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THE CATALYTIC SYNTHESIS OF CARBOXYLIC ACIDS AND THEIR ESTERS FROM CARBON MONOXIDE, ALKENES, AND ALCOHOLS

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1. INTRODUCTION

More than 100 years have passed since Berthelot's discovery[1] of the reaction between carbon monoxide and caustic alkali to give formates:

$$CO+KOH \rightarrow HCOOK.$$

This process formed the basis of the modern industrial preparation of formic acid. Subsequently, during the first quarter of the 20th century, a number of new reactions of carbon monoxide were discovered, and these have played an important part in the development of organic synthesis. In these reactions, carbon monoxide and hydrogen in the presence of heterogeneous catalysts give either hydrocarbons — methane[2] or a mixture of higher aliphatic hydrocarbons of the synthine type[3] — or oxygen-containing compounds — methanol and its homologues[4] or mixtures of

aliphatic alcohols; aldehydes, ketones, and acids, of the synthol type[5,6]. Most of these processes have been applied in industry and are widely described in the literature.

In the past 20 years, new reactions of carbon monoxide have acquired considerable importance. The distinguishing feature of these reactions is that the carbon monoxide combines with another organic reagent, entering the molecule of the organic compound in the form of a carbonyl group. This leads to the production of a new oxygen-containing functional group — aldehyde, ketone, acid, ester, etc.

Reactions of this type include the formylation[7-9] of olefinic compounds with carbon monoxide and hydrogen to give aldehydes and alcohols. This reaction was discovered by Roelen[10,11] and is also known as the oxo-process:

$$R{-}CH{=}CH_2+CO+H_2 \longrightarrow \begin{cases} R{-}CH_2CH_2CHO \\ R{-}CH(CHO)CH_3 \end{cases}.$$

Even before this reaction was reported, chemists in the USSR carried out the hydrocondensation of carbon monoxide with alkenes[12-14]: in these reactions, carbon monoxide, hydrogen, and alkenes react to form olefinic and paraffinic hydrocarbons with higher molecular weight. Unlike the oxo-process, which is carried out at 150–200 atm in the presence of cobalt carbonyl, this process is carried out over a cobalt catalyst at atmospheric pressure.

In the oxo-process, hydrogen can be replaced by reagents containing labile hydrogen in the molecule.

The present review examines reactions which are being studied fairly widely abroad but only on a comparatively small scale in the USSR. These include the reactions of carbon monoxide with alcohols or ethylenic compounds and a third compound with a labile carbon atom, leading to the synthesis of carboxylic acids and their esters.

All these processes are catalytic and in most cases take place at high pressures. Important catalysts include acidic reagents such as phosphoric acid, sulphuric acid, and boron trifluoride, or nickel, cobalt, and iron compounds which during the reaction are converted into carbonyls or carbonyl hydrides, which are the true catalysts in these processes.

Some of these reactions were described in 1947[15] and in an article by Orchin and Wender in 1957.[16] Since then, however, new material has accumulated and a further review is necessary. A recent review by Bird[17] dealt only with reactions involving metal carbonyls, but almost no reference was made to the work reviewed in the present article.

2. REACTIONS OF CARBON MONOXIDE WITH ALCOHOLS

The direction of the reaction of carbon monoxide with alcohols depends to a considerable extent on the nature of the catalysts used and the conditions of the process. The reaction products may be formates:

$$CO+ROH \rightarrow HCOOR, \quad (1)$$

higher carboxylic acids:

$$CO+ROH \rightarrow RCOOH, \quad (2)$$

or their esters:

$$CO+2ROH \rightarrow RCOOR+H_2O.$$

According to Stähler[18], reaction (1) occurs with aliphatic alcohols at 40–190° and 120–400 atm, using the corresponding sodium alkoxide as catalyst. Later, potassium alkoxide was used for the same purpose[19,20]. The true catalyst in the reaction may, however, be the alkali metal formate[21], formed by Berthelot's reaction from carbon monoxide and the alkali metal hydroxide, into which the alkoxide is converted by moisture which is unavoidably present. The formate then reacts with the alcohol to form the formic ester and the alkali hydroxide:

$$HCOONa+ROH \rightarrow HCOOR+NaOH.$$

Reaction (1) possibly takes place under the influence of sodium hydroxide. It was reported[22] that methyl formate is formed from carbon monoxide and methanol at 100 atm in the presence of NaOH. This synthesis was studied[23] at 50–60°, 70–220 atm, and a $CO:CH_3OH$ molar ratio of 0.75–1.7. The apparent activation energy is 15.7 kcal mole^{-1}. Reaction (1), which also takes place with cyclic alcohols such as cyclohexanol and benzyl alcohol[24], is reversible[25]. The kinetics of the reaction have been studied in detail for methanol, ethanol, both propanols, and all four butanols[26,27]. The rate constants for the formation of formates from these alcohols at 40° are given in Table 1.

The alkoxides were prepared by dissolving metallic sodium in the corresponding alcohols. Metallic potassium was used only in the experiments with t-butanol, since sodium butoxide is sparingly soluble in this alcohol. Table 1 shows that the reaction rate is lowest for methanol and highest for s- and t-butanols. The reaction rates for primary alcohols with the iso-structure are double those for the corresponding normal alcohols.

At first a number of basic catalysts were used[28-30]. The reaction was carried out in the vapour phase at 250–500° and 50–300 atm in the presence of catalysts containing the oxides of various metals, chiefly from Groups IV and VI, together with alloys, particularly those of copper, silver, gold, and lead, or individual metals of Group VIII (iron, cobalt, or nickel), and also alkali or alkaline earth metal hydroxides. It was reported[31] that a 1% solution of sodium methoxide in methanol has been used as a catalyst to synthesise acetic acid in 80% yield from CO and methanol at 60–100° and 10 atm. It is doubtful if these data are correct, however. A large number of acidic catalysts were then proposed: inorganic acids (boric, arsenic, molybdic, uranic, phosphoric, tungstic, and titanic), hetero-acids (molybdophosphoric, tungstosilicic, molybdosilicic, uranosilicic, etc.), and the acid salts of these acids[15]. These catalysts are generally used on carriers (carbon, graphite, coke, or silica gel) and promoted with various metals, chiefly those of Group VIII but also copper, manganese, chromium, vanadium, and some Group IV metals (titanium, zirconium, and thorium). Metal salts have also been proposed as promoters, particularly the phosphates and

TABLE 1.

Original alcohol	Rate constant for the formate formation, $10^8 K$, s^{-1}
Methanol	81
Ethanol	288
Propanol	443
Butanol	411.5
Isopropanol	836.3
Isobutanol	884.8
s-Butanol	1473
t-Butanol	1098

arsenates of the Group II metals, copper, aluminium, manganese, and chromium. The oxides of various metals, containing metal nitrates or the methyl esters of the simplest carboxylic acids; halides, including fluorides, and other fluorine compounds, particularly boron trifluoride, have also been used. For example, dibasic carboxylic acids or their esters have been prepared [32] from aliphatic hydroxycarboxylic acids or their esters and CO in the presence of boron trifluoride at 75–300° and 400–1000 atm. The ratio of the original acid to boron trifluoride was 3 : 1 and the hydroxyl group should be separated from the carboxyl group by at least two carbon atoms. Adipic acid is formed from CO and butane-1,4-diol in the presence of BF_3 and H_3PO_4 at 300° and 300 atm. [33]

Dolgov and Abarenkova [34] concluded that basic catalysts bring about reaction (1) and acidic catalysts bring about reaction (2). The possibility that the reaction can take place in two directions depending on the nature of the catalysts was attributed to the ability of the alcohol to dissociate in two days with the formation of either a hydrogen cation or a hydroxide anion. In the first case, in the presence of basic catalysts, the reaction with carbon monoxide gives formates, and in the second case, under the influence of acidic catalysts, the reaction gives esters of higher acids. Thus, according to Dolgov and Abarenkova, acidic catalysts act as dehydrating agents. In the case of methanol, the alcohol can decompose to the methylene radical and water with the subsequent formation of the keten and then acetic acid:

$$CH_3OH \rightarrow \dot{C}H_2 + H_2O,$$

$$\dot{C}H_2 + CO \rightarrow CH_2{=}CO,$$

$$CH_2{=}CO + H_2O \rightarrow CH_3COOH.$$

These authors [34] prepared acetic acid from carbon monoxide and methanol in the presence of chromium metaphosphate deposited on a porous carrier. Under the optimum conditions (400° and 100 atm) the reaction product contained 13% of acetic acid.

Hardy [35] found that the formation of acetic acid from methanol vapour and carbon monoxide is exothermic. The heat of reaction is 24.84 kcal per mole of acetic acid in the vapour state. Earlier, on the basis of the calculated equilibrium constant, Shilov [36] concluded that the reaction is thermodynamically possible, and Hardy confirmed this conclusion by showing that the equilibrium favours the synthesis of acetic acid up to 370° at atmospheric pressure. Increase in pressure to 50 atm at 327° decreases the degree of decomposition of this acid from 25% to 4%. At 330–340° and 150 atm with circulation of the carbon monoxide in the presence of 87% phosphoric acid containing 2% copper phosphate, the reaction product contained 5.8% of acetic acid, 13.5% of methyl acetate, and 1.3% of dimethyl ether. The total yield of acetic acid and methyl acetate increased with increase in the quantity of catalyst, rate of circulation, and pressure. In experiments lasting 14 h, it reached 45% of the original quantity of methanol and 81% of the methanol reacting. The degree of conversion of the carbon monoxide in one passage was 0.5%. Up to 4.8% of the original methanol was converted into carbon during the reaction.

A large quantity of carbonaceous deposit was also observed by Singh and Krase [37] during the formation of acetic acid from CO and methanol in the vapour phase in the presence of phosphoric acid under pressure at 410–480°. They obtained the best results with active carbon impregnated with syrupy phosphoric acid. The rate of formation of acid in experiments with recirculation of the gas was double that in experiments with a flow system.

Lel'chuk and Karpov [38] studied a number of catalysts consisting of phosphoric acid on active carbon with various additives, for the synthesis of acetic acid from carbon monoxide and methanol at 350° and 200 atm in a circulation system. The additives were uranium and titanium nitrates and chromium phosphates and pyrophosphate. Molybdophosphoric acid was also used. The most active and stable catalyst was phosphoric acid containing uranium nitrate: the rate of formation of acetic acid amounted to 18.2 g h^{-1} and its concentration in the condensate was 12–18%. A number of undesirable products were formed simultaneously, including macromolecular aromatic compounds which caused sintering of the catalyst. The authors concluded that more stable or more readily regenerated catalysts should be used for this synthesis since the phosphoric acid catalysts have a low stability.

Acetic acid can be synthesised by the reaction of CO with $CH_3OH.BF_3$ at 160–220° and 765–1120 atm. [39] It was suggested that under these conditions $CH_3OH.BF_3$ is converted into $(CH_3)_2O.BF_3$ and $H_2O.BF_3$, which react with CO. The rate of formation of acetic acid is proportional to the $CH_3OH.BF_3$ concentration. The apparent activation energy is 15 kcal $mole^{-1}$. Under the optimum conditions (200°, 1000 atm, molar ratio $H_2O.BF_3 : CH_3OH.BF_3 = 1.5$, duration 2 h), the yield of acetic acid was 92%.

Hardy [40] used 87% phosphoric acid containing copper phosphate for the reaction of the homologues of methanol with carbon monoxide in a circulation system at 200 atm. From ethanol at 250–370° he obtained oily polymers of ethylene, some propionic acid and ethyl propionate, and traces of acetaldehyde and volatile hydrocarbons. n-Propanol and isopropanol at 200–250° were converted into a mixture of isobutyric acid, unsaturated hydrocarbons, isobutyl methyl ketone, and diisopropyl ketone. The yield of acids amounted to 40% or 46%, relative to the original alcohols (calculated on the carbon). Hardy concluded that these alcohols, before reacting with carbon monoxide, are dehydrated to propene, which simultaneously undergoes polymerisation to higher hydrocarbons and reacts with carbon monoxide and water vapour to form isobutyric acid (see p. 443). From the isomeric butanols, at 200–210° in the presence of the same catalyst, Hardy [41] obtained a mixture of trimethylacetic and ethylmethylacetic acids, higher ketones, and hydrocarbon polymers. The yield of acids relative to the weight of original alcohol amounted to 24%, 28%, and 22% in the experiments with n-butanol, s-butanol, and isobutanol respectively. In this case also it was assumed that the alcohols are first dehydrated with the formation of butenes, which simultaneously polymerise and react with CO and H_2O to form C_5 acids; mutual isomerisation of the butenes also takes place and this explains, for example, the fact that trimethylacetic acid is obtained from n-butanol.

Considerable progress in this field of chemistry was achieved when the carbonyls of Group VIII metals were first used as catalysts.

In 1941, Reppe and coworkers [42] showed that mixtures of a metal carbonyl and halide act as effective catalysts in the synthesis of carboxylic acids from carbon monoxide and alcohols. The reaction takes place at 250–270° and 200–300 atm. Carbonyl-forming metals with added cuprous chloride or iodine can also be used as catalysts [43]. The

catalytic activity of nickel halides increases considerably in the order: chloride < bromide < iodide. Reaction does not take place in the absence of halides or halogens. The reaction rate and yield of carboxylic acids can be increased by adding to the Co, Ni, and Fe catalysts not only halides or hydrogen halide acids but also polyfunctional compounds such as aminoacetic acid, ethanolamine, *m*-aminophenol, salicylic, tartaric, pyruvic, and adipic acids, or succinodinitrile [44,45]. The reaction can also be carried out in the presence of complexes of Co, Ni, and Fe, for example, $[Co(H_2N-NH_2)_2]I_2$, $[Ni(H_2NCH_2CH_2NH_2)_2]BrI$, $Hg[Co(CO)_4]$, $Ag[Co(CO)_4]$, or compounds of the type Y_2ZX_2, where Y = tetraalkylammonium or triphenylalkylphosphonium ions, Z = Co or Ni, and X = Br or I. [46-50] Advantages of the complex salts relative to simple salts are their stability and ready solubility in the original alcohol and the non-formation of volatile metal carbonyls.

Carboxylic acids are formed more readily from the higher alcohols [43]. The reaction with methanol to give acetic acid takes place with difficulty even at 250–350° and 250–300 atm. Methanol gives only acetic acid, and ethanol gives only propionic acid. Higher alcohols give acids with normal and iso-structures, the latter predominating. Alcohols with high molecular weight give acids with normal structure almost exclusively. The reaction with dihydric alcohols gives dibasic acids:

$$HO(CH_2)_nOH \rightarrow HOOC(CH_2)_nCOOH.$$

These acids in turn can be reduced to dihydric alcohols, which are then used to synthesise $\alpha\omega$-dibasic acids with a longer chain.

Methylglutaric and adipic acids were prepared from butane-1,3-diol. Higher $\alpha\omega$-diols are converted almost exclusively into the corresponding $\alpha\omega$-dibasic acids.

The best catalyst for the reaction is nickel iodide. The use of nickel chloride or bromide leads to side reactions involving the removal of water from the alcohol to yield ethers; the higher alcohols also give alkenes.

Adkins and Rosenthal [51] carried out the reaction in the presence of nickel carbonyl, nickel chloride, hydrochloric acid, and water. Nickel carbonyl and water were taken in excess, but nickel chloride and concentrated hydrochloric acid were taken in "catalytic" quantities. The reaction temperature was 300° for the primary alcohols and 275° for the secondary and tertiary alcohols. Primary alcohols react least readily and give the lowest yield of acids. Primary and secondary aliphatic alcohols with the same number of carbon atoms in the molecule are converted into the same acid with one more carbon atom and a methyl radical in the α-position to the carboxyl group. This was taken as proof that the same α-alkene is formed as intermediate product. Butan-1-ol and butan-2-ol gave α-methylbutyric acid in 47% and 70% yield respectively; heptan-1-ol and heptan-2-ol gave α-methylheptanoic acid in 33% and 70% yield; octan-1-ol and octan-2-ol gave α-methyloctanoic acid in 30% and 76% yield. Pentan-1-ol did not react readily and was converted into α-methylvaleric acid in 16% yield. Neopentanol gave C_6 acids in 21% yield and the tertiary alcohol gave $\alpha\alpha$-dimethylbutyric acid in 35% yield. 2-Ethylbutan-1-ol gave α-methyl-α-ethylbutyric acid in 40% yield. The cyclic alcohols studied were cyclopentanol, 3-cyclohexylpropan-1-ol, 4-methylcyclohexanol, and decahydro-β-naphthol, which were converted into cyclopentanecarboxylic, α-methylcyclohexanepropionic, 4-methylcyclohexanecarboxylic, and decahydronaphthoic acids in 84, 49, 53, and 35% yield respectively. In the case of glycols, one hydroxyl group was carboxylated and the other was reduced. Thus pentane-1,5-diol and hexane-1,6-diol were converted into α-methylvaleric and α-methylhexanoic acids respectively. The hydrogen necessary for the reduction was obtained by the reaction

$$CO+H_2O \rightarrow H_2+CO_2.$$

Aliphatic-aromatic alcohols were converted into alkylbenzenes, again by reduction. 2-(2-Hydroxyethyl)naphthalene gave a resin, apparently as a result of the polymerisation of 2-vinylnaphthalene, the dehydration product of the original alcohol.

The synthesis of carboxylic acids and esters from carbon monoxide and alcohols at 200–300° and 200–400 atm with Ni, Co, and Fe catalysts was studied in detail by Bhattacharyya and coworkers [52-58], who tested a number of Ni and NiI_2 catalysts deposited on silica gel. These showed a high activity. NiI_2 was prepared by precipitating nickel hydroxide from the nitrate with potassium hydroxide and dissolving the precipitate in hydriodic acid.

The maximal yield of acetic acid in the vapour-phase synthesis from methanol was achieved at 180–230°, 260 atm and a concentration of NiI_2 on silica gel equal to 84.2%. After 2 h at 180°, 46% of the methanol was converted into acetic acid, 4% into methyl acetate, and 10% into gaseous products [52,53].

The synthesis of acetic acid from CO and methanol in the vapour phase in the presence of 84.7% $FeI_2.4H_2O$ on silica gel was also studied [59]. The catalyst was found to be highly active. After 2 h at 260 atm and 175°, 11% of the 95% methanol was converted into acetic acid, 4.2% into methyl acetate, and 16.5% into gaseous products. The nickel catalyst gave a smaller quantity of gaseous products and more acetic acid.

The activity of the metals decreases in the order: nickel > cobalt > iron, and that of the halides decreases in the order: iodide > bromide > chloride.

At 210°, an initial pressure of 135 atm, and a contact time of 2 h, nickel, cobalt, and iron, deposited as the metals, chlorides, or bromides on kieselguhr or silica gel, were found to have only low activity. The degree of conversion of methanol into acetic acid was only 0.5–4%. A slightly higher activity was shown by the catalysts FeI_2/SiO_2 (85:15) and CoI_2/SiO_2 (84:16), with which the degree of conversion at 175° amounted to 8.1% and 16.0% respectively. The highest activity was shown by catalysts containing NiI_2; for NiI_2 without carrier, the degree of conversion was 11.5%. Catalysts consisting of NiI_2 on kieselguhr, pumice, and kaolin, with an NiI_2 : carrier ratio of 70:30, gave degrees of conversion equal to 24.0, 21.2, and 14.5% respectively. The addition of CuI, MgO, and ThO_2 reduced the activity.

The best catalyst was found to be NiI_2/SiO_2 (84:16), with which the degree of conversion of the methanol was 37%. Under the optimal conditions (265 atm and 200°) on this catalyst, 40% of the methanol was converted into acetic acid. The best cobalt catalyst was CoI_2/SiO_2 (84:16), with which the degree of conversion under these conditions was 18.8%. Table 2 gives the equilibrium constants for the reaction [53]:

$$CH_3OH(gas) + CO(gas) \rightarrow CH_3COOH(gas). \quad (3)$$

TABLE 2.

Temperature, °C	Pressure, atm	Equilibrium constant, K_{equil}
25	1	$3.55 \cdot 10^{14}$
150	1	$9.772 \cdot 10^{7}$
210	1	$1.059 \cdot 10^{6}$
250	1	$1.00 \cdot 10^{5}$
400	1	$1.514 \cdot 10^{2}$
300	1	$7.943 \cdot 10^{3}$
300	100	$1.299 \cdot 10^{4}$
300	200	$1.496 \cdot 10^{4}$
300	300	$1.552 \cdot 10^{4}$

Reaction (3) is accompanied by side reactions, including

$$CH_3COOH+CH_3OH \rightarrow CH_3COOCH_3+H_2O,$$
$$CH_3OH \rightarrow CO+2H_2,$$
$$CH_3COOH \rightarrow 2CO+2H_2,$$
$$CH_3COOH \rightarrow CH_4+CO_2,$$
$$CO+H_2O \rightarrow CO_2+H_2,$$
$$CO+3H_2 \rightarrow CH_4+H_2O,$$
$$2CO \rightarrow C+CO_2.$$

Bhattacharyya and coworkers [53] also studied the formation of propionic acid from ethanol and carbon monoxide. At 210°, initial pressure 135 atm, and duration of contact 2 h, Ni, Co, and Fe in the form of the metals, chlorides, or bromides on carriers showed only low activity. The degree of conversion of ethanol into propionic acid was 1.7–4.0%. In the presence of the catalysts CoI_2, NiI_2, and FeI_2 on SiO_2 in the ratio $MI_2/SiO_2 = 85:15$, the degree of conversion at 175° was 14.6, 25.3, and 8.1% respectively. Under the optimal conditions (230° and 280 atm), the degree of conversion on CoI_2 and NiI_2 catalysts was 22.3% and 37.3%.

Table 3 gives values of the equilibrium constant for the reaction

$$CH_3CH_2OH(gas) + CO(gas) \rightarrow CH_3CH_2COOH(gas). \quad (4)$$

The main reaction (4) is accompanied by the side reactions

$$C_2H_5COOH+C_2H_5OH \rightarrow C_2H_5COOC_2H_5+H_2O,$$
$$C_2H_5COOH \rightarrow C_2H_6+CO_2,$$
$$C_2H_5COOH \rightarrow 2CO+H_2+CH_4,$$

and others.

Natta and Pino [60] used nickel carbonyl for the synthesis of acetic acid from carbon monoxide and methanol at 230–250° and 400–600 atm. Up to 0.4 mole of dimethyl ether and 0.2 mole of methyl bromide per mole of methanol were added to the anhydrous reaction mixture. The yield of acetic acid was 66.5%.

TABLE 3.

Temperature, °C	Pressure, atm	Equilibrium constant, K_{equil}
25	1	$1.514 \cdot 10^{11}$
210	1	$5.105 \cdot 10^{2}$
400	1	$1.349 \cdot 10^{-1}$
300	1	3.715
300	100	6.7
300	200	8.0
300	300	8.6

Various cobalt catalysts can be used in the synthesis of saturated acids of low molecular weight and their esters from carbon monoxide and alcohols. Cobalt acetate can be used for the synthesis of acetic acid and methyl acetate [61]. Ethylene bromide and a large excess of dimethylacetamide are added to the reaction mixture. The reaction is carried out at 200–700 atm and 200–250°. The reaction product contains 79% acetic acid and 5% methyl acetate.

The reaction can be carried out to give only the ester. In the reaction of carbon monoxide with methanol at 220° and 650–700 atm in the presence of 2–10% (relative to the alcohol) of cobalt carbonyl, cobalt carbonyl hydride, metallic cobalt, or cobalt oxide, up to 15% methyl acetate is formed in 1 h. [62] The reaction temperature should not exceed 300° to avoid the formation of acetic acid and propionaldehyde. Methyl acetate is obtained under these conditions in the presence of cobalt acetate. The degree of conversion of the methanol is 7% in 0.5 h. Water is also present in the reaction medium. Small quantities of hydrogen increase the reaction rate. The degree of conversion after 0.5 h increases to 25% if the $CO:H_2$ ratio is 3:1. [63] When an alloy with Ni:Co = 17:1 is used as catalyst with the addition of small quantities of NH_4I and BiI_2 (or Bi + I_2), CO and butane-1,4-diol give adipic acid in 45% yield and CO and butyrolactone give glutaric acid [64].

Acetic acid can be synthesised from CO and methanol with a catalyst consisting of a silver halide or its mixture with another metal halide [65] in the presence of water at 300° and 100 atm.

Koch and Haaf [66,67] synthesised carboxylic acids by the reaction of alcohols (or alkenes) with formic acid at atmospheric pressure in the presence of a large excess of concentrated sulphuric acid, which serves both to dehydrate the formic acid and alcohols with the formation of CO and alkenes respectively and also to catalyse the addition of CO to the alkenes. Carbon monoxide adds on according to Markovnikov's rule, and in all cases acids branched in the α-position to the carboxyl group are obtained. The reaction was carried out at room temperature and an alcohol: :formic acid:sulphuric acid molar ratio of 1:2–4:8–12. Thus the reaction medium was kept saturated with carbon monoxide throughout. The reaction product was decomposed with water and the carboxylic acid was extracted from the organic layer produced.

Propanol does not give acids under these conditions, but both n-butanols are converted to α-methylbutyric acid in moderate yield. t-Butanol is converted almost exclusively into trimethylacetic acid in good yield. Pentan-1-ol and pentan-2-ol give 80% yields of a mixture of 80% αα-dimethylbutyric acid and 20% of higher acids, chiefly C_{11} acids. 2,3,3-Trimethylbutanol gives ααββ-tetramethylbutyric acid in 90% yield.

αα-Dimethylbutyric acid has been synthesised from neopentanol, a 1:2 mixture of αα-dimethylvaleric and α-ethyl-α-methylbutyric acids from 2,2-dimethylbutanol, and a 1:2 mixture of αα-dimethylhexanoic and α-ethyl--α-methylvaleric acids from 2,2-dimethylpentanol. In these syntheses the yield of acids was 82–85%.

The reaction with cyclopentanol gave a 1.7:1 mixture of cyclopentanecarboxylic acid and the dimeric *cis*-decalincarboxylic acid in 26% yield. Cyclohexanol was converted in 78% yield into a mixture of 78% 1-methylcyclopentanecarboxylic acid, 9% cyclohexanecarboxylic acid, and 13% of C_{13} acids. β-Decalol gives a 1:4 mixture of *trans*- and *cis*-decalincarboxylic acids in 95% yield. An extremely

uniform product is given by primary cyclic alcohols of the neopentanol type. Thus 1-methyl-1-hydroxymethylcyclopentane is converted, with expansion of the ring, exclusively into 1-methylcyclohexanecarboxylic acid in 95% yield. 1-Methyl-1-hydroxymethylcyclohexene and 1-ethyl--1-hydroxymethylcyclohexane react with preservation of the six-membered ring and elongation of the side chain to give 1-ethylcyclohexanecarboxylic and 1-n-propylcyclohexanecarboxylic acid respectively in 86–87% yield.

Carboxylic acids have been synthesised[68,69] by the reaction of an alcohol with carbon monoxide at 50–90 atm and 15–20° in the presence of concentrated sulphuric acid. This synthesis can be regarded formally as the addition of CO to the alcohol with the simultaneous isomerisation of the hydrocarbon radical:

$$ROH+CO \rightarrow R_1COOH,$$

where R_1 is a more highly branched radical than R, with the same number of carbon atoms.

In its first stage, however, this process may involve either dehydration of the alcohol to the alkene:

$$RCH_2CH_2OH \rightarrow RCH=CH_2+H_2O,$$

which then reacts according to the schemes:

$$R_1R_2C=CR_3R_4+H_2SO_4 \rightarrow R_1R_2HC-\overset{+}{C}R_3R_4+\overset{-}{O}SO_3H \xrightarrow{CO}$$

$$\xrightarrow{CO} R_1R_2HC-CR_3R_4\overset{+}{C}O + \overset{-}{O}SO_3H \rightleftarrows R_1R_2HCR_3R_4C-\underset{\underset{O}{\|}}{C}OSO_3H$$

(I) (II)

or

$$\text{(I) [or (II)]} + HX \longrightarrow R_1R_2HC-R_3R_4C-\underset{\underset{O}{\|}}{C}-X,$$

or direct conversion of the alcohol into the carbonium ion, according to the reaction

$$RCH_2CH_2OH + H_2SO_4 \longrightarrow RCH_2\overset{+}{C}H_2 + \overset{-}{O}SO_3H + H_2O.$$

The second direction is more probable. This is confirmed by the preparation of carboxylic acids from alcohols of the neopentanol type, which cannot be dehydrated directly to alkenes[67].

The synthesis of the acids and their esters was carried out in such a way that the alcohol, CO, and sulphuric acid reacted in the first stage, and in the second stage an excess of water or methanol was added to the reaction mixture. In the first case, carboxylic acids were obtained, and in the second case their methyl esters, with traces of the carboxylic acids themselves, were obtained. The total yield of esters and acids from the aliphatic C_3–C_5 alcohols increased with increase in the molecular weight of the alcohol and reached 85%. Alcohols with the iso-structure reacted more readily than those with normal structure and the same molecular weight. The yield of esters and acids from the aliphatic C_6–C_9 alcohols was approximately on the same level (76–82%), irrespective of the molecular weight. The yield of esters and acids from the cyclic alcohols (cyclohexanol and menthol) reached 91–94%.

The following acids and their esters were obtained as the chief reaction products: isobutyric acid from propanol and isopropanol, α-methylbutyric acid from n-butanol, trimethylacetic acid from isobutanol, αα-dimethylbutyric and α-ethylbutyric acids (in the ratio 1.7 : 1) from n-pentanol, αα-dimethylbutyric acid from isopentanol, αα-dimethylvaleric and α-ethylvaleric acids from n-hexanol, αα-dimethylhexanoic and α-ethylhexanoic acids from n-heptanol, αα-dimethyloctanoic acid from n-nonanol, 1-methylcyclopentane-1-carboxylic and cyclohexanecarboxylic acids from cyclohexanol, and menthanecarboxylic acid (4-isopropyl-1--methylcyclohexane-3-carboxylic acid) from menthol.

The data in this section show that the reaction of carbon monoxide with alcohols may take place in three different directions, with the formation of formates, carboxylic acids, and esters respectively. Formates are produced in the presence of alkali metal alkoxides at increased temperature (100–300°) and high pressure (200–1000 atm). The synthesis of carboxylic acids and their esters is carried out at about the same temperatures and pressures in the presence of cobalt, nickel, and iron catalysts or acidic catalysts (phosphoric acid and boron trifluoride). In the presence of concentrated sulphuric acid the synthesis can be carried out at room temperature and a pressure of 50–90 atm, in two stages. In the first stage, the alcohol, CO, and sulphuric acid react, and in the second stage an excess of water or methanol is added to give the corresponding carboxylic acids or their esters.

3. REACTIONS OF CARBON MONOXIDE WITH ALKENES AND WATER

In a study of the reaction of carbon monoxide with alcohols, Hardy[35] suggested that the alcohols are first dehydrated to alkenes, which then react with carbon monoxide and water to form carboxylic acids. This he confirmed experimentally by preparing carboxylic acids from alkenes, carbon monoxide, and water at 200–300° and 150–200 atm in the presence of 87% phosphoric acid[70].

The synthesis of carboxylic acids from alkenes, carbon monoxide, and water at 130–375° and pressures up to 700 atm was described in a number of patents. The catalysts used were phosphoric, boric, arsenic[71], and monochloroacetic acids, acetyl chloride on active carbon[72], and Ba and Ca halides[73]. Boron trifluoride is often used[74]. 2,2,3-Trimethylbutyric acid was prepared in quantitative yield from tetramethylethylene and CO at 75–77° and 400 atm in the presence of $BF_3.3H_2O$.[75] Ethyl αα-dimethylbutyrate was prepared from ethylene, propene, and CO at 110° and pressures up to 900 atm in the presence of BF_3.[76] Ethyl α-ethyl-α-methylbutyrate was prepared from a 3 : 5 mixture of C_2H_4 and CO in the presence of $BF_3.1.7H_2O$ under the same conditions[77].

Compounds of general formula $RR_1C=CR'CH_2X$, where R may be a hydrogen atom, a C_1–C_6 alkyl group, or the phenyl group, and R′ an alkyl or phenyl group (but not H, since in this case no reaction occurs) and X a halogen, react with CO at 60–150° and 200–2000 atm in the presence of $BF_3.2H_2O$ to give αα-dialkyl-β-halogenopropionic acids[78]. Dibasic carboxylic acids and their esters are obtained by the reaction of aliphatic unsaturated monocarboxylic acids and their esters with CO and water at 75–300° and 400–1000 atm in the presence of BF_3. The original acid : BF_3 : : water ratio was 3 : 1 : 3. In the molecule of the original acid the double bond should be separated from the carboxyl group by at least two carbon atoms[32].

In the synthesis of carboxylic acids from alkenes, CO, and water, the catalysts used are the carboxylic acids which should be formed during the reaction, or others[79]. Ethylene, CO, and water in the ratio 0.9 : 1 : 2 at 290° and initial pressure 133 atm in the presence of propionic acid gave the same acid in 71% yield.

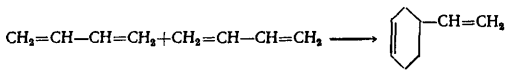
Nickel and cobalt carbonyls and nickel and cobalt salts which are converted into carbonyls during the reaction have been widely used as catalysts in the reaction of alkenes with CO and water. The use of finely divided metallic nickel as a catalyst for this reaction was reported as early as 1934.[80]

In 1940, the method developed by Reppe and coworkers for the carboxylation of acetylenic compounds in the presence of nickel carbonyl and nickel salts was extended to olefinic compounds in order to obtain saturated carboxylic acids and their derivatives[42]. The catalyst used in these reactions was nickel carbonyl. The starting materials in the reactions were alkenes and their functional derivatives — unsaturated alcohols, acids, etc.[81] The carboxylation of the olefinic compounds, like that of the acetylenic compounds[82], can be carried out either with stoichiometric quantities of nickel carbonyl in the presence of the acid necessary to dissolve the nickel, in which case the carbonyl acts as the source of CO (method A), or by using CO and "catalytic" quantities of nickel carbonyl, nickel salts, or metallic nickel (method B). The alkene and the compound with the labile hydrogen react simultaneously. The reaction takes place at higher temperatures and pressures than in the case of the acetylenic compounds, namely 100–200 atm and 160–190° in method A and 230–285° in method B. The high pressures in method B make it possible to avoid the addition of acid to combine with the nickel, since under these conditions the metal forms nickel carbonyl.

The reaction products are saturated carboxylic acids or their derivatives. The resulting acid may be converted into the anhydride by the further action of the alkene and CO:

$$CH_3CH_2COOH + CO + H_2C{=}CH_2 \longrightarrow (CH_3CH_2CO)_2O.$$

Branched acids, chiefly α-methyl-substituted acids, are formed in addition to acids with the normal structure. Propionic acid and its anhydride were obtained in a smooth reaction from ethylene. Propene was converted into a mixture of approximately equal quantities of butyric and isobutyric acids; isobutene into a mixture of isovaleric acid and a trace of trimethylacetic acid; and 2-ethylhex-1-ene into a mixture of 2-ethyl-2-methylhexanoic and 3-ethylheptanoic acids. Cyclohexene, cyclooctene, and octadec-1-ene gave cyclohexanecarboxylic, cyclooctanecarboxylic, and α-methylstearic acids respectively. Buta-1,3-diene, by diene synthesis, gave 1-vinylcyclohex-3-ene



which was subsequently converted into a mixture of 2- and 3-vinylcyclohexanecarboxylic and α- and β-(cyclohex-3-enyl)propionic acids. Under the more severe conditions of method B (CO + nickel carbonyl), a mixture of dicarboxylic acids, namely α- and β-(3- and 4-carboxycyclohexyl)propionic acids, was formed. Biallyl gave 2- and 3-methyl-4-vinylbutyric acids and the corresponding dicarboxylic acids. An attempt to carboxylate styrene did not give satisfactory results, since the acid polymerised under these conditions. Unsaturated alcohols were converted into hydroxy-acids, hemi-esters, and lactones. Allyl alcohol, however, gave crotonic acid (apparently by dehydration of the initial γ-hydroxybutyric acid), the lactone, and a polymer of methacrylic acid. Carboxylation of unsaturated carboxylic acids containing a double bond gave saturated dicarboxylic acids and their derivatives. Oleic acid gave a mixture of heptadecane-1,8-dicarboxylic and heptadecane-1,9-dicarboxylic acids and small quantities of hydroxystearic acid.

In the case of the reaction in the liquid phase, inert liquids (aromatic and naphthenic hydrocarbons, ketones) are used[83] and in the case of the reaction in the gaseous phase, carbon dioxide is used as diluent and also serves to suppress the water–gas reaction. Under these conditions, at 300–375° and 450–740 atm in the presence of nickel carbonyl, ethylene gave a 40% yield of propionic acid, and propene gave a 76% yield of butyric and isobutyric acids in the ratio 2 : 1.

4-Methyloctanoic acid was obtained in 33% yield from oct-1-ene at 300° and 300 atm in the presence of a catalyst containing 65% nickel carbonyl, 10% nickel chloride, and 25% hydrochloric acid[84].

The reaction takes place more rapidly and with higher yields of acids in the presence of an Ni catalyst promoted with HI.[85] At 300° and 400 atm in the presence of nickel acetate, hex-1-ene reacts with CO and water more slowly than pent-1-ene; pent-2-ene reacts even more slowly and 2-methylbut-2-ene does not react at all. If 0.013 mole of HI per 1–1.5 mole of alkene is added to the nickel catalyst, the rate of carboxylation of pent-1-ene, pent-2-ene, and hex-1-ene is increased by a factor of 40, but the rate of reaction of 2-methylbut-2-ene is only one-half of this value. The total yield of acids reaches 90%. Pent-1-ene and pent-2-ene both gave hexanoic and 2-methylvaleric acids, hex-1-ene gave a mixture of heptanoic and 2-methylhexanoic acids, and 2-methylbut-2-ene gave a mixture of at least three acids: 3-methylvaleric, 4-methylvaleric, and 2,3-dimethylvaleric acids. In the presence of an unpromoted catalyst, pent-1-ene and hex-1-ene gave products containing 40% of straight-chain acids and 60% of branched-chain acids; the corresponding figures for pent-2-ene were 30% and 70% respectively. With a promoted catalyst, the quantity of straight-chain acids increased to 47% and 44% respectively.

Cobalt-based catalysts have also been widely used in this reaction. Propionic acid was prepared from ethylene, CO, and water at 270–290° and 300–600 atm in the presence of cobalt carbonyl[86]. At 285° and 200 atm the yield was 85%.[87,88]

Ercoli[89] studied the conditions for the synthesis of carboxylic acids from alkenes, CO, and water in the presence of $Co_2(CO)_8$. The use of solvents decreases the reaction temperature to 120–125° and the pressure to 100–300 atm. The yield of acids reaches 80–90%. The ease of reaction decreases with increased extent of branching of the original alkene. The cobalt catalyst, however, tends to produce side reactions; for example, considerable quantities of diethyl ketone are formed in the carboxylation of ethylene[83].

The rate of carboxylation of cyclohexene in the presence of cobalt octacarbonyl is proportional to the water concentration and to the square root of the cycloalkene concentration. The maximal reaction rate at 156° is achieved at 165–210 atm. At lower pressures the rate of reaction is directly proportional to the pressure, and at higher pressures (above 340 atm) the reaction rate is inversely proportional to the pressure. The reaction rate increases with increase in the Co concentration[90].

Propionic acid was synthesised in 50–85% yield in the presence of cobalt propionate or butyrate in aqueous

medium at 200–250°, 135–270 atm and $C_2H_4 : CO = 1 : 3$. Diethyl ketone and CO_2 are formed in side reactions. The catalyst is deactivated when the reaction medium contains more than 28% CO_2.[91] Propionic acid was obtained in 55% yield from ethylene, CO, and water in the presence of cobalt formate in aqueous trimethylamine solution at 220° and 300 atm.[92] Propionic acid was prepared from a 1 : 1 mixture of C_2H_4 and CO at 180° and 340 atm in the vapour phase on a Co–Fe–ThO_2–MgO–kieselguhr (30 : 1 : 2 : 2 : 65) catalyst reduced in a current of H_2 at 400°; the degree of conversion after 3 h was 10–13%.[93] In the presence of CoI_2/SiO_2 and NiI_2/SiO_2 (50 : 50) at 230–300° and 300 atm the yield of this acid after 3 h was 7.3% and 27.9% respectively[54]. The main reaction

$$C_2H_4 + CO + H_2O \longrightarrow C_2H_5COOH,$$

was accompanied by a number of side reactions, including

$$n\,C_2H_4 \longrightarrow (C_2H_4)_n,$$

$$C_2H_4 \longrightarrow 2C + 2H_2,$$

$$C_2H_4 \longrightarrow C + CH_4,$$

$$C_2H_4 + CO + H_2 \longrightarrow C_2H_5CHO.$$

Polyethylene is formed on catalysts subject to prolonged reduction.

Carboxylic acids can also be synthesised from alkenes and CO in the presence of aqueous solutions of iron salts[94].

These data show that the single-stage synthesis of carboxylic acids from alkenes, CO, and water when all the original reagents are present in the reaction mixture requires the use of increased temperatures (100–350°) and high pressure (200–1000 atm).

A new development was the two-stage synthesis of carboxylic acids, carried out in 1955 by Koch[95,96]. In the first stage, the alkene reacted with CO in the presence of 96% sulphuric acid, and in the second stage, decomposition of the reaction complex with water gave the carboxylic acid. The acids were obtained in good yield under very mild conditions at 0–50° and 1–100 atm with vigorous stirring. The reaction usually obeys Markovnikov's rule. Propene was converted only into isobutyric acid, but-1-ene and but-2-ene into α-methylbutyric acid, and isobutene chiefly into trimethylacetic acid. Increase in pressure retards the polymerisation of the alkenes and the isomerisation of the carbon chain. Pent-2-ene at 5 atm was converted in 59% yield into a mixture of approximately equal quantities of C_6, C_{11}, C_{16}, and C_{21} acids, the only C_6 acid being αα-dimethylbutyric acid. At 100 atm, pent-2-ene gave a 70% yield of a mixture of α-methylvaleric and α-ethylbutyric acids with a small quantity of αα-dimethylbutyric and higher acids. The same acids were formed from pent-1-ene. The three n-hexenes gave four isomeric C_7 acids; α-methylhexanoic, αα-dimethylvaleric, α-ethylvaleric, and α-ethyl-α-methylbutyric. These acids were also obtained from 2-methylpent-1-ene, 2-ethylbut-1-ene, and 3-methylpent-2-ene, but ααβ-trimethylbutyric acid was obtained from 2,3-dimethylbut-2-ene and 2,3-dimethylbut-1-ene. "Diisobutylene" and "triisobutylene" gave 2,2,4,4-tetramethylvaleric and methyldineopentylacetic acids respectively. It was subsequently shown that in the presence of a large excess of sulphuric acid CO can be replaced by formic acid, and in this case the reaction takes place at atmospheric pressure[66]. When this method was used, pent-2-ene gave a mixture of acids containing 80% αα-dimethylbutyric acid and 16% of dimeric C_{11} acids; hex-1-ene gave αα-dimethyl valeric, α-ethyl-α-methylbutyric and dimeric C_{13} acids; and dec-1-ene gave exclusively C_{11} acids, chiefly tertiary acids, in 84% yield. In the product obtained from branched alkenes, the acid with one carbon atom more than the original alkene is not the chief component and the mixture obtained contains all the isomers of the dimeric acids, together with acids containing a different number of carbon atoms.

The original alkene can be replaced by an alcohol or alkyl chloride[68–69].

An extremely interesting development of this method established the possibility of synthesising carboxylic acids from paraffins under conditions of acid catalysis[97]. Mixtures of an alkene (or alcohol) with an isoalkane (or cycloalkane) with the addition of formic acid or an excess of sulphuric acid gave, in addition to the expected acids, other acids derived from the saturated hydrocarbon. This reaction can be attributed to the transfer of a hydride ion from the isoalkane or cycloalkane to the carbonium ion formed by the reaction of the alkene with sulphuric acid. Thus the saturated hydrocarbon forms a new carbonium ion which reacts further with carbon monoxide and water to give carboxylic acids. Thus t-butanol and isopentane give αα-dimethylbutyric acid in addition to trimethylacetic acid. The yield of exchange acid reaches 74%. The yield of exchange acid decreases with increase in the chain length of the isoalkane and increase in the distance between the branching and the end of the straight chain. Cycloalkanes containing no side-chain give carboxylic acids with a smaller ring: cyclohexane gives 1-methylcyclopentane-1-carboxylic acid, cycloheptane gives 1-methylcyclohexane-1-carboxylic acid, and cyclooctane gives 1-ethylcyclohexane-1-carboxylic acid. The synthesis of carboxylic acids from alkanes by the hydride migration method can also be brought about by the reaction with carbon monoxide under pressure in the presence of a large excess of sulphuric acid. Favourable reaction conditions can be selected using the fact that the carbonium ion initially formed from the alkene may react further in two ways: by the direct addition of carbon monoxide or by an exchange reaction with alkanes. Only the former is facilitated by high pressure, so that the synthesis of the exchange acids takes place only at pressures below 20 atm. For example, the maximum yield of acids (52%) in the synthesis from propene–methylcyclopentane vapour is achieved at a pressure of 5 atm.

The data in this section show that the reaction of carbon monoxide with alkenes and water takes place with the formation of the carboxylic acids and esters which are produced in the reaction of carbon monoxide with the corresponding alcohols. The two reactions take place in the presence of the same catalysts — cobalt, nickel, and iron compounds, phosphoric acid, and boron trifluoride — and under approximately the same conditions — at increased temperature (100–350°) and high pressure (200–1000 atm). The reaction can also be carried out in two stages and under very mild conditions (0–50°, 1–100 atm) with high yield of carboxylic acids in the presence of acidic catalysts, particularly sulphuric acid. In the first stage the alkene and carbon monoxide react with the catalyst and in the second stage the third component — water — is introduced.

4. REACTIONS OF ALCOHOLS AND ALKENES WITH CARBON MONOXIDE

When the formation of carboxylic acids from alkenes and carbon monoxide takes place in the presence of alcohols,

esters may predominate in the reaction products. Thus the reaction of alkenes, alcohols, and CO over active carbon impregnated with phosphoric acid gave a mixture of carboxylic acid, esters, and ethers[98]. Reppe and coworkers[82] synthesised esters from alkenes, alcohols, and CO in the presence of carbonyl-forming metals or their derivatives. The reactions were carried out at 100–200 atm and 160–190° with stoichiometric quantities of $Ni(CO)_4$ (method A) and at 270–285° with CO and "catalytic" quantities of the Ni compounds (method B). Activators, for example mineral acids, which increase the yield of esters, may also be used. Ethyl isononanate was obtained in up to 95% yield in the liquid phase using inert solvents in the presence of NiI_2 and acetic acid. Ethylene, CO, and butanol in the presence of small quantities of propionic acid and $Ni(CO)_4$ gave butyl propionate in 72% yield. 12% of propionic anhydride was formed simultaneously[99,100]. In the presence of Ni halides the main reaction is accompanied by a number of side reactions, such as esterification, trans-esterification, ester hydrolysis, and carboxylation. Higher acids and polyalkenes are also formed. The hydrogen produced by the water–gas reaction does not hydrogenate the alkene but is consumed in the formylation of the alkene to aldehydes and hydrogenation of the latter to alcohols.

Natta, Pino, and their coworkers[101,102], in the synthesis of esters from alkenes, carbon monoxide, and alcohols, made extensive use of catalysts based on cobalt. Their experience with the carboxylation of acetylene to acrylates was applied to the reaction with alkenes, cycloalkenes, and polyalkenes. They used metallic cobalt deposited on diatomite. The reaction was carried out at 100–200° and 10–200 atm. Cyclohexene, CO, and an excess of methanol gave methyl cyclohexanecarboxylate in 76–86% yield[103]. Small quantities of hexahydrobenzaldehyde were formed in the side reaction

$$C_6H_{10} + CO + H_2 \longrightarrow C_6H_{11}CHO.$$

Under the same conditions, cyclohexene, CO, and a small excess of butanol gave a mixture of hexahydrobenzyl butyrate, butyl hexahydrobenzoate, hexahydrobenzyl, hexahydrobenzoate, butyl butyrate, hexahydrobenzyl alcohol, methyl hexahydrobenzoate, and hexahydrobenzaldehyde[104]. Methyl crotonate, methanol, and CO at 192 atm and 200° gave methyl methylsuccinate containing a little β-formylbutyric acid. Butyl crotonate, butanol, and CO gave butyl methylsuccinate in 70–79% yield. Butyl butyrate and β-formylbutyrate were formed in side reactions. Butene, CO, and methanol gave methyl valerate in 25% yield[105]. Esters of propionic, butyric, and isobutyric acids were synthesised in analogous fashion. The yield of esters when methanol was used was much greater than that for higher alcohols, since side reactions play a smaller part. The thermodynamic conditions for the carboxylation reaction are evidently more favourable than those for carbonylation (the oxo-process), but in practice the carboxylation takes place more slowly because of kinetic factors[103,106]. The cobalt salts of carboxylic acids were used as catalysts[105]. On these catalysts a ternary mixture of CO, alkenes, and secondary alcohols reacts to form ketones. CO, ethylene, and isopropanol in the presence of cobalt butyrate and cobalt(II) oxide gave acetone and diethyl ketone in quantitative yield. In analogous fashion, ethylene and cyclohexanol gave diethyl ketone and cyclohexanol in 70% yield. The reaction takes place at 225–300° and 600–750 atm.[107]

The reaction of cyclohexene with CO and a large excess of methanol at 165° and 60–390 atm in the presence of $Co_2(CO)_8$ gives methyl cyclohexanecarboxylate containing the dimethylacetal of hexahydrobenzaldehyde. The formation of the acetal is favoured by a low molar alcohol : alkene ratio, a high concentration of Co salt solution, low CO pressure, and high temperature. The reaction is of zero order with respect to alkene and first order with respect to methanol. Its rate passes through a maximum at a pressure of 60–90 atm.[108]

Bhattacharyya and coworkers[54] used CoI_2, NiI_2, and FeI_2 deposited on SiO_2 in the ratio 50 : 50. At 300 atm and 230–300°, ethylene, CO, and methanol gave methyl propionate in yields of 26.0, 20.0, and 27.1% respectively. Ethyl propionate was obtained in yields of 25.1, 24.4, and 23.5% when methanol was replaced by ethanol. Table 4 gives the equilibrium constants for the reaction

$$C_2H_4(gas) + CO(gas) + CH_3CH_2OH(gas) \rightarrow CH_3CH_2COOC_2H_5(gas).$$

The reaction between alkenes, CO, and alcohols can be carried out at 80–200° and 600–1000 atm in the presence of the alcohol-soluble salts of the noble metals of Group VIII (Pt, Pd, Rh, and Ir) and the alcohol-soluble salts of tin and germanium. Under these conditions, ethylene, CO, and methanol, ethanol, isopropanol, butanol, or cyclohexanol gave respectively methyl, ethyl, isopropyl, butyl, and cyclohexyl propionates. In analogous fashion allene or allylene, CO, and methanol gave methyl methacrylate, and *cis*-but-2-ene, CO, and methanol gave methyl α-methylbutyrate[109].

Thus the synthesis of the esters of carboxylic acids, like that of the carboxylic acids themselves, takes place under severe conditions and requires the use of increased temperature and high pressure. In 1958 the authors of the present paper achieved a two-stage synthesis of the esters of carboxylic acids under much milder conditions at 20–40° and 20–80 atm.[110–118]

Solutions of carboxylic acids in concentrated sulphuric acid readily esterify methanol[119]. It is suggested that the reaction of carboxylic acids with sulphuric acid gives acylsulphuric acids which react with methanol to give esters. Koch[67,95,96] obtained carboxylic acids by using water to decompose a reaction mixture formed from alkenes and CO in the presence of concentrated sulphuric acid. After a comparison of these results and an analysis of the possible nature of the reactive complex from CO, an alkene and sulphuric acid, we suggested that in this case acylsulphuric acids should be formed. These may be present in equilibrium with acylinium ions:

$$R_1R_2C{=}CR_3R_4 + H_2SO_4 \longrightarrow R_1R_2HC{-}\overset{+}{C}R_3R_4 + \overline{O}SO_3H \xrightarrow{CO}$$

$$\xrightarrow{CO} \underset{(III)}{R_1R_2HC{-}C(R_3R_4)\overset{+}{C}O} + \overline{O}SO_3H \rightleftarrows \underset{(IV)}{R_1R_2HC{-}C(R_3R_4)CO{-}OSO_3H}.$$

TABLE 4.

Temperature, °C	Pressure, atm	Equilibrium constant, K_{equil}
25	1	$1.135 \cdot 10^{15}$
100	1	$6.86 \cdot 10^{8}$
200	1	$4.06 \cdot 10^{3}$
300	1	1.610
230	1	$2.79 \cdot 10^{2}$
230	100	$4.378 \cdot 10^{2}$
230	200	$4.639 \cdot 10^{2}$
230	250	$4.64 \cdot 10^{2}$

Forms (III) and (IV) should exhibit acylating properties and should convert compounds with labile hydrogen into derivatives of carboxylic acids:

$$\text{(III) [or (IV)]} + HX \longrightarrow H_2SO_4 + R_1R_2HC{-}R_3R_4C{-}\underset{\underset{O}{\|}}{C}X.$$

In the particular case where X = OH, they should give carboxylic acids according to Koch's reaction. When X = OR, *i.e.* with alcohols, forms (III) and (IV) should be converted into esters, as confirmed in our experiments. The reaction of the complex formed from an alkene, CO, and sulphuric acid with methanol or ethanol gave the corresponding esters. The yield of esters was 60–85% relative to the original alkene, or 70–100% relative to the CO absorbed. The starting materials in the carbalkoxylation reaction were C_4–C_{10} α-alkenes with normal structure, isobutene, all the isomeric pentenes, and the cycloalkenes: cyclopentene, cyclohexene, and dihydrodicyclopentadiene. The chief reaction product from α-alkenes with normal structure are the esters of $\alpha\alpha$-dimethylalkanoic acids with one carbon atom more than the original alkene. But-1-ene gave α-methylbutyrate, isobutene gave trimethylacetate, pent-1-ene, hex-1-ene, hept-1-ene, oct-1-ene, non-1-ene, and dec-1-ene gave $\alpha\alpha$-dimethylbutyrate, $\alpha\alpha$-dimethylvalerate, $\alpha\alpha$-dimethylhexanoate, $\alpha\alpha$-dimethylheptanoate, $\alpha\alpha$-dimethyloctanoate, and $\alpha\alpha$-dimethylnonanoate. The isomeric pentenes gave chiefly $\alpha\alpha$-dimethylbutyrate; cyclopentene gave esters of cyclopentanecarboxylic and *cis*-decalin-9-carboxylic acids, cyclohexene gave esters of 1-methylcyclopentanecarboxylic and cyclohexane carboxylic acids in almost equal quantities. Dihydrodicyclopentadiene gave the ester of 4,7-endomethylenehydrindancarboxylic acid.

In the synthesis of esters of carboxylic acid from CO, alcohols, and alkenes in the presence of sulphuric acid, as in the case of the synthesis of the carboxylic acids themselves from alkenes, CO, and water (see p. 443), saturated hydrocarbons may take part in the reaction as a result of the hydride transfer process. In this case the starting materials are mixtures of alkanes or cycloalkanes with alkenes or alcohols. The carbonium ions formed in the first stage from the alkenes or alcohols combine with the hydride ions produced from the alkanes or cycloalkanes containing hydrogen or a tertiary carbon atom. The latter give up hydride ions and are converted into carbonium ions. Thus in the first stage, carbonium ions are produced from the alkanes and these add on CO and are converted into acylinium ions. In the second stage, methanol is added and this reacts with the acylcarbonium ions to form the methyl esters of carboxylic acids.

The hydride ion transfer reaction proceeded to the greatest extent in isopentane–t-butanol vapour; in this case 93% yield of the esters was obtained from isopentane and only 7% from t-butanol. The ratio of the esters obtained by exchange and direct synthesis from isopentane–menthol vapour was 1 : 1, that from isopentane–cyclohexane vapour 1 : 1.3–1.5, and that for isopentane–isononene vapour 1 : 2.2. Methylcyclohexane underwent the hydride transfer reaction with t-butanol, triisobutene, cyclohexene, and isononenes to the extent of 80, 73, 50, and 24% respectively. The hydride transfer reaction does not take place between n-hexane and t-butanol, cyclohexene, or isononenes, evidently because there is no hydrogen on the tertiary carbon atom.

Thus the simultaneous reaction of carbon monoxide with alkenes and alcohols gives esters of carboxylic acids containing some of the carboxylic acids themselves.

The formation of the esters of carboxylic acids takes place under the same conditions and on the same catalysts as the reaction of carbon monoxide with alcohols and the reaction of carbon monoxide with alkenes and water.

5. MECHANISM OF CARBOXYLATION REACTIONS

In carboxylation by means of carbon monoxide and particularly in the synthesis of acids and esters by this method, the catalysts used are mineral acids, particularly phosphoric and sulphuric acids, their salts (phosphates), BF_3, the metals Co, Ni, and Fe in the reduced state, and their oxides, halides, and carbonyls. The mechanism of the carboxylation naturally depends to a considerable extent on the catalyst used.

According to Hardy [41], in the synthesis of carboxylic acids from alkenes, CO, and water in the presence of concentrated phosphoric acid, the alkene molecule is first activated by the formation and subsequent decomposition of alkyl phosphates. The activated alkene molecules then add on CO with the formation of complexes which react with water to give carboxylic acids.

For the reaction in the presence of $BF_3 . 1.7H_2O$ the following ionic scheme has been assumed [77]:

$$C_2H_4 + \overset{+}{H} \longrightarrow CH_3\overset{+}{C}H_2 \xrightarrow{C_2H_4} CH_3CH_2CH_2\overset{+}{C}H_2 \rightleftarrows CH_3CH_2CH_2\overset{+}{C}H_2 \xrightleftharpoons{C_2H_4}$$

$$\xrightleftharpoons{C_2H_4} CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{+}{C}H}CH_2CH_3 \rightleftarrows CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{+}{C}H}CH_2CH_3 \rightleftarrows CH_3CH_2\underset{\underset{CH_3}{|}}{CH}\overset{+}{C}H_2 \xrightarrow{CO}$$

$$\xrightarrow{CO} (CH_3CH_2)_2\underset{\underset{CH_3}{|}}{C}\overset{+}{C}O \xrightarrow[-\overset{+}{H}]{H_2O} (C_2H_5)_2\underset{\underset{CH_3}{|}}{C}COOH \xrightarrow{C_2H_4} (C_2H_5)_2\underset{\underset{CH_3}{|}}{C}COOC_2H_5.$$

The tendency of primary and secondary carbonium ions to undergo conversion into tertiary ions is evidently extremely high, since no products corresponding to the intermediate ions were obtained.

In a discussion of the mechanism of the carboxylation of acetylene in the presence of nickel carbonyl, Reppe [82] considers the possibility that the CO reacts with the iso-form of acetylene with the intermediate formation of methyleneketen which subsequently can react readily with water or alcohol to give acrylic acid or its esters:

$$H_2C{=}C{+}CO \longrightarrow (H_2C{=}C{=}CO) \xrightarrow[ROH]{H_2O} \begin{matrix} H_2C{=}CHCOOH \\ H_2C{=}CHCOOR \end{matrix}.$$

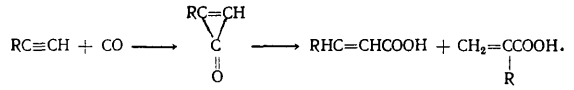
The keten scheme cannot, however, explain either the reactivity of symmetrically disubstituted acetylenes or the formation of two reaction products. The ester of cinnamic acid, which should be the only reaction product formed according to this scheme from phenylacetylene, CO, and alcohol:

$$C_6H_5C{\equiv}CH + CO \longrightarrow \begin{matrix} H_5C_6 \\ H \end{matrix}\!\!>\!C{=}C{-}CO \xrightarrow{ROH} \begin{matrix} H_5C_6 \\ H \end{matrix}\!\!>\!C{=}CHCOOR$$

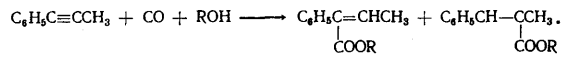
is not formed, the product being the ester of α-phenylacrylic acid.

It was therefore suggested [120,121] that the carboxylation, like the carbonylation of alkenes (the oxo-process), involves the formation of an intermediate hypothetical cyclopropene

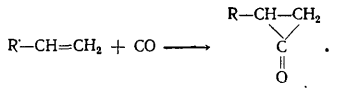
ring from acetylene and CO, and that this opens under the influence of compounds with a labile hydrogen atom:



If molecular hydrogen is used instead of a compound with labile hydrogen, the reaction does not give satisfactory results. It can be seen from this scheme that two products should in general be formed. In actual fact, methylphenylacetylene, for example, gives two esters: α-phenylcrotonate and α-phenylcinnamate:



In the carboxylation of alkenes an intermediate cyclopropanone derivative is formed instead of the cyclopropenone derivative:

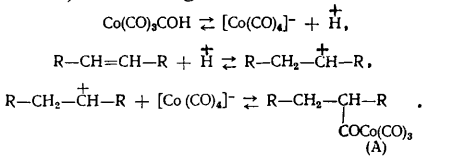


Ghis gives aldehydes with H_2, acids with water, and esters with alcohols, and in this case also the formation of two derivatives is possible.

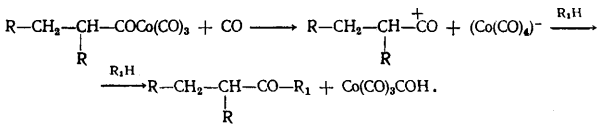
Doubts have been cast on this mechanism[122]. It has been pointed out that the formation of cyclopropanone derivatives should not be related to the presence of compounds with labile hydrogen. At the same time, in the absence of such a compound, these cyclic derivatives are never formed. Moreover, the reversibility of the oxo-process is not in accordance with the properties of derivatives with a saturated three-membered carbon ring. Another mechanism was therefore proposed[122], according to which the reagent with labile hydrogen reacts with the metal carbonyl catalyst to give intermediate compounds which in turn react with alkenes to form new intermediate compounds in which one carbon atom in the alkene is joined directly to the central atom of the metal carbonyl. This mechanism explains the difference in the reaction rates when different compounds with labile hydrogen are used, but it cannot explain the difference in the behaviour of nickel and cobalt in the synthesis of esters.

When it was suggested[123] that cobalt carbonyl hydride $Co(CO)_3COH$ [hydrogen tetracarbonylcobaltate(I) (Ed. of Translation)] is formed as an intermediate product in the oxo-process and it was pointed out[124] that the reaction of cobalt carbonyl with CO precedes its reaction with a reagent containing labile hydrogen, Natta and Pino[104] suggested a new mechanism for the carboxylation of alkenes with carbon monoxide in the presence of a catalyst based on metallic cobalt. According to their scheme, the active catalyst, as in the case of carbonylation reactions (the oxo-process), is an intermediate cobalt carbonyl hydride $Co(CO)_3COH$. This adds on to the double bond of the alkene to form an intermediate compound which then reacts with the compound containing labile hydrogen.

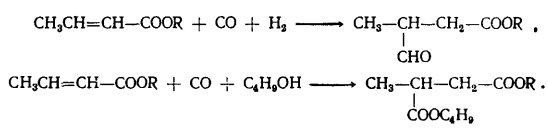
Cobalt carbonyl hydride exhibits the properties of a strong acid. It may therefore be assumed that it adds on to alkenes in the same way as hydrochloric, sulphuric, and similar acids, according to the scheme:



The compound (A) has a low stability and reacts with a CO molecule to form the $[Co(CO)_4]^-$ ion and an active carbonium ion, which rapidly reacts with the compound containing active hydrogen to regenerate cobalt carbonyl hydride:



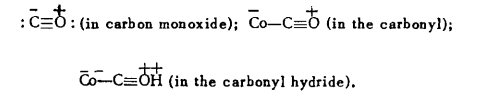
Natta and Pino[104] put forward some evidence in support of this mechanism. They point out that as a result of the part played by cobalt carbonyl hydride, aldehydes are formed, both in the oxo-process and in the carboxylation reaction. This is a stage common to both reactions. In both cases, when the reactions are carried out with esters of crotonic acid, only one reaction product is obtained, in which the formyl or carbalkoxy-groups respectively are found in the β-position:



α-Formyl butyrate is not formed in the oxo-process, and ethyl malonate is not formed in the carboxylation process. This also confirms the analogy between the mechanisms of the two reactions.

The formation of cobalt carbonyl hydride does not require the presence of large quantities of hydrogen, and small quantities of water or hydrogen sulphide are sufficient[125]. In the synthesis of esters, water is formed by the dehydration of the alcohols to ethers and hydrogen is formed by the dehydrogenation of the alcohols to aldehydes. This is confirmed by the presence, in the reaction products, of small quantities of water or, in the case of alcohols higher than methanol, of aldehydes and ketones.

In compound (A), the bond between the $[Co(CO)_4]^-$ ion and the positively charged carbon atom of the carbonium ion is formed *via* the carbon atom of one of the CO groups[104]. It is possible that in this case, under the influence of electrophilic reagents, the $[Co(CO)_4]^-$ ion becomes asymmetric, with the production of higher reactivity in one of the CO groups relative to the three others. The formation of a bond to the central Co atom at the centre of the tetrahedron formed by the four CO groups is unlikely. A bond *via* the oxygen of a CO group is also unlikely, since as in the case of the CO molecule, the oxygen in carbonyls and carbonyl hydrides tends to retain a positive charge[126].



From this mechanism it can be seen that cobalt carbonyl hydride cannot be regenerated without the participation of a compound with labile hydrogen R'H, and that without this compound the reaction cannot take place. The reaction rate therefore depends on the reactivity of R'H. The greatest activity is shown by hydrogen itself, which may react in the presence of water, alcohols, etc. In our opinion, this feature does not quite fit into the proposed mechanism, since the hydrogen in the H_2 molecule can hardly be regarded as labile.

A very similar mechanism was proposed by Kirch and Orchin[127]:

$$2HCo(CO)_4 + RCH{=}CH_2 + CO \longrightarrow (HCo(CO)_4)_2 \cdot RCH{=}CH_2 \cdot CO \longrightarrow$$
$$\longrightarrow Co_2(CO)_8 + RCH_2CH_2CHO.$$

This was based on the observed formation of a stable $2HCo(CO)_4$.alkene.CO complex in the reaction of an alkene, CO, and carbonyl hydride at room temperature and atmospheric pressure. This complex begins to decompose even at 25°, with the liberation of CO and the formation of aldehyde.

Breslow and Heck[128] suggested that the reaction proceeds with the participation of cobalt carbonyl hydride according to the scheme:

$$RCH{=}CH_2 + HCo(CO)_4 \longrightarrow RCH_2CH_2Co(CO)_4 \longrightarrow RCH_2CH_2COCo(CO)_3 \xrightarrow{CO}$$
$$\xrightarrow{CO} RCH_2CH_2COCo(CO)_4 \xrightarrow{HCo(CO)_4} RCH_2CH_2CHO + Co_2(CO)_8.$$

This scheme is confirmed by the synthesis of compounds $RCo(CO)_4$, where R = CH_3, C_2H_5, $C_6H_5CH_2$, from $NaCo(CO)_4$ and RX; these compounds add on one CO molecule to form the intermediate compound of the last stage $CH_3CO{-}Co(CO)_4$, which reacts with cobalt carbonyl hydride to give the aldehyde and cobalt carbonyl:

$$CH_3COCo(CO)_4 + HCo(CO)_4 \longrightarrow CH_3CHO + Co_2(CO)_8.$$

This mechanism, however, does not agree with the fact that the reduction of $CH_3COCo(CO)_4$ with hydrogen at 25° and 200 atm stops completely at high CO pressure. The compound being reduced is probably $CH_3COCo(CO)_3$, and not $CH_3COCo(CO)_4$. The retarding action of CO can be attributed to the conversion of the acylcobalt tricarbonyl into the inactive acylcobalt tetracarbonyl. Thus a more probable scheme is

$$RCH{=}CH_2 + HCo(CO)_3 \longrightarrow RCH_2CH_2Co(CO)_3 \xrightarrow{CO} RCH_2CH_2COCo(CO)_3 \xrightarrow{H_2}$$
$$\xrightarrow{H_2} RCH_2CH_2COH + HCo(CO)_3.$$

The reactivity of alcohols decreases with increase in molecular weight[104]. When small quantities (1–10 mole %) of methanol are present in the butanol, the reaction products contain considerable quantities of methyl esters. In the case of butanol the reaction is initiated by the hydrogen liberated on dehydrogenation. Butyraldehyde is detected. In the case of methanol, no significant quantities of formaldehyde are produced, but dehydration to dimethyl ether takes place readily. Considerable quantities of methyl acetate are detected, probably formed according to the reaction

$$CH_3OCH_3 + CO \rightarrow CH_3COOCH_3.$$

The methyl acetate cannot be formed from acetic acid, since the latter is not obtained by direct synthesis from CO and methanol at temperatures below 250° and in the absence of halides or halogens.

For carboxylation reactions in the presence of metallic nickel and nickel halides on carriers, Bhattacharyya[129] proposed two basic schemes with intermediate metal carbonyl halide complexes or carbonium ions. The first scheme gives complexes of the type $M(CO)I_2$ (where M = Co, Fe, Ni), which subsequently react with other reagents; CO may be added on with the liberation of halogen. For example,

$$NiI_2 + CO \longrightarrow Ni(CO)I_2 \xrightarrow{3CO} Ni(CO)_4 + I_2,$$

$$NiCOI_2 + CH_3OH \longrightarrow CH_3COOH + NiI_2.$$

Here NiI_2 is regenerated.

In the reaction of Fe and Co halides under pressure, complexes of composition $Co(CO)I_2$, $Fe(CO)_2I_2$, $[Fe(CO)_3Br_2]_3$, etc. are formed[125,130,131]. $Co(CO)I_2$ is obtained[129] at 200 atm and 100° in the form of a dark red crystalline substance with a very high CO dissociation pressure even at room temperature. The analogous nickel complexes could not be isolated, although they may be formed as unstable intermediate products. The electronic configurations of Ni, Co, and Fe indicate that the stability of these complexes decreases in the order Fe > Co > Ni. This may explain the above order of decrease in activity, depending on the nature of the metal and halogen. On the one hand, the Ni complexes are the least stable and hence more reactive. On the other hand, iodide forms complexes more readily than bromide and chloride. The scheme involving intermediate carbonyl halide complexes cannot, however, explain the activating action of traces of water on the catalyst. The other scheme, based on the carbonium-ion theory, is therefore more probable, in view of the acidic character of the catalysts on silica gel.

It was mentioned above that the presence of traces of water is necessary to preserve the activity of the MX_2 catalysts. This is evidently required for the formation of HI according to the reaction

$$NiI_2 + H_2O \longrightarrow NiO + 2HI,$$

or, according to Reppe,

$$NiI_2 + 5CO + H_2O \longrightarrow Ni(CO)_4 + 2HI + CO_2.$$

Traces of nickel oxide are in fact detected in the spent catalyst. The function of the HI may be to displace the extremely active CO from the nickel carbonyl with regeneration of NiI_2:

$$2HI + Ni(CO)_4 \longrightarrow NiI_2 + 4CO + H_2,$$

or to activate other components of the reaction

$$CH_3OH + HI \rightleftharpoons (CH_3HOH)^+ + I^- \rightleftharpoons \overset{+}{C}H_3 + H_2O + I.$$

The resulting carbonium ion reacts with CO:

$$\overset{+}{C}H_3 + :\overset{-}{C}:::\overset{+}{O}: \rightleftharpoons CH_3C:::\overset{+}{O} \rightleftharpoons CH_3{-}\overset{+}{C}::O:.$$

Water then reacts, with the formation of acetic acid:

$$CH_3\overset{+}{C}::O: + H_2O \longrightarrow \underset{\underset{OH}{|}}{CH_3C}::O + \overset{+}{H}.$$

The H^+ then attacks another alcohol molecule and the reaction continues. The mechanism of other reactions involving the formation of acids and esters may be represented in this way[110–118].

A mechanism for the carboxylation of alcohols with CO in the presence of an Ni catalyst has been proposed[43]:

$$R{-}CH_2OH + HI \longrightarrow R{-}CH_2I + H_2O,$$

$$R{-}CH_2I + CO + H_2O \xrightarrow[Ni(CO)_4]{} R{-}CH_2COOH + HI.$$

The HI necessary for this reaction is obtained in the formation of $Ni(CO)_4$ from NiI_2 and CO. The $Ni(CO)_2I_2$ acts as active CO carrier. One further reaction takes place:

$$Ni(CO)_4 + 2HI \longrightarrow NiI_2 + 4CO + H_2.$$

The reactions leading to the conversion of CO have been described earlier[43]. Carboxylic acids with the iso-structure are obtained in the carboxylation of higher alcohols as a result of isomerisation of the intermediate primary halogeno-derivative to secondary and tertiary derivatives.

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