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# Carbonylation of Mono-olefinic and Monoacetylenic Hydrocarbons

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The review deals with catalytic reactions involving the carbonylation of monoacetylenic and mono-olefinic hydrocarbons by carbon monoxide.
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## I. INTRODUCTION

Reactions involving the carbonylation of unsaturated compounds by carbon monoxide under conditions of homogeneous catalysis in the presence of Group VIII metals and their compounds or acid catalysts are of considerable theoretical and practical interest. They permit the synthesis of valuable products: alcohols, aldehydes, ketones, saturated and unsaturated mono-, di-, and poly-carboxylic acids, their esters, chlorides, amides and lactones, and quinones, [1-9]. Some of these reactions have been achieved industrially[10]. As a result of numerous studies, the optimum reaction conditions have been investigated in detail, active catalysts have been selected, and the compositions of the reaction products have been determined.

New catalysts based on Group VIII noble metals have been found in recent years and certain features of the carbonylation mechanism have been elucidated.

The review deals with the reactions of mono-olefinic and monoacetylenic hydrocarbons with carbon monoxide, with the exception of hydroformylation reactions, which were described previously[11].

## II. CARBONYLATION OF MONOACETYLENIC HYDROCARBONS

Acetylenic hydrocarbons are carbonylated in the presence of Group VIII metal carbonyls and hydrocarbonyls according to the overall equation

$$RC{\equiv}CH + CO + HX \rightarrow CH_2{=}CH(R)C\langle^{O}_{X},$$

where HX is a compound with mobile hydrogen.

Acrylic acid was obtained from acetylene, carbon monoxide, and water; acetylenealdehyde and acetylenedialdehyde were not formed. When water is replaced by other compounds with mobile hydrogen (alcohol, mercaptans, ammonia, amines, or carboxylic acids), derivatives of acrylic acid (esters, thioesters, amides, and anhydrides) are obtained[7,12,13]. These reactions are used at present for the industrial manufacture of acrylic acid and its derivatives. $\alpha\beta$-Unsaturated carboxylic acids (the hydrocarboxylation reaction), their esters (hydroalkoxycarbonylation), and other acid derivatives were obtained in the carbonylation of acetylene homologues. The addition of elements of formic acid (H−COOH) to the triple bond took place in accordance with the Markovnikov rule[14]. $\alpha$-Phenylacrylic acid and not cinnamic acid was obtained from phenylacetylene[12]. The reactions were carried out by stoichiometric or catalytic methods.

The stoichiometric method consists in the reaction of acetylene with nickel, cobalt, or iron carbonyls at a pressure of 1−10 atm and 30−85°C in organic solvents: alcohols, acetone, ethyl methyl ketone, dioxan, tetrahydrofuran (THF), ethyl acetate, pyridine, and anisole, containing an inorganic (HCl, $H_3PO_4$) or organic (acetic) acid[15-24]. The reactions can be represented by the equation

$$4C_2H_2 + 4C_2H_5OH + Ni(CO)_4 + 2HCl \rightarrow 4CH_2{=}CH{-}COOC_2H_5 + NiCl_2 + H_2.$$

The nickel salt formed is then converted into a hexamine salt, which is treated in dilute aqueous solution with carbon monoxide at 100°C and 100 atm with formation of nickel carbonyl.

Methyl, ethyl, butyl, phenyl, tetrahydrofuryl, $\alpha$-decalyl and other esters of acrylic acid were synthesised in high yields by this method. The reaction is autocatalytic, the duration of the induction period depending on the structure of the initial acetylenic hydrocarbons, the solvent, the acid, and the reaction temperature[25]. If an additional amount of the reactant is added after the induction period, the nickel complex formed as an intermediate acts as a catalyst. The rate and mode of reaction are influenced by the addition of water, acid, or base, for example pyridine, and also by the solvent. In anhydrous solvents, vigorous hydrogenation takes place: NiCl is formed as an intermediate from $Ni(CO)_4$ and then reacts with HCl to give $NiCl_2$ and $H_2$. This results in a decrease of the amount of final product. In the absence of acid the reaction does not occur. The acid strength does not influence the yield of acrylic acid, but does affect the yield of its esters[2]. The presence of oxidants in the reaction mixture inhibits the reaction, while reductants do not affect it[25].

The carbonylation of phenylacetylene, hex-1-yne, and methylacetylene by stoichiometric amounts of $Ni(CO)_4$ has been investigated in detail[26-30]. The reactivity of acetylenic hydrocarbons decreases with molecular weight. The addition of acetylene itself sharply increases the rate of reaction of homologues and increases the yield of the final products. Disubstituted acetylenes formed substituted acrylic acids[26,31,32]. Ethyl $\alpha$-phenylcinnamate was obtained from diphenylacetylene and ethanol in benzene,

while in dioxan the main product was 2,3,4,5-tetraphenylcyclopent-2-en-1-one together with the above ester[32]. In the latter case the reaction probably proceeds via bis-(diphenylvinyl) ketone with its subsequent Nazarov cyclisation[2]. The carbonylation of diphenylacetylene in saturated sodium hydroxide in methanol in the presence of an excess of $Ni(CO)_4$ takes place with formation of *trans*-α-phenylcinnamic acid and 1,2,3,4-tetraphenylbutadiene in 25 and 67% yields respectively. The source of carbon monoxide is the intermediate dark-red $[Ni_3(CO)_8]^{2-}$ anion[33]. When diphenyl- and dimethyl-acetylenes react with $Fe(CO)_5$ under ultraviolet irradiation, tetraphenylcyclopentadienone and tetramethylcyclohexadienone are formed respectively and are isolated as complexes with iron tricarbonyl[34-37].

It is suggested that in the stoichiometric method a carbonium ion, which is formed initially during the acid catalytic process, reacts with $Ni(CO)_4$. In this stage four CO groups are transferred by a series of $Ni(CO)_X-C_2H_2$ complexes[38]. When the reactant ratios are accurately regulated, only "catalytic" amounts of $Ni(CO)_4$ and HCl are required for the carbonylation reaction.

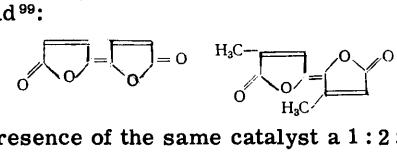
The carbonylation of acetylenic hydrocarbons by the catalytic method takes place at 150–200°C and about 30 atm in a homogeneous system containing 0.5–5% (relative to the solvent) of the catalyst, for which mainly complexes of Group VIII metals, and their halides, sulphides, carbonyls, etc. were employed[7,8,17,20,21,39-43]. Gaseous carbon monoxide is usually taken in an equimolar amount in relation to acetylene. Water, alcohols, tetrahydrofuran, pyran, dioxan, ketones, glycol monoethers, lactones, and *N*-alkyl-lactams are used as solvents[18,20,21,42,44]. Catalysts based on nickel have been investigated in greatest detail. The catalytic activity increases from the chloride via the bromide to the iodide, which, however, promotes also the acrylate polymerisation processes. The best catalyst proved to be $NiBr_2$, since it forms with carbon monoxide an unstable reactive complex NiCOBr, which readily gives up active carbon monoxide on regeneration of $NiBr_2$.[39,45] The active complexes are those of nickel, containing triaryl- or trialkylphosphines, trialkylstibines, and trialkylarsines, for example: $[(C_6H_5)_3P]_2.NiX_2.RX$, $[(C_6H_5)_3P]NiBr_2$, $[(C_6H_5)_3P]_2NiBr_2(C_6H_5Br)$, $[(C_6H_5)_3P]NiI_2C_6H_5Br$,[7,17,46-49] $(R_3P)_XNi(CO)_{4-X}$,[50] $NiBr_2[(C_6H_5)_3N(C_4H_9Br)]_2$, $NiCl_2[(CH_3)(C_2H_5)C_6H_5N]_2$, $[(C_6H_5)_3P.C_4H_9Br]_2C_5H_5N.NiBr_2$, $(C_6H_5)_3P(C_5H_5N.C_4H_9Br).NiBr_2$, $(C_5H_5N.C_4H_9Br).C_6H_5N.NiBr_2$,[51,52] $[(C_6H_5)_3P].[Ni(CN)_2]_3$,[53] $(R_3Sb)_XNi(CO)_{4-X}$,[54] $(R_3Sb)_2NiX_2$,[53,55-58] complexes of $NiI_2$ or $Ni(CN)_2$ and an alkali metal[59-61], complexes of $NiCl_2$ and acyclic and cyclic acid amides[62], halogen-containing organic complexes of phosphorus, arsenic, and antimony with carbonyl-forming substances[63,64], complexes of $NiX_2$ with oxygen-containing saturated heterocyclic compounds[64,65], a mixture of metallic nickel and nickel thiocyanate[58], metallic nickel on a carrier containing iodine[66], nickel halides on silica gel[67-75], nickel salts of naphthenic acids, nickel-dimethylglyoxime or a complex of $NiCl_2$ with 1-nitro-2-naphthol, and $NiBr_2$ complexes with ethanolamine, benzoxazole, and 1,3,4-thiadiazole-2,5-dithiol[76,77]. Metallic copper and mercury or their salts and also metallic nickel in an amount of 3–20% of the weight of the catalyst[76,78-81] and $HgCl_2$ (in the stoichiometric process) in an amount of 5–10% of the solvent[82] have been employed as activators of the carbonylation catalysts. The stability of the catalyst was increased by $CuSO_4$, antimony and arsenic chlorides, and hydroquinone[52].

The carbonylation of methylacetylene in the presence of $Ni(CO)_4$ yielded methyl methacrylate[83-85]. In the presence of methacrylic acid at 130°C and 13 atm the overall yield of methacrylic acid and its ester reached 85%. Methyl methacrylate was also obtained at 170–180°C and 10 atm when nickel halides, nickel complexes with $(C_6H_5)_3P$, and cobalt and chromium carbonyls were employed[85]. The side products of the reaction were methyl *trans*-crotonate, methyl isobutyrate, and acetone. Nickel and cobalt carbonyls showed the highest activity. In the carbonylation of butylacetylene in the presence of $[(XC_6H_4)_3P]_2NiBr_2$, where X = H, $CH_3$, or $OCH_3$, the activity of the catalyst increased when electron-donating substituents were introduced into the benzene ring of the ligand. The rate of reaction increased in the series X = H, $CH_3$, and $OCH_3$ and was proportional to the concentration of butylacetylene and the catalyst. The overall yield of esters was about 80%, the main product being butyl α-butylacrylate together with small amounts of butyl β-butylacrylate[86].

The rate of carbonylation of acetylene in a butanol–methyl acrylate solution at 30–75°C in the presence of $Ni(CO)_4$ depends on the partial pressure of carbon monoxide, being determined by the rate of diffusion of carbon monoxide, and decreases in the presence of an excess of acetylene greater than 40%. Above 75°C the rate of reaction falls by a factor greater than 2. An increase in the amount of the catalyst leads to the acceleration not only of the main reaction but also of the side processes, in particular the polymerisation of acetylene. Dilution of the initial acetylene–carbon monoxide mixture with nitrogen shortens the induction period, and, when the supply of hydrogen chloride is stopped, the reaction ceases rapidly. Cobalt and iron carbonyls are inactive under these conditions[25]. The solvent and the overall pressure have little effect on the rate, but affect significantly the mode of reaction in the range 4–150 atm. In the presence of water the main acetylene carbonylation products were acrylic acid and in *N*-vinylpyrrolidinone the products were saturated dicarboxylic acids[24].

In the presence of cobalt carbonyls and water in a neutral solvent, succinic acid and its homologues are the main products from acetylenes, together with cyclopentanone and monocarboxylic acids[87-89]. Bifurandione is formed in acetone solution[90-93] and in methanol and water solution or in methyl ether the product is dimethyl succinate together with small amounts of methyl acrylate[94-96]. In the presence of cobalt catalysts a mixture of methyl esters of acrylic, succinic, and γ-hydroxypimelic acids and the trimethyl ester of ethanetricarboxylic acid were obtained from acetylene, carbon monoxide and methanol[95-97].

In contrast to the analogous reaction of olefins (see below), the carbonylation of acetylene takes place at a high rate also in the absence of halides and halogens[98]. In the presence of $Co_2(CO)_8$ at 120°C and 250 atm, *cis*- and *trans*-octa-2,4,6-triene-1,4,5,8-diolides were obtained from acetylene, carbon monoxide, and acetic anhydride and, when acetylene was replaced by $CH_3C{\equiv}CH$, the products were *cis*- and *trans*-2,6-dimethylocta-2,4,6-triene-1,4,5,8-diolides[93], which were oxidised to 2,6-dimethylsuberic acid[99]:



In the presence of the same catalyst a 1 : 2 : 1 acetylene–carbon monoxide–hydrogen mixture in an excess of ethanol under a pressure of 50–80 atm and at a temperature of 100–120°C, gives rise to a mixture of products

containing ethyl propionate, propionaldehyde, its acetal, and diethyl succinate and γγ-diethoxybutyrate. When ethyl alcohol was replaced by isopropyl alcohol, a mixture of isopropyl γγ-di-isopropoxybutyrate, succinate, and β-formylpropionate was obtained[98,100]. Acetylene, carbon monoxide, and water in the presence of cobalt hydrocarbonyl yielded hydroquinone[101]. The carbonylation of acetylene derivatives in non-aqueous media catalysed by iron carbonyls leads to the formation of cyclic compounds[102].

In the synthesis of acrylate esters from acetylene, carbon monoxide, and alcohols, nickel, cobalt, and iron halides deposited on silica gel are employed as catalysts. The activity decreases in the series Ni > Co > Fe and I > Br > Cl. The reaction conditions were milder and the yield of the ester higher the higher was the molecular weight of the initial alcohol. Nickel naphthenate on silica gel proved to be the best catalyst for the synthesis of acrylic acid itself[67-75].

The carbonylation of acetylene in the presence of ruthenium compounds {the carbonyls $Ru_2(CO)_9$ and $[Ru(CO)_4]_3$, the salt $RuCl_3$, chelate complexes of ruthenium with acetyl acetonate} takes place at 160°C in water, methanol, acetone, or dioxan with formation of hydroquinone and quinhydrone. The amount of catalyst is 1% of the weight of the solvent. The yield of hydroquinone, which reaches 65%, depends on the reaction temperature and the $H_2O/C_2H_2$ ratio, but is little affected by the partial pressure of carbon monoxide in the range 53–160 atm.[103-105] Hydroquinone and quinhydrone were obtained similarly using rhodium compounds: $RhCl_3$, $Rh(CO)_2Cl$, rhodium carbonyl, and chelate complexes with acetylacetonate[103-106]. However, in a silver-lined autoclave acetylene was converted in the presence of hydrogen chloride and small amounts of $RhCl_3.3H_2O$ into a mixture of acrylic and 3-chloropropionic acid chlorides[107].

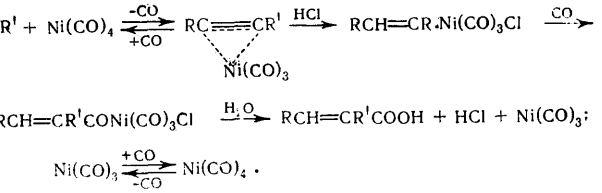
By reaction with $Rh(CO)_2Cl$ in benzene, diethylacetylene was converted into tetraethylcyclopentanephenol [tetraethylcyclopentanophenol ?], isolated as a complex with $RhCl_3$, and partly into 2,3,5,6-tetraethyl-1,4-benzoquinone, and diphenylacetylene was converted into 2,3,4,5-tetraphenylcyclopentadienylrhodium chloride and partly into hexaphenylbenzene[108] [wrong reference (Ed. of Translation)].

In the presence of palladium salts, the carbonylation of acetylene occurred under milder conditions: 60–125°C and 1–45 atm of carbon monoxide with formation of a mixture of saturated and unsaturated mono- and di-carboxylic acids. The butyl esters of acrylic, propionic, maleic, and fumaric acids were obtained in proportions of 24:9:38:10 from a 1:1 acetylene–carbon monoxide mixture in butanol containing 0.1% $CdCl_2$, 1.1% $I_2$, and 1.8% $H_2O$. An increase of the concentration of carbon monoxide in the mixture promoted an increase in the yield of the dicarboxylic acid esters. The replacement of $I_2$ by HI and of $PdCl_2$ by $PdSO_4$ did not influence the reaction. The addition of $SnCl_2.2H_2O$ inhibited the reaction[109].

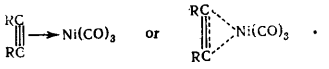
The carbonylation of acetylene in benzene solution in the presence of a $PdCl_2$ complex with dibenzonitrile proceeds with preferential formation of muconic acid chloride containing an admixture of fumaric and maleic acid chlorides[97,110,111].

In the presence of phosphine complexes of palladium, a specific role of the solvent was observed. In a 5:1 chloroform–alcohol mixture at 40°C and 1 atm, acrylate esters were formed. When chloroform was replaced by benzene, toluene, or xylene, catalytic activity was not shown below 80°C, which can be accounted for by the formation in the first case of the complex $Pd[(C_6H_5)_3P]_2.CHCl_3$ which is probably converted during the reaction into the hydride complex $Pd(H)Cl[(C_6H_5)_3P]_2$. A similar complex, obtained by the reaction of chloroform with $Pd[(C_6H_5)_3P]_4$, also catalysed the carbonylation of acetylene under analogous conditions[112].

The carbonylation of acetylenic compounds by the stoichiometric method may be represented by the following scheme[113]:

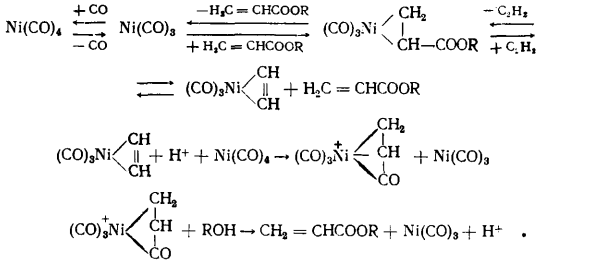


The acetylenic compound reacts with $Ni(CO)_4$ forming a π complex, which is converted under the influence of a proton into a σ-alkenyl and then alkenoyl organometallic compound:

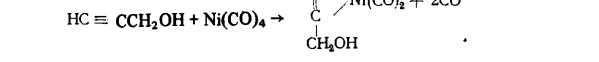


The complexes of nickel, cobalt, and iron carbonyls with acetylenic compounds are widely known. For example, $Co_2(CO)_9.C(C_3H_7)\equiv CH$, $Co_2(CO)_9C(CH_3)\equiv CH$, and $Co_2(CO)_9.CH\equiv CH$ were obtained from $Co_2(CO)_8$, CO, and acetylenic hydrocarbons at 70°C and 190 atm.[114-115]

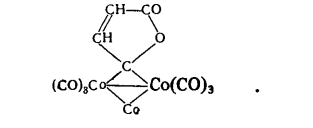
The carbonylation by the catalytic method has been represented by the following scheme[25,108]:



Thus $Ni(CO)_3$ is regenerated on formation of the reaction products. The dissociation of the metal carbonyl with simultaneous formation of coordination-unsaturated intermediates may proceed with the immediate evolution of two CO molecules, as was observed in the carbonylation of propargyl alcohol[108]:



Analogous intermediate complexes, which are of the type of π complexes of the catalyst and the substrate, were also formed in the case of cobalt, iron and other Group VIII metal carbonyls[115]. Cobalt carbonyl complexes with acetylene are known to be capable of reacting with several CO molecules under the conditions of the carbonylation reaction, forming complexes of the type



Such complexes may be converted further into dicarboxylic acids or into cyclic compounds[114,116].

Recently a major role in the carbonylation reaction has been attributed to hydrocarbonyls. It is assumed that nickel catalysts form in the first stage nickel hydrocarbonyl, which is in fact the true reaction catalyst[85]:

$$Ni(CO)_4 \underset{-nCO}{\overset{+HX}{\rightleftharpoons}} HNi(CO)_{4-n}X \xrightarrow{CH\equiv CR} CH_2=C(R)Ni(CO)_{4-n}X + RCH=CHNi(CO)_{4-n}X \xrightarrow{CO}$$
$$\xrightarrow{CO} CH_2=C(R)CONi(CO)_{4-n}X + RCH=CHCONi(CO)_{4-n}X \xrightarrow{R'OH} CH_2=C(R)COOR' + RCH=CHCOOR' + HNi(CO)_{4-n}X,$$

where HX = $H_2O$, an organic acid, or an inorganic acid and R′ = H or alkyls.

The data presented in this section show that the carbonylation of monoacetylenic hydrocarbons leads to the formation mainly of $\alpha\beta$-unsaturated carboxylic acids, their esters, and other derivatives. The reaction proceeds in the presence of catalysts based on Group VIII metal carbonyls of hydrocarbonyls.

## III. CARBONYLATION OF MONO-OLEFINIC HYDROCARBONS.

### 1. Reactions in the Presence of Catalysts Based on Group VIII Metals

The carbonylation of olefinic hydrocarbons[7,117] takes place under more severe conditions than that of acetylenic hydrocarbons: at 120–280°C and 100–300 atm of carbon monoxide in the presence of cobalt or nickel halides or carbonyls, sometimes activated by magnesium, aluminium, manganese, $Cr_2O_3$, tin, CuI, and RbI. Complex salts of the type $K_2[Ni(CN)_4]$, nickel and cobalt complexes of amines, and aqueous solutions of iron and cobalt salts of organic acids have also been used as catalysts. The results of earlier studies in this field are compiled in a previous review[1]. The carbonylation of olefins takes place on heating to 160–170°C in a mixture with a stoichiometric amount of nickel or cobalt carbonyl in the presence of water and acetic acid according to the mechanism

$$4RCH=CH_2 + 4H_2O + Ni(CO)_4 + 2CH_3COOH \rightarrow 4[RCH(CH_3)COOH + RCH_2CH_2COOH] + (CH_3COO)_2Ni + H_2 .$$

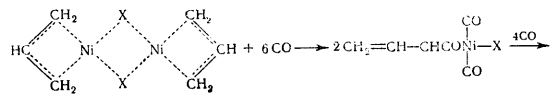
The principal characteristics of the carbonylation reaction are the same for both olefins and acetylenic hydrocarbons[7,98,117–120], certain reactive olefins, such as for example, bicyclo-[2,2,1]heptene, react under the same conditions as acetylenic hydrocarbons[121]. Straight-chain $\alpha$-olefins enter into the reaction most readily with formation of a mixture of straight-chain and $\alpha$-methyl-substituted carboxylic acids in proportions of 1 : (1.5–2.5) in the presence of nickel catalysts and 3 : 1 in the presence of cobalt catalysts[120–122]. Activators of nickel catalysts ($I_2$, HI, $CH_3I$, KI) accelerate the reaction and increase the yield of the straight-chain acids. In the presence of the $Ni(CO)_4 + NiI_2$ catalyst, $C_2$–$C_4$ olefins are converted into acids in yields up to 90%, which increase when solvents such as methanol, acetone, and dioxan, which readily dissolve both the olefin and water, are employed[119].

In the presence of $Ni(CO)_4 + NiI_2$, mainly propionic acid (85%) is obtained from ethylene, a mixture of butyric and isobutyric acids (48 : 52) from propene, a mixture of trimethylacetic and $\alpha$-methylbutyric acids (60 : 40) from isobutene, and a mixture of caproic and $\alpha$-methylvaleric acids from pent-1-ene. Qualitatively, the same acids are formed from $\beta$-olefins as from $\alpha$-olefins. In the carbonylation of olefins, higher carboxylic acids, aldehydes, and polymers are formed as side products[120]. In the synthesis of butyric acids (yield 96%) from propene, carbon monoxide, and water, in the presence of $Co_2(CO)_8$, the reaction is of first order with respect to water, of zero order with respect to propene, and of a fractional order (0.6–0.8) with respect to the catalyst[122]. When water is replaced by methanol, butyric acid esters are obtained, whose yield increases with increase of carbon monoxide pressure from 25 to 208 atm, with increase of the catalyst concentration, and with decrease of reaction temperatures from 250° to 145°C.[123] The relative amounts of the isomers in the reaction products are influenced by carbon monoxide pressure, reaction temperature, and the nature of the catalyst metal: $Co_2(CO)_8$, $Ni(CO)_4$, or $Ru_3(CO)_{12}$.[124] In order to increase the catalytic activity, tributylphosphine[125] or small amounts of pyridine are added to $Co_2(CO)_8$. Pyridine accelerates the reaction and increases the yield of unbranched products[126–128]. The presence in the reaction zone of small amounts of $H_2$ does not prevent the formation of acids and their esters, but the hydroformylation of the olefins with formation of an aldehyde or an acetal takes place at the same time[129,130].

For the synthesis of propionic acid and its methyl and ethyl esters, nickel, cobalt, and iron halides deposited on silica gel (1 : 1), which proved more effective as a carrier than kieselguhr, pumice, and kaolin, are employed as catalysts. The catalysts can be arranged in the following sequences in terms of their activity[69–72,131]: Ni > Co > Fe and I > Br > Cl. It is suggested that the complexes $M(CO)I_2$, where M = Co, Ni, and Fe, are formed initially. They react further with carbon monoxide or methanol:

$$NiI_2 + CO \rightarrow Ni(CO)I_2 \xrightarrow[CH_3OH]{3CO} \begin{matrix} Ni(CO)_4 + I_2 \\ CH_3COOH + NiI_2 \quad \text{etc.} \end{matrix}$$

The iodides form complexes more readily than the bromides and chlorides. The stability of the complexes $M(CO)I_2$ obtained from the halides and carbon monoxide under pressure[39] decreases in the series Fe > Co > Ni, in opposition to the catalytic activity series[132]. When carbon monoxide was passed through solutions of $\pi$-allylnickel halides at 0°C, about ten moles per mole of the dimer were absorbed. The formation of a coordination bond corresponding to butenoylnickel dicarbonyl halides was observed by infrared spectroscopy:




$$\rightarrow 2CH_2=CHCH_2COX + 2Ni(CO)_4 .$$

In the presence of $Ni(CO)_4$, the carbonylation reaction is promoted by traces of acid (HCl), necessary for the formation of halogenonickel dicarbonyl hydride, which is apparently the actual reaction catalyst[133]:

$$HX + Ni(CO)_4 \underset{+2CO}{\overset{-2CO}{\rightleftharpoons}} HNi(CO)_2X \xrightarrow{RCH=CH_2} [RCH_2CH_2Ni(CO)_2X +$$
$$CH_3CH(R)Ni(CO)_2X] \xrightarrow{CO} [RCH_2CH_2CONi(CO)_2X + CH_3CH(R)CONi(CO)_2X] \rightarrow$$
$$\xrightarrow{R'OH} RCH_2CH_2COOR' + CH_3CH(R)COOR' + HNi(CO)_2X.$$

Data have been obtained in support of an analogous mechanism of the carbonylation reactions in the presence of a cobalt catalyst[134–137]. Acylcobalt carbonyl $RCOCo(CO)_4$, formed when the hydrocarbonyl $HCo(CO)_4$ absorbs a mole of carbon monoxide and a mole of olefin, was isolated. When $HCo(CO)_4$ was allowed to react with $RCOCo(CO)_4$, an aldehyde and $Co_2(CO)_8$ were obtained.

A mechanism has been proposed for the hydroformylation of olefins[134]:

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

The reduction of $CH_3COCo(CO)_4$ by hydrogen at 25°C [138,139] ceases completely at high carbon monoxide pressures, which suggests that this acyl cobalt carbonyl is relatively inactive[139]. Therefore a different mechanism was adopted in which the catalyst is cobalt tricarbonyl hydride[136]:

$$HCo(CO)_4 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} HCo(CO)_3 \underset{-RCH=CHR}{\overset{RCH=CHR}{\rightleftharpoons}} \underset{HCo(CO)_3}{RCH=CHR} \rightleftharpoons$$
$$\rightleftharpoons RCH_2CH(R)Co(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} RCH_2CH(R)Co(CO)_4 \rightleftharpoons$$
$$\rightleftharpoons RCH_2CH(R)COCo(CO)_3 \begin{cases} \xrightarrow{HCo(CO)_4} RCH_2CH(R)CHO + Co_2(CO)_7 \\ \xrightarrow[H_2]{} RCH_2CH(R)CHO + HCo(CO)_3 \end{cases}.$$

Cobalt hydrocarbonyl catalyses also the migration of the double bond in olefins when it forms an intermediate $\pi$ complex with the olefin[136,140].

The interconversion of alkylmetal carbonyl and acylmetal carbonyl takes place similarly also for the manganese compounds[141]. This is accompanied by the isomerisation of the carbon skeleton, for example:

$$CH_3CH_2CH_2CH_2COCo(CO)_n \rightleftharpoons \begin{matrix} H_5C_2 \\ H_3C \end{matrix}\!\!>\!CHCOCo(CO)_n .$$

The rate of isomerisation greatly depends on the size of the alkyl group[142].

In the carbonylation and hydroformylation reactions, the true catalyst is probably cobalt hydrocarbonyl[137] which in the absence of gaseous hydrogen is formed from $Co_2(CO)_8$ and the hydrogen of the solvent. Acylcobalt carbonyls are hydrolysed or alchoholysed with formation of a carboxylic acid or an ester and the regeneration of the hydrocarbonyl. Acryloyl-, pent-4-enoyl, and allylcobalt tricarbonyls form with sodium methoxide the sodium salt of the corresponding acid, an ester, or an ether. Alkylcobalt and acylcobalt carbonyls form at 0°C stable complexes with $(C_6H_5)_3P$, carbon monoxide being evolved[135]. Trialkyl- and triaryl-phosphine derivatives $RCOCo(CO)_n$ react with sodium methoxide, forming free phosphines, $NaCo(CO)_n$, and carboxylic acid esters[137].

Iron carbonyls proved to be active catalysts in the carbonylation of olefins with formation of alcohols:

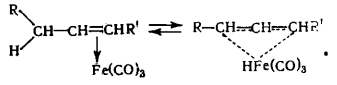
$$C_nH_{2n} + 3CO + 2H_2O \rightarrow C_{n+1}H_{2n+3}OH + 2CO_2 .$$

The reaction proceeds at 60–80°C and 100–200 atm in an aqueous alkaline solution of $Fe(CO)_5$.[143] The replacement of CO in the carbonyl by $(C_6H_5)_3P$ leads to an increase of catalytic activity by a factor of about ten[144]. The complexes formed from iron carbonyls, tertiary amines, and water are also active catalysts of this reaction[145], which occurs at a pressure as low as 10–25 atm. In the presence of ammonia, amines are formed[146].

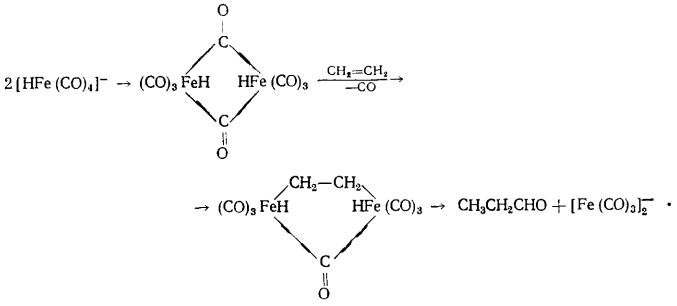
The synthesis of butyl alcohols by this method, has been achieved under industrial conditions[147]. Trimethyl-, and triethyl-amines and *N*-ethylpiperidine are most effective as the amine components of the catalyst. In this case the yield of alcohols reaches 56%. The effectiveness of pyridine and its derivatives is very low[148]. The complex of iron hydrocarbonyl with n-butylpyrrolidine also proved to be an active catalyst for the synthesis of primary butyl alcohols from propene. The conversion of carbon monoxide reached 75%, that of propene 86%, and the content of isobutyl alcohol was 25%.[149] The formation of some alcohols with the iso-structure indicates an isomerising effect of $Fe(CO)_5$.[145] The reaction probably proceeds via a $\pi$ complex of iron hydrocarbonyl with the olefin in equilibrium with the $\sigma$ compound[150]:

$$\begin{matrix} RCH=CHR \\ \downarrow \\ HFe(CO)_3 \end{matrix} \rightleftharpoons \begin{matrix} RCH-CH_2R \\ \downarrow \\ Fe(CO)_3 \end{matrix} .$$

The formation of a $\pi$ complex of the olefin with iron tricarbonyl, which is subsequently converted into a $\pi$-allyl complex of iron hydrocarbonyl, is also possible:



The complexes obtained by the reaction of $Fe(CO)_5$ with bases catalyse also the migration of the double bond in olefins. The olefin replaces one CO group and an aldehyde is obtained from the complex formed[151]:



In the carbonylation of olefins in the presence of ammonia or amines using cobalt catalysts at an elevated pressure, carboxylic acid amides are obtained. In the presence of iron catalysts, mainly primary, secondary, and ternary amines are formed, while the yield of the amides is low. The amides can be synthesised also on the catalyst for the Fischer–Tropsch synthesis (Co–$ThO_2$–MgO–kieselguhr) at 200°C and 150 atm. *N*-(n-propyl)propionamide, 2-ethyl-3,5-dimethylpyridine, and 4-ethyl-3,5-dimethylpyridine were synthesised from ethylene, ammonia, and a 1 : 1 carbon monoxide–hydrogen mixture in hexane. In the absence of hydrogen, *N*-(n-propyl)propionamide was obtained from ethylene, carbon monoxide, and n-propylamine in 60, 55, and 30% yields in the presence of the cobalt catalyst, Co + $Fe(CO)_5$, and $Fe(CO)_5$ respectively.

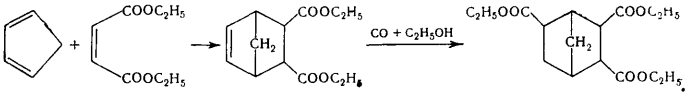
Unsubstituted cyclohexanecarboxamide was synthesised from cyclohexene, carbon monoxide, and ammonia. When ammonia was replaced by a primary amine, the reaction proceeded more smoothly; in the presence of hydrogen, amines are formed as side products[152].

The carbonyls $[C_6H_5Fe(CO)_2]_2$, $[C_6H_5Mo(CO)_3]_2$, and $[Co(CO)_4]_2$ catalyse the reaction of olefins, carbon monoxide, and carbon tetrachloride with formation of compounds having the general formulae RCH(COCl), $CH_2CCl_3$, and $RCHClCH_2CCl_3$.[153]

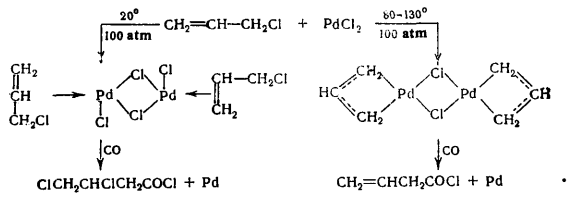
Group VIII noble metals, their salts, and complexes proved to be active catalysts for the carbonylation of olefins. Metallic palladium was active only in the presence of HCl. In the presence of "catalytic" amounts of these metal halides, carboxylic acid chlorides, anhydrides, and esters were formed from olefins, carbon monoxide, and hydrogen chloride in inert solvents at 150–200°C and 600–1000 atm.[154–157]. The reaction of carbon monoxide in benzene solution at 20°C and 50 atm with the Π complex

$C_2H_4.PdCl_2$, prepared by the reaction of ethylene with powdered $PdCl_2$ in benzene, gave β-chloropropionyl chloride in 40% yield relative to the initial *II* complex[155]. An ester of the β-chloroacid is formed in alcoholic solution. The corresponding esters of β-chloroacids were also obtained from $C_3-C_5$ olefins, carbon monoxide reacting with the terminal carbon atom of the double bond. However, hex-1-ene gave an ester with a branched structure as the main product. An ester of *trans*-2-chlorocyclohexanecarboxylic acid was obtained from cyclohexene. The yields of acid chlorides and esters are low due to the decomposition of a considerable proportion of the π complex with formation of an olefin or a chloro-derivative[158]. At 100 atm and 80°C, ethyl propionate with an admixture of ethyl β-hydroxypropionate and γ-oxocaproate was obtained from ethylene in ethanol saturated with hydrogen chloride in the presence of small amounts of $PdCl_2$, propene gave ethyl n-butyrate and isobutyrate (2:1), and styrene gave ethyl α- and β-phenylpropionates (2:1) with an admixture of α-chloroethylbenzene[155].

In the presence of the complex $[(C_6H_5)_3P]_2PdCl_2$, the carbonylation of olefins leads to the formation of carboxylic acids. In the presence of $[(C_6H_5)_3P]Pd$ and small amounts of hydrogen chloride at 90°C and 700 atm, about 60% of isobutyric acid, 3% of butyric acid, and 36% of methyl butyrate were obtained from propene, carbon monoxide, and methanol.[159] Products of the Diels–Alder synthesis, which are unstable at high temperatures, were carbonylated with the aid of palladium complexes:



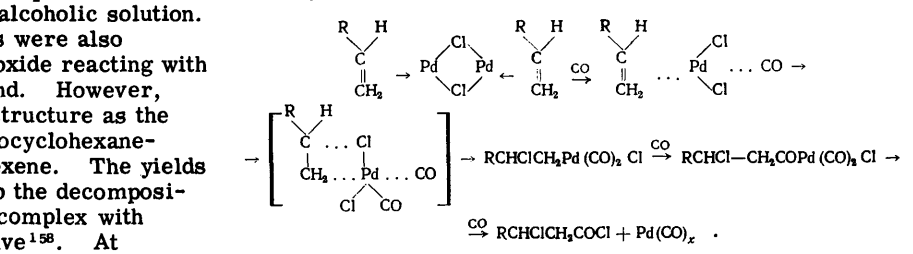
Triethyl cyclohexane-1,2,5-tricarboxylate was synthesised from butadiene by a similar reaction[160]. The differences sometimes observed in the mode of carbonylation depending on the reaction conditions, with formation of β-chlorocarboxylic acid chlorides or esters at 20°C and the analogous derivatives of β-unsaturated acids at 80–130°C, may be explained by the formation of different olefin–$PdCl_2$ π complexes,[158,161]:



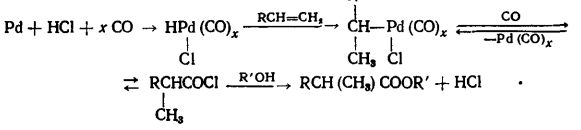
Carbonylation with retention of the double bond takes place with allyl chlorides and allyl alcohols, the same products being obtained from different isomers in consequence of the formation of the same π complex with $PdCl_2$.[159]

In the presence of Group VIII metal halides and chelate complexes in pyridine, olefins react with carbon monoxide and water, also with formation of ketones. Diethyl ketone was obtained from ethylene at 200°C and 1000 atm together with propionic acid, while propene gave acetone, isopropyl ketone, and isobutyrate together with isobutyric acid[162].

In the formation of acid chlorides and esters, the π complex of the olefin with $PdCl_2$ is coordinated to one or two carbon monoxide molecules; in the resulting complex the Cl atom migrates from palladium to the carbon atom of the coordinated olefin and a σ-organometallic compound is formed and reacts further with carbon monoxide. The latter is inserted between the alkyl group and palladium with formation of a β-chloroacylpalladium compound, which is subsequently converted into the chloride of the β-chlorocarboxylic acid:

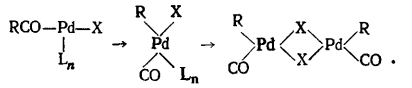


The structure of the initial π complex has been confirmed by NMR data[163]. A mechanism has been proposed for the formation of esters from olefins in the presence of the $PdCl_2$ in ethanol, where the true catalyst is palladium hydrocarbonyl chloride[164–168]:



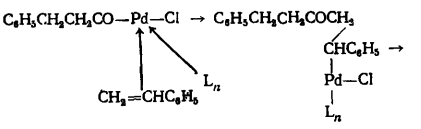
The $C_2H_4-PdCl_2$ complexes are carbonylated with formation of β-chloropropionic acid anhydride, while metallic palladium catalyses the carbonylation of olefins with formation of esters and aldehydes. These reactions are reversible: acid chlorides and aldehydes are decarbonylated to the olefins with intermediate formation of the acyl-palladium bond[165–167]. The first stage in the carbonylation of mono-olefins in the presence of hydrogen halides is believed to be the formation of palladium(II) in the form of metal hydride complexes, whose formation by oxidative addition of the hydrogen halide or hydrogen to transition metals is well known[169,170]. These complexes play an important role as catalysts, not only in carbonylation reactions but also in hydrogenation, double bond migration, and addition reactions.

A number of stages in carbonylation, catalysed by metal carbonyls, including the carbonylation of the phosphine complexes of palladium and platinum, are reversible[171]. The last decarbonylation stage—the conversion of the acylpalladium complex in the absence of carbon monoxide into an alkylpalladium complex proceeds via a "stable tetracoordinate bridge" halogenocarbonyl complex[172] [wrong reference (Ed. of Translation)]:



Subsequently the alkyl–palladium bond is cleaved with formation of an olefin and hydrogen halide or hydrogen. An alkyl palladium–phosphine complex with a β-hydrogen atom in the alkyl group is converted into an olefin and palladium hydride, which decomposes into palladium and hydrogen halide[173].

The decarbonylation of β-phenylpropionic acid anhydride gives 1,5-diphenylpent-1-en-3-one according to the mechanism[165]:



where L = phosphine.

The presence of activators (acids), the solvent, and reaction temperature have a major influence on the redistribution of bonds within the palladium complexes on coordination of carbon monoxide and the dissociation of Pd–Cl bridge bonds[174].

The decarbonylation of carboxylic acid chlorides also takes place under the influence of rhodium complexes:

$$RCH_2CH_2COCl + RhCl[(C_6H_5)_3P]_3 \rightarrow RCH{=}CH_2 + HCl + \underset{\displaystyle CO}{\overset{\displaystyle |}{Cl{-}Rh}}[(C_6H_5)_3P]_2 .$$

The chlorocarbonyl complex formed could be isolated[165].

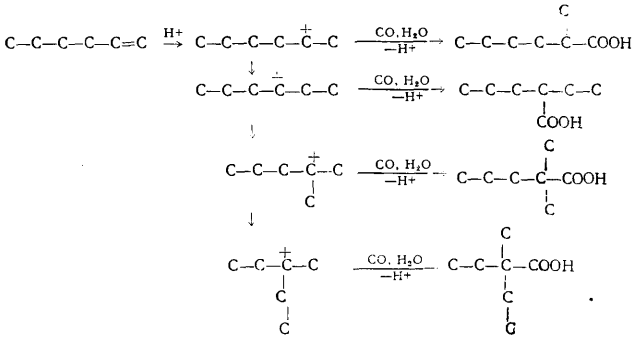
The decarbonylation of aldehydes leads to the formation of an alkane and the complex $ClRh(CO)[(C_6H_5)_3P]_2$.[166] This complex was also obtained by the reaction of the transition metal salts with alcohols, and proved to be an active catalyst for the decarbonylation of aldehydes and acid chlorides[175,176]. Analogous carbonyl halide hydrides are formed by the reaction of hydrogen chloride with carbonylbis(triphenylphosphine)iridium chloride[170] and of methyl chloride with iodo(methyl)bis(triethylphosphine)-platinum[177]. In the presence of soluble variable-valence metal salts, with a positive oxidation potential higher than that of platinum, for example $CuCl_2$, platinum catalyses at 120–150°C and 150–200 atm the carbonylation of olefins in an alcoholic medium with formation of unsaturated and β-alkoxy-substituted carboxylic acid esters. Oxygen was added in portions to the reaction medium[178]. αβ-Unsaturated carboxylic acid esters have been synthesised electrochemically[178,179] from carbon monoxide and olefins in the presence of carbonyl complexes of platinum. It has been suggested that the catalytic activity of Group VIII metal carbonyls in the carbonylation of unsaturated hydrocarbons is associated with the acidic properties of the hydrocarbonyls of these metals, rhodium carbonyl showing the greatest effectiveness in the hydrocarboxylation and hydromethoxycarbonylation reactions of the above hydrocarbons[180].

Ruthenium and rhodium halides and chelate complexes also catalyse the carbonylation of olefins. Propionic acid is formed from ethylene in concentrated hydrochloric acid and in cyclohexane solution mixed with anhydrous hydrogen chloride the products are propionic anhydride and propionyl chloride. The reaction proceeds at 150–210°C and a high carbon monoxide pressure (600–1000 atm).[154]

The data quoted in this section show that the carbonylation of mono-olefins with formation of saturated carboxylic acids in an aqueous medium or of their esters in an alcoholic medium proceeds in the presence of catalysts based on Group VIII metals; cobalt, nickel, iron, platinum, palladium, ruthenium, and rhodium. The true catalysts are the intermediate hydrocarbonyl complexes. One of the primary stages may be the formation of a π complex of the metal hydrocarbonyl with the olefin. An important stage is the conversion of the alkyl into acyl complexes. Catalysts based on Group VIII noble metals, particularly complexes with ligands of the type of triarylphosphines, are already active at 20–50°C and the reaction products can be also acid chlorides, anhydrides, and chlorocarboxylic acids.

## 2. Reactions in the Presence of Acid Catalysts

The carbonylation of olefins can be achieved in the presence of various acid catalysts[1]. Initially the reaction was carried out at an elevated temperature (100–300°C) and high carbon monoxide pressures (200–1000 atm) in the presence of all the starting materials in the reaction zone. Subsequently the process was achieved in two stages: the reaction of the olefin with carbon monoxide in the presence of 96% sulphuric acid at 0–50°C, and 1–100 atm carbon monoxide pressure and the decomposition of the reaction complex by water with formation of carboxylic acids and regeneration of sulphuric acid[181,182]. The addition of the elements of formic acid (H–COOH) takes place in accordance with the Markovnikov rule. Acids with a quaternary atom, such as αα-dimethyl- and α-ethyl-α-methylalkanoic acids, are always formed from straight-chain α-olefins together with the expected acids having a tertiary carbon atom in the α-position; unbranched carboxylic acids are absent from the reaction products. The number of possible isomers is given by the equation $y = x - 2$, where $x$ is the number of carbon atoms in the initial olefin. All the expected isomeric acids were obtained from straight-chain $C_5$–$C_{10}$ olefins[183]. The results obtained are described satisfactorily by a mechanism according to which carbonium ions are formed as intermediates:



Olefins branched at the double bond can form only tertiary carbonium ions and the latter are converted exclusively into carboxylic acids with a quaternary α-carbon atom.

Small amounts of the carbonylation products of the dimeric form of the olefin are formed together with the normal reaction products. Trimethylacetic[181,184] and ααγγ-tetramethylvaleric acid were obtained from isobutene. Lower olefins branched at the double bond disproportionate at a carbon atom with subsequent carbonylation. Thus a mixture of $C_{11}$ acids and also equivalent amounts of trimethylacetic and αα-dimethylvaleric acid are formed from 2-methylbut-2-ene together with αα-dimethylbutyric acid. The formation of $C_5$ and $C_7$ acids is due to the disproportionation of the isodecene formed initially into $C_4$ and $C_6$ olefins. ααγγ-Tetramethylvaleric and methylneopentylacetic acids were obtained from di- and triisobutenes respectively.

For cyclic mono-olefins, the number of possible isomeric acids cannot be determined from the equation derived for unbranched acyclic olefins, since the isomerisation is affected by the ring size and ring strain and also the reaction conditions. 1-Methylcycloheptane- and 1-ethylcycloheptane-carboxylic acids were obtained from cyclo-octene; the products of the direct carbonylation of cyclononene and cyclodecene could not be obtained either[185].

When carbon monoxide is replaced by formic acid, the reaction in the presence of concentrated sulphuric acid proceeds at atmospheric pressure and room temperature[186–188]. Carboxylic acids are obtained in high yields for the molar ratios olefin: $HCOOH : H_2SO_4 = 1 : 4 : 8$. Carboxylic acids with one carbon atom more than in the initial olefin and with a quaternary carbon atom in the α-position were largely formed from unbranched olefins.

A mixture of the carbonylation products of the monomeric and dimeric forms and of the olefins produced by the disproportionation of the dimer was obtained from the olefins branched at the double bond. Cyclo-olefins without a six-membered ring usually undergo ring contraction or expansion with formation of cyclohexanecarboxylic acids. Cyclohexene gives 1-methylcyclopentanecarboxylic acid and alkylcyclohexenes are converted into acids with retention of the six-membered ring. Bi- and poly-cyclic systems are carbonylated in high yields (up to 95%). Thus 5-methyl-bicyclo[2,2,1]hept-2-ene gives 2-*endo*-methylbicyclo[2,2,1]heptano-*exo*-2-carboxylic acid[186].

In the synthesis of carboxylic acid esters using carbon monoxide, a two-stage method is employed, in which the reaction complex formed by the interaction of the olefin with carbon monoxide at 20–40°C and 70–80 atm carbon monoxide pressure in the presence of sulphuric acid is decomposed by methanol or ethanol[189-191]. $C_5-C_{10}$ olefins[192-195] and cyclo-olefins[196,197] have been hydroalkoxycarbonylated by this method. Methyl and ethyl esters, predominantly with a quaternary $\alpha$-carbon atom, are obtained in high yields[198]. At atmospheric pressure the yield of esters is low, but, on raising the carbon monoxide pressure in the range 5–75 atm, the overall yield of esters increases; however, in the case of isobutene the content of esters with quaternary and tertiary $\alpha$-carbon atoms shows little change. In the reactions of straight-chain $\alpha$-olefins, skeletal isomerisation processes are retarded, which leads to a lowering of the yield of esters with a quaternary $\alpha$-carbon atom[199,200]. An increase of the $H_2SO_4$ : olefin molar ratio increases the overall yield and the content of the main reaction product for but-1-ene but decreases the content of the main product for isobutene. An increase of reaction temperature has an unfavourable effect[201].

The hydroalkoxycarbonylation of olefins and cyclo-olefins is readily achieved by the reaction with formic acid in the presence of concentrated sulphuric acid at atmospheric pressure close to room temperature with subsequent addition of the alcohol in the second stage of the process. The reaction has been investigated for aliphatic straight-chain $C_5-C_9$ olefins, $C_5-C_6$ olefins with the iso-structure[202-205], and also cyclo-olefins: cyclopentene, cyclohexene, 1-alkylcyclopentenes, and 1-alkylcyclohexenes[205-208]. $C_1-C_5$ saturated alcohols were used in the second stage. In all these reactions the main products were carboxylic acid esters with quaternary or tertiary carbon atoms in the $\alpha$-position relative to the alkoxycarbonyl group. The corresponding free carboxylic acids were present in the reaction products. The position of the double bond in the initial olefin molecule did not affect the course of the reaction. The relative yield of esters fell and that of free acids increased with increase in the number of carbon atoms in the molecule of the alcohol added in the second stage[209-211].

An increase of the concentration of sulphuric acid, the addition to it of some $P_2O_5$, an increase of the relative amount of the alcohol added in the second stage, and in increase of temperature lead to an increase of the yield of esters. Thus in the case of pent-1-ene an 80% yield is achieved and the content of the main products in the mixture is 90–98%.

The isomerisation of the carbon skeleton of the initial olefin takes place in the alkylcarbonium ion stage and the acylium ion formed subsequently by the reaction $R^+ + CO \rightarrow R\overset{+}{C}O$, the carboxylic acid, and its ester do not isomerise. A certain amount of carboxylic acids is produced already in the first reaction stage due to the water contained in the sulphuric and formic acids and liberated on decomposition of the latter. Esters are formed both by the reaction of acylium ions with alcohols:

$$R\overset{+}{C}O + R'OH \rightarrow RCOOR' + H^+$$

and by the esterification of the carboxylic acids already formed in the first stage[212-214].

It has been noted[215] that concentrated $H_3PO_4$ does not catalyse the carbonylation of olefins at all. However, this proved true only of the reaction conditions described: 5–10°C and 100 atm carbon monoxide pressure. Subsequently it was found that at a higher temperature phosphoric acid is active in this reaction[216]. In the presence of 95–100% $H_3PO_4$, $H_4P_2O_7$, and polyphosphoric acids, $C_5-C_{12}$ olefins of different structures were converted into carboxylic acids at 75–150°C. Under the reaction conditions, $H_3PO_4$ gives up the water necessary for the formation of a carboxylic acid, and is converted into $H_4P_2O_7$. When a stoichiometric amount of water is added, the catalyst and the reaction product collect in different layers[217]. The catalytic properties of $H_3PO_4$ were investigated in reactions involving the carbonylation by carbon monoxide of straight-chain $C_5-C_{10}$ olefins, isobutene, di-isobutene, and cyclohexene[218-222]. A mixture of $\alpha\alpha$-dimethyl-, $\alpha$-ethyl-$\alpha$-methyl-, $\alpha$-ethyl-, and $\alpha$-methyl-alkanoic acids is formed as the main products.

Straight-chain $C_7-C_{10}$ $\alpha$-olefins yielded only acids derived from their monomeric form, i.e. with the $C_8-C_{11}$ composition. $C_5-C_6$ $\alpha$-olefins form in addition small amounts of acids derived from their dimeric form ($C_{11}-C_{13}$ acids), disproportionation products, and also the isomers and dimers of the initial olefin. Isobutene and di-isobutene give rise to the same reaction products: trimethylacetic acid and $C_6-C_8$ and $C_{13}$ acids. 1-Methylcyclopentanecarboxylic acid, cyclohexanecarboxylic acid, and a mixture of *cis*- and *trans*-decalin-9-carboxylic acid were obtained from cyclohexene. The optimum concentration of $H_3PO_4$ in the carbonylation of $C_7-C_{10}$ $\alpha$-olefins increases with the number of carbon atoms in the olefin molecule; in the case of $C_5-C_6$ olefins, this concentration is below 94%. At higher concentrations the olefin dimerisation and disproportionation processes become intensified. With the increase in the number of carbon atoms in the molecule of the initial olefin from four to seven, the overall yield of acids rises with a relative decrease of the yield of acids having a quaternary carbon atom in the $\alpha$-position and also derivatives of the dimeric form of the olefin. The optimum reaction temperature is in the range 125–175°C, i.e. higher by about 100°C than in the carbonylation in the presence of sulphuric acid. The optimum carbon monoxide pressure is 70–80 atm, which is higher by 20–30 atm than for sulphuric acid[220].

"Solid" phosphoric acid, prepared by mixing 90% phosphoric acid with kieselguhr and subsequent heat treatment at 200–370°C,[223] catalyses the carbonylation reaction at 50–100°C and 150 atm.

Hydrogen fluoride has also been used as a catalyst for the carbonylation of olefins. Carboxylic acid fluorides are formed from unbranched olefins and carbon monoxide in the presence of anhydrous HF, while in the presence of aqueous hydrofluoric acid the products are carboxylic acids and their esters. When methanol is added, esters are produced. $\alpha$-Methylbutyric and isononanoic acids and their s-butyl esters were synthesised from but-1-ene at 30°C and a carbon monoxide pressure of 20–30 atm in the presence of HF containing 5% of water. Olefins branched at the double bond are carbonylated more readily than straight-chain olefins, but the reaction products are

carboxylic acid and their fluorides. Esters are not obtained under these conditions because of the instability of the intermediate tertiary alcohols, which are decomposed by hydrogen fluoride. Esters are obtained from $C_3-C_{20}$ olefins and carbon monoxide at higher pressures in the presence of hydrogen fluoride and up to 15% of water. When the initial compounds are measured out accurately, hydrogen fluoride can be reused without additional purification [224-227].

Catalysts based on $BF_3$, which can be separated from the reaction products without diluting the reaction mixture with water or alcohols, are also employed in the olefin carbonylation reactions. The $BF_3-H_2SO_4$ systems, prepared by passing $BF_3$ into 45 and 85% sulphuric acid at 0° and 100°C, are used only for branched olefins [215,228,229] and the $BF_3-H_3PO_4$ system, with component ratios ranging from 1.2 : 0.8 to 0.8 : 1.2, is used for the carbonylation of both branched and unbranched olefins. The greater the amount of carboxylic acids with a quaternary $\alpha$- carbon atom in the reaction products, the more complete and rapid is their separation from the catalyst [230-232].

The $BF_3-CH_3OH$ system, obtained by passing $BF_3$ into methanol, may be regarded as monomethoxyfluoroboric acid $H(BF_3OCH_3)$; it is active in the hydroalkoxycarbonylation of olefins, particularly cyclic olefins, but it results in a homogeneous reaction mixture [233], which does not separate into the catalyst and the reaction product. In the presence of this system at 15°C and a carbon monoxide pressure of 150 atm, high yields were obtained of the methyl esters of 1-benzylcyclohexanecarboxylic, 1-benzylcycloheptanecarboxylic, and 1-benzylcyclooctanecarboxylic acids from 1-benzylcyclohexene, 1-benzylcycloheptene, and 1-benzylcyclo-octene respectively [234], the methyl esters of $C_{12}$ and $C_{23}$ acids from undec-1-ene, and also the corresponding esters of acids derived from oct-1-ene, isononene, isobutene, tetradec-1-ene, 2-ethylhex-1-ene, and octahydronaphthalene. A mixture of alkoxyfluoroboric acid with boron trifluoride hydrate, containing between one and two moles of a mixture of water and alcohol per mole of $BF_3$, also catalyses effectively the carbonylation of olefins. When a stoichiometric amount of water is added, the catalyst is readily separated from the reaction products, which consist of a mixture of 70-90% of carboxylic acids and 3-20% of their esters [235].

The $BF_3-2H_2O$ system, obtained when $BF_3$ is passed into water at 0°C, is active in the carbonylation of olefins. Branched olefins are converted below 10°C and at 50-100 atm into acids in 85% yield. In the presence of $BF_3 . 1.5H_2O$, the trimer of propene reacts at 20°C, giving a high yield of a mixture of not less than eight isomeric $C_{10}$ acids [215,236]. The optimum yield of trimethylacetic acid is obtained from isobutene at a carbon monoxide pressure of 100 atm, 30°C, and the molar ratio $C_4H_8 : BF_3 . 2H_2O = 1 : 1$. [237]

The data presented in this section show that two-stage olefin hydrocarboxylation and hydroalkoxycarbonylation reactions involving carbon monoxide, a compound with a mobile hydrogen atom, and an acid catalyst permit the synthesis of branched carboxylic acids with tertiary and quaternary carbon atoms in the $\alpha$-position, their esters, and certain derivatives.

The acid catalysts are concentrated sulphuric acid, concentrated phosphoric acid, hydrogen fluoride, and boron trifluoride complexes.

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