24 (1942) "Der
      gegen-wartige Stand der Chemie der Metallcarbonyle"

[3]) A.A.Blanchard & P.Gilmont – J.Am.Chem.Soc. 62
   1192 (1940)

under pressure. These reactions were always carried out in small copper-lined autoclaves, and the hydro-carbonyl formed was recovered by blowing off the contents of the autoclave via a cold trap. Although cobalt hydrocarbonyl in concentrated form rapidly decomposes at temperatures over -20°C, it is rather stable in dilution in other gases, and consequently only a minor part decomposed during the blowing-off of the autoclave (some cobalt metal deposit was al-ways found in the expansion valve).

As an example the following experiments were quoted:

a. $Co + H_2S + CO \xrightarrow{\hspace{2cm}} CoH(CO)_4$
1 at. 200 ats 150°C quantitatively

b. $Co + H_2S + CO \xrightarrow{\hspace{2cm}} CoH(CO)_4$
15 ats 200 ats 65°C 65% of Co converted

In these cases the sulphur from the H_2S is taken up by the copper of the autoclave liner.

c. $Co + H_2 + CO \xrightarrow{\hspace{2cm}} CoH(CO)_4$
50 ats 200 ats 200°C
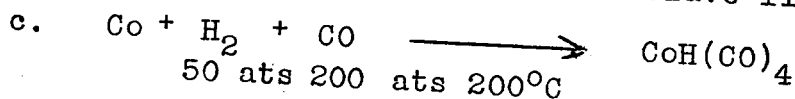
Hieber is convinced that in the latter case the reaction proceeds via the tetracarbonyl

$$2\,Co + 8\,CO \xrightarrow{\hspace{1cm}} \left[Co(CO)_4\right]_2 + H_2 \xrightarrow{\hspace{1cm}} 2\,CoH(CO)_4$$
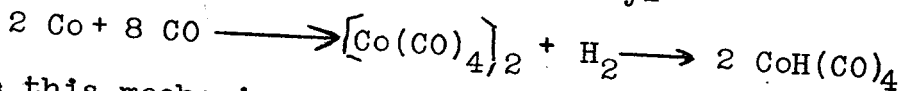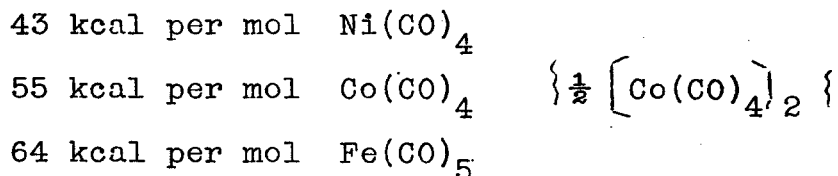
Since this mechanism should be tested by carrying out flow-experiments and as Prof. Hieber had not had other equipment at his disposal than small autoclaves, he had no definite proof for this opinion.

When asked about the heat of formation of the tetracarbonyl and the hydrocarbonyl, Prof. Hieber stated not to have carried out any calorific measure-ments on these compounds. He was inclined to assume the formation of the hydrocarbonyl from the tetra-carbonyl to be an exothermic reaction:

$$Co(CO)_4 + \tfrac{1}{2} H_2 \xrightarrow{\hspace{1cm}} CoH(CO)_4 + Q$$

The formation of the "full" carbonyls from the

metals Ni, Co and Fe and CO is also an exothermic reaction, the relative heats of formation amounting to:

43 kcal per mol $Ni(CO)_4$

55 kcal per mol $Co(CO)_4$ $\{\frac{1}{2}\left[Co(CO)_4\right]_2\}$

64 kcal per mol $Fe(CO)_5$

The heat of polymerisation from cobalt tetra-carbonyl monomer to its dimer may be taken to be negligibly low.

Whereas the dissociation pressure of nickel-carbonyl at various temperatures is well-known, no such data have been published for iron- and cobalt-carbonyl. According to Prof.Hieber the latter car-bonyls do not give a clearcut dissociation; they de-compose into lower carbonyls and CO, as follows:

$$2\ Co(CO)_{4\ 2} \longrightarrow \left[Co(CO)_3\right]_4 + 4\ CO$$

$$2\ Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO$$
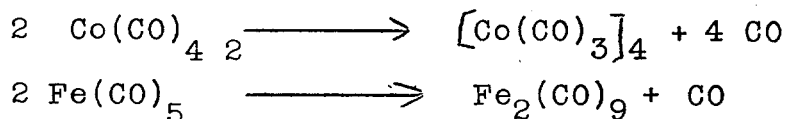
and are partly converted into carbides.

However, Prof.Hieber had been able to measure the decomposition pressure for one specific iron double carbonyl, viz.: for the reaction $FeJ_2 + 4\ CO \rightleftarrows Fe(CO)_4J_2$, the dissociation pressure for the complex carbonyl being found at abt. 6 ats.CO at room temperature.

As stated above, no such transition pressures could be measured for those carbonyls most interest-ing in connection with the Oxo-synthesis, cobalt hydrocarbonyl and iron hydrocarbonyl.