Translated from *Uspekhi Khimii* **58** 118–137 (1989) U.D.C. 661.727.1 + 66.095.5

The synthesis of ethylene glycol from formaldehyde

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ABSTRACT. The literature and patent data on the hydroformylation of formaldehyde to glycolaldehyde—an intermediate in the synthesis of ethylene glycol—are surveyed. The principal types of catalytic systems based on rhodium and cobalt carbonyl complexes and the characteristic features of the reaction are examined and compared with the hydroformylation of olefins. The reaction mechanism is discussed in the light of the reactions of the formaldehyde complexes of transition metals.
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I. Introduction

The wide-scale employment of ethylene glycol in various fields has led to an increasing requirement for this compound. The world output of ethylene glycol in 1983 was 4.5 million tonnes.[1] It is obtained industrially from ethylene as the raw material, the cost of which has been continuously growing.

The search for new methods of synthesising ethylene glycol, especially without involving ethylene, is of practical interest. Methods based on the use of the synthesis gas (Table 1) are recognised as being the most promising.

According to technical-economic forecasts,[1] processes involving the carbonylation of formaldehyde are especially attractive. Information about them is available in recently published monographs[3–6] and reviews.[2,7–15]

Apart from the procedures listed in Table 1, the following methods of synthesis of ethylene glycol are known.

(1) Condensation of formaldehyde:

$$2\,CH_2O \rightarrow HOCH_2CHO \xrightarrow{H_2} CH_2OH{-}CH_2OH.$$

The process is carried out[16] in the presence of alkaline catalysts, deposited on zeolites, at 90–100 °C using aqueous formaldehyde solutions. The yield of glycolaldehyde is about 12% and the rate of its formation is 2.5–4.5 mol litre^{-1} h^{-1}.

(2) Redox reaction (radical coupling, radical condensation):[8,17–20]

$$CH_3OH + CH_3OH \rightarrow CH_2OH{-}CH_2OH + (H_2),$$
$$CH_3OH + CH_2O \rightarrow CH_2OH{-}CH_2OH.$$

The reaction is carried out either in the liquid phase or in the gas phase at a pressure of 5–14 MPa at 225–350 °C using radical generators. The yield of ethylene glycol is 200 kg m^{-3} h^{-1}.

(3) The coupling of methyl formate with formaldehyde:[5,21]

$$HCOOCH_3 + CH_2O \rightarrow HOCH_2COOCH_3.$$

Table 1. The synthesis of ethylene glycol and its derivatives.[1]

Starting materials	Catalyst	Temperature, °C	Pressure MPa	Products	Selectivity, %	Turnover number, 10^3 s^{-1}
$CO + H_2$	$Cs_3Rh_{17}(CO)S_2$	200	100	ethylene glycol methanol	69 21	18.1
$CH_3OH + CO + O_2$	PdI_2—$CuSO_4$	120	2	dimethyl oxalate dimethyl carbonate	78 22	37.0
	Pd/γ-Al_2O_3—NO	120	2	dimethyl oxalate dimethyl carbonate	80 20	21.7
$HCHO + CO + H_2O$	HF	50	2	glycolic acid	94	0.07
$CH_2OCH_2OCH_2O + CO + H_2O$	$RhCl_3$—HI	150	7	glycolic acid acetic and formic acids	39 61	6.4
Paraformaldehyde + H_2 + CO	$Co_2(CO)_8$	120	10	glycolaldehyde methanol	77 23	11.6
	$RhCl(CO)(PPh_3)_2$—NEt_3—PPh_3			glycolaldehyde methanol and carbohydrates	76 24	148.0
Paraformaldehyde + BuOH + H_2 + CO	$Co(OAc)_2(C_5Me_5)$	160	19	monobutyl ether of ethylene glycol dibutyl ether of ethylene glycol methanol	62 6 4	18.8
$H_2C(OMe)_2 + CO + H_2$	$Co_2(CO)_8$	180	20	methyl ether of ethylene glycol dimethyl ether of ethylene glycol methanol and others	46 9 45	3.1

The reaction is performed at atmospheric pressure and a temperature of about 90 °C in the presence of strong acids—HF, H_2SO_4, etc. (selectivity up to 90%). The replacement of methyl formate by formic acid leads to the formation of glycolic acid.

This review considers the method of synthesis of glycolaldehyde (the intermediate in the synthesis of ethylene glycol) by the hydroformylation of formaldehyde:

$$HCHO + CO + H_2 \rightarrow HOCH_2CHO \xrightarrow{H_2} CH_2OH{-}CH_2OH.$$

II. The state of research into formaldehyde hydroformylation processes

Hitherto this reaction has been usually carried out as a homogeneous-catalytic process in solutions of cobalt and rhodium complexes. The subsequent reduction of glycolaldehyde to ethylene glycol was carried out in the same reactor using ruthenium catalysts.[22]

A process involving the hydroformylation of formaldehyde on heterogeneous rhodium catalysts modified by tertiary phosphines immobilised on solid carriers has been patented:[23] at 25 MPa and 120–160 °C, the degree of conversion of formaldehyde into glycolaldehyde in the liquid-phase process is 60–80%. Paraformaldehyde, trioxan, or an aqueous formaldehyde solution can serve as the starting material. In the last case, the selectivity with respect to the target product is low because of the acceleration of the side reaction involving the hydrogenation of glycolaldehyde to methanol. The use of trioxan makes it necessary to carry out the reaction at high temperatures (~300 °C) in order to form monomeric formaldehyde; for the depolymerisation of paraformaldehyde it is sufficient to carry out the reaction at temperatures in the range 90–130 °C,[24] which makes formaldehyde the most suitable reagent.

The high reactivity of formaldehyde and glycolaldehyde leads to many side and secondary reactions, which lower the selectivity of the hydroformylation. Among them, the main reactions are the Cannizzaro–Tishchenko reaction, hydrogenation to methanol and its conversion into higher homologues, and the aldol condensation of formaldehyde to carbohydrates. The last three reactions are catalysed by the components of the catalytic system and the condensation involves the target product (glycolaldehyde) in undesirable reactions. Undesirable side and secondary reactions are accelerated particularly strongly by cobalt catalysts. Thus in the hydroformylation of formaldehyde in the presence of $Co_2(CO)_8$ in dioxan at 120 °C, the maximum selectivity does not exceed 40%; under the same conditions, $RhCl(CO)(PPh_3)_2$ affords glycolaldehyde in 85% yield.[25]

The severe hydroformylation conditions (pressure 15.0–25.0 MPa, temperature 150–170 °C), the low selectivity, and the low rate of reaction in the presence of cobalt catalysts (turnover number 11.6 s^{-1} [26] compared with 148.0 s^{-1} for the rhodium system[27]) made it necessary to give preference to rhodium catalysts. The patent and scientific publications in recent years have been concerned predominantly with processes occurring in solutions of rhodium complexes.

Satisfactory parameters (selectivity up to 95%, degree of conversion of formaldehyde more than 95%, catalyst turnover number about 150 × 10^3 s^{-1}) are attained when promoting agents are introduced into the phosphine–rhodium catalytic system: acids of organic[28] and inorganic[29] origin, organometallic compounds or metal salts,[30–35] and bases.[36,37]

The technological formulation of the synthesis of ethylene glycol by the hydroformylation of formaldehyde is at present in the research and development stage; in the versions proposed, either a single-stage process, combining the hydroformylation of formaldehyde and the hydrogenation of glycolaldehyde in a single reactor,[38] or a two-stage process,[39] in which the catalyst of the first stage is a rhodium complex (in solution, in the form of a suspension, or deposited on a solid carrier), are used. It has been proposed that the process be carried out with a low degree of conversion of formaldehyde[40] in order to reduce the amount of condensation products.

Rhodium catalysts modified with PAr_3 are most often used; they are deactivated, as in the hydroformylation of olefins,[41,42] by the transformation of the phosphine ligand resulting from the *ortho*-metallation of the aromatic substituent.[43] There is no information about the regeneration of such catalysts.

The catalyst can be returned to the cycle when a phosphine amide ligand is used. The following solvent system is employed for this purpose: a low-boiling solvent (acetonitrile), a non-polar high-boiling solvent (*m*-xylene), and a small amount of a second low-boiling solvent (diethyl ether) to decompose the acetonitrile–methanol azeotrope. The most complete regeneration is attained when the ligand is 3-(diphenylphosphino)-*N*-methyl-*N*-oxadecylpropionamide $PPh_2(CH_2)_2C(O)N(CH_3)(C_{18}H_{37})$. A selectivity with respect to glycolaldehyde up to 93–99% is then ensured; the degree of conversion of formaldehyde after the first cycle is reduced by 13% and the residual rhodium content in glycolaldehyde is 26 p.p.m.[44,45]

Glycolaldehyde may be hydrogenated to ethylene glycol in the presence of heterogeneous hydrogenation catalysts: Raney nickel (100% conversion of formaldehyde for 49% selectivity with respect to ethylene glycol is achieved at 110 °C and 7.0 MPa), palladium on charcoal (70 °C, 70 MPa, 100% conversion, 73% selectivity), etc.[46,47] Methods for the hydrogenation of glycolaldehyde to ethylene glycol in quantitative yields have been patented.[48,49]

There exists an example of the selective homogeneous hydrogenation of glycolaldehyde in a static system in solution of $Rh(acac)CO_2$ in *m*-xylene, tetraglyme, or dioxan containing PPh_3: the yield of ethylene glycol is 90.2 mole % at 80 °C, a pressure of 10 MPa, and a $CO:H_2$ ratio of 1:1.[50]

The catalytic method for the hydroformylation of formaldehyde which have been described can be arbitrarily divided into two groups: (a) with participation of carboxylic acid *NN*-dialkylamides in the coordination sphere of rhodium; (b) based on the activation of the catalytic system with the aid of solvents or promoting agents which exhibit a very pronounced basicity ensuring the ionisation of the catalytic complex.

III. Hydroformylation of formaldehyde in solution in amides

The study of the characteristic features of the catalytic hydroformylation of formaldehyde has shown[51] that, in contrast to the reaction with olefins, high rates of formation of glycolaldehyde in the presence of rhodium complexes are attained only when carboxylic acid *NN*-dialkylamides are used as solvents. Only methanol is formed in other solvents (Table 2).

Best results have been obtained in dimethylacetamide using chlorine-containing triphenylphosphine rhodium complexes, especially $RhCl(CO)(PPh_3)_2$, as precursors of the catalyst. The inhibition of the reaction by glycolaldehyde has been noted.[51]

Among other features distinguishing this reaction from the hydroformylation of olefins, the presence of chlorine in the coordination sphere of the active rhodium species and the independence of the rate and selectivity of the reaction of the basicity of the ligand are important. The exclusion of the ligand PR_3 from the catalytic system renders it inactive, which is also uncharacteristic of the hydroformylation of olefins.

The kinetic study of the reaction in the presence of $RhCl(CO)(PPh_3)_2$—the catalyst precursor—in dimethylformamide (DMF) showed that [25,52] the introduction of $Et_3N.HCl$ or Et_3N

into the reaction mixture does not alter the initial rate of hydroformylation. Since the hydroformylation of olefins in the presence of $HRh(CO)(PPh_3)_3$ proceeds at higher rates than in the presence of $RhCl(CO)(PPh_3)_2$ and the catalytic activity of the latter is attributed to the reaction[53,54]

$$RhCl(CO)(PPh_3)_2 + Et_3N + H_2 \rightleftarrows HRh(CO)(PPh_3)_2 + Et_3N \cdot HCl,$$
$$RhCl(CO)(PPh_3)_2 + H_2 \rightleftarrows HRh(CO)(PPh_3)_2 + HCl,$$

the addition of $Et_3N.HCl$ should reduce the rate of reaction, while the addition of Et_3N or the use of $HRh(CO)(PPh_3)_3$ from the very beginning should increase it. The absence of these effects as well as the absence of an induction period when $RhCl(CO)(PPh_3)_2$ is used and also the detection of this complex among the hydroformylation products permitted the conclusion that chlorine enters into the composition of the catalytically active complex.

Table 2. Hydroformylation of formaldehyde in the presence of various catalyst precursors and solvents.[51]

Catalyst precursor	Solvent	Yield, %	
		of glycolaldehyde	of methanol
$HRh(CO)(PPh_3)_3$	acetic acid	0.0	18.6
	acetone	0.0	42.0
	acetonitrile	2.8	43.0
	benzene	0.0	19.7
	1,4-dioxan	0.0	31.7
	pyridine	2.8	4.4
	dimethylacetamide	5.6	4.1
	dimethylformamide	12.3	4.7
$RhCl(CO)(PPh_3)_2$*	"	39.8	2.3
	formamide	0.0	0.0
	methylformamide	0.0	0.0
	methylphenylformamide	0.0	0.0
	dimethylacetamide	49.7	1.2
$Rh_4(CO)_{12}$	dimethylformamide	0.0	0.0
$RhCl(CO)_2(PPh_3)$	"	19.6	0.4
$Rh(C_8H_{12})(PPh_3)_2 \cdot BPh_4$	"	3.8	26.7

Note. Reaction conditions: [Rh] = 5×10^{-3} M, [HCHO] = 2 M, $CO:H_2$ = 1:1, temperature 110 °C, pressure 8 MPa, reaction time 3 h, 100 ml of solvent.
*[HCHO] = 1 M, pressure 13 MPa.

Taking the above into account, the mechanism of the hydroformylation of formaldehyde must provide for the presence of Cl in the intermediates; overall, it resembles the familiar mechanism of the hydroformylation of olefins:[25]

$$RhCl(CO)(PPh_3)_2 \overset{k_1}{\rightleftarrows} RhCl(CO)(PPh_3) + PPh_3,$$
$$RhCl(CO)(PPh_3) + H_2 \overset{k_2}{\rightleftarrows} RhH_2Cl(CO)(Ph_3P),$$
$$RhH_2Cl(CO)(PPh_3) + HCHO \overset{k_3}{\rightleftarrows} RhHCl(CO)(PPh_3)(CH_2OH),$$
$$RhHCl(CO)(PPh_3)(CH_2OH) + CO \overset{k_4}{\rightleftarrows} \underset{(I)}{RhHCl(CO)(PPh_3)(COCH_2OH)},$$
$$(I) \overset{k_5}{\rightleftarrows} RhCl(CO)(PPh_3) + HOCH_2CHO.$$

On the assumption that the initial rate of reaction is $v_0 = k_5[I]$ when $RhCl(CO)(PPh_3)_2$ with an excess of PPh_3 in solution in a dimethylamide is used, the rate constants for the individual stages (k_1, k_2, k_3, and k_4) were determined and it was shown that the equation derived, namely

$$v_0 = {}^1/_2 k_1 k_2 k_3 k_4 k_5 P_{H_2} P_{CO} [HCHO]_0 \left\{ \left(1 + \frac{4[Rh]_0}{k_1 (1+X)} \right)^{1/2} - 1 \right\}, \quad (1)$$

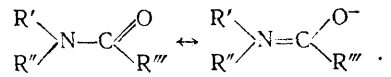
where

$$X = k_2 P_{H_2} + k_2 k_3 P_{H_2} [HCHO]_0 + k_2 k_3 P_{H_2} P_{CO} [HCHO]_0,$$

describes satisfactorily the experimental kinetics.[52] The activation energy for the reaction is 18.3 kcal mol^{-1}.

It is noteworthy that the proposed mechanism does not provide for the participation in the reaction of the chlororhodium dicarbonyl complex with PPh_3, namely $RhCl(CO)_2(PPh_3)$, since such species were incapable of activating H_2 in the oxidative addition reaction in the first stage. At the same time, it is known that the strength of the Rh–CO bond in chlororhodium monocarbonyl complexes of this kind is high and the mobility of the CO group is therefore low.[54] The hydroformylation conditions favour the stabilisation of the dicarbonyl derivative,[55] which may be formed in the reaction with CO or as a result of the decarbonylation of the amide or formaldehyde.[55,56] Such a derivative is characterised by the lability of the carbonyl ligand.[54,55]

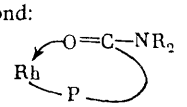
The inhibition of the hydroformylation of formaldehyde by an excess of the phosphine ligand[46,51] confirms a dissociative mechanism analogous to that of the hydroformylation of olefins. Here *NN*-dialkylamides are regarded as electron-donating ligands. A specific feature of such molecules is the presence of resonance structures:



There are numerous data supporting the coordination interaction of the amide with the transition metal. In the vast majority of cases, the coordination is to the oxygen atom of the carbonyl group of the amide[57,58] but there are data also for other types of coordination.[56,59] The possibility of rotation about the C–N bond makes it possible to explain the absence of the activating influence of asymmetrically substituted amides (for example *N*-methyl-*N*-phenylformamide—see Table 2) on the hydroformylation of formaldehyde by the steric hindrance to the coordination.[51]

The coordination interaction of the amide with rhodium has been confirmed as a result of a study[45] in which the hydroformylation of formaldehyde was investigated (130 °C, pressure of 1:1 CO + H_2 mixture 12.9 MPa) in the presence of two different rhodium catalysts: $RhCl(CO)(PPh_3)_2$ (Spencer's catalyst) and $RhCl(CO)[PPh_2(CH_2)_2.(CO)N(CH_3)_2]_2$. When acetonitrile is used as the solvent, the degree of conversion of formaldehyde after 3 h in the presence of a rhodium catalyst with the *NN*-dimethyl-3-(diphenylphosphino)-propionamide ligand was 62% for a selectivity with respect to glycolaldehyde of 75% (the yield of methanol was 2%), i.e. higher parameters were attained than in the presence of $RhCl(CO)(PPh_3)_2$.

On the other hand, when an *NN*-dialkylamide was used as the solvent, no differences were observed between the catalytic activities of Spencer's catalyst and the catalyst with the *NN*-dimethyl-3-(diphenylphosphino)propionamide ligand, which indicates the similarity of the catalytic systems. It has been suggested[51,60] that the phosphineamiderhodium catalyst contains the Rh–amide coordinate bond:



The chelate effect in this complex apparently decreases the concentration of the amide groups in the reaction medium.

The hydroformylation of formaldehyde under mild conditions (80 °C, 5.0 MPa) with a conversion close to 100% and a selectivity up to 64% proved to be possible when the dimeric rhodium thiolate complex $Rh_2(\mu\text{-}S\text{-t-Bu})_2(PPh_3)_2$ (A) was used as the precursor of the catalyst with an excess of PPh_3 in solution in *NN*-dialkylamides.[61] After the reaction had been carried out, the complex was isolated unchanged. The complex $Rh_2(\mu\text{-}S\text{-t-Bu})_2(CO)_4$ (B), which has no phosphine ligands, was inactive, as in the hydroformylation of olefins.[62] An excess of the ligand hinders the transformation (A) → (B) and thereby prevents the deactivation of the catalyst. The replacement of the PPh_3 ligands by the more electron-donating PMe_3 ligands promotes the formation of methanol.

In the presence of $RhCl(CO)(PPh_3)_2$, the selectivity with respect to glycolaldehyde can be increased by carrying out the hydroformylation of formaldehyde in pyridine (selectivity 98%, conversion 83.7%, pressure 9.0 MPa, H_2:CO = 2:1),[48] while in the presence of the complex (A) the use of this solvent did not allow the attainment of such high parameters.[61] The employment of the catalyst precursor (A) produces best results in *NN*-dialkylamides and the reaction then proceeds under milder conditions and at higher rates than in the case when Spencer's catalyst is used. Parameters of the hydroformylation of formaldehyde analogous to those obtained using Spencer's catalyst in DMF [51] are attained in the given instance at a pressure of 1.5 MPa, while the use of hexamethylphosphoramide makes it possible to avoid hydrogenation to methanol. Since the observed selectivity and activity are not the same as those obtained in the presence of $RhCl(CO)(PPh_3)_2$ and are attained under milder conditions, while the dinuclear rhodium thiolate complex remains unchanged after the reaction, it has been suggested that the catalysis is affected by another active species of unknown nature.

It has been established that, in the hydroformylation of olefins in the presence of the rhodium complex (A), the dinuclear carbonyl phosphine rhodium thiolate species is active.[62]

The selective hydroformylation of formaldehyde in solution in DMF using $Rh_4(CO)_{12}$ modified with PPh_3 and promoted with HI as the catalyst precursor has been reported.[63]

IV. Hydroformylation in the presence of basic promoting agents or solvents

Another group of catalytic systems used in formaldehyde hydroformylation reactions includes a basic promoting agent, for example, amines or highly basic solvents, which makes it possible to eliminate amides from the composition of the catalytic solution. Table 3 presents data indicating the influence of the nature of the solvent on the yield of the formaldehyde hydroformylation products.[43] The use of pyridine and its derivatives increases significantly the activity and selectivity of the process.

In the hydroformylation in the presence of rhodium complexes promoted by organic bases or alkalis,[27,37,64] the active catalytic system is formed from neutral or cationic rhodium complexes both containing and not containing chlorine, while the employment of amide or highly basic solvents is not obligatory in this instance (Table 4). Thus the addition of a small amount of triethylamine to the $RhCl(CO)(PPh_3)_2$ system in tetraglyme (Table 4) made it possible to increase the degree of conversion of formaldehyde in the hydroformylation reaction almost from zero to 90% for a selectivity with respect to glycolaldehyde of 76%.

Table 3. The influence of the nature of the solvent on the hydroformylation of formaldehyde.[43]

Solvent	Yield, %		
	glycol-aldehyde	ethylene glycol	methanol
γ-Picoline	49.4	0.3	0.4
β-Picoline	43.0	0.3	0.2
Pyridine	42.9	0.4	0.2
4-Pentylpyridine	39.7	0.4	0.4
3,5-Diethylpyridine	35.1	0.1	0.1
Triethylamine	9.4	0.0	0.4
Dimethylformamide	4.3	0.0	0.1
Dioxan	0.8	0.0	0.1
Dimethyl sulphoxide	7.4	0.0	0.2
Acetone	~0	~0	0.1

Note. $[CH_2O]$ = 19.1 mM, $[RhCl(CO)(PPh_3)_2]$ = 0.05 mM, temperature 70 °C, pressure of 1:1 CO + H_2 mixture 5 MPa, reaction time 3 h.

Table 4. Promotion of the rhodium catalysts $RhCl(CO)(PPh_3)_2$ + $n PPh_3$ by bases.[27]

n	Solvent	Base	Concentration of base, M	Reaction time, min	Conversion of CH_2O, %	Selectivity, %		
						glycol-aldehyde	methanol	condensation products
0	tetraglyme	—		30	traces			
0	»	NEt_3	$1\cdot10^{-2}$	30	84	71	6	
0	»	NEt_3	$2\cdot10^{-2}$	30	90	76	6	
8	»	NaOAc	$1.8\cdot10^{-2}$	15	94	14	11	
30	*NN*-dubutyl-formamide	KOH	$5\cdot10^{-3}$	60	75	56	20	
30	»	KOH *	$2.5\cdot10^{-2}$	30	62	2	10	
30**	*NN*-dimethyl-acetamide	NEt_3	$0.84\cdot10^{-2}$	30	43	86	5	9
30**	»	NEt_3	$1.8\cdot10^{-2}$	30	95	71	2	27
30**	»	NEt_3	$45\cdot10^{-2}$	15	95	17	6	77

Note. Reaction conditions: $[Rh] = 5 \times 10^{-3}$ M, $[CH_2O]$ = 2 M, $CO:H_2$ = 1:1, 17.5 MPa, 110 °C.
*The reaction is carried out in the presence of the 18-crown-6 ether to improve the dissolution of KOH.
**Pressure 21.0 MPa.

When the formaldehyde hydroformylation reaction was carried out in the presence of $HRh(CO)_2(PPh_3)_2$, it was established that the catalytic system includes, together with $HRh(CO)_2(PPh_3)_2$, also the anionic species $[Rh(CO)_4]^-$ and $[Rh(CO)_2(PPh_3)_2]^-$.[27] It was suggested that the amine additive serves as a bifunctional promoting agent for the catalytic system. By deprotonating the rhodium carbonyl hydride, it gives rise to an anionic species, to which catalytic activity is attributed:

$$HRh(CO)_2(PPh_3)_2 \rightleftarrows [Rh(CO)_2(PPh_3)_2]^- .$$

Furthermore, the amine serves as a source of protons, which are essential for the formation of the hydroxymethyl complex:

$$[R_3NH]^+ + CH_2O + [Rh(CO)_3(PPh_3)]^- \rightarrow HOCH_2Rh(CO)_3(PPh_3) + R_3N.$$

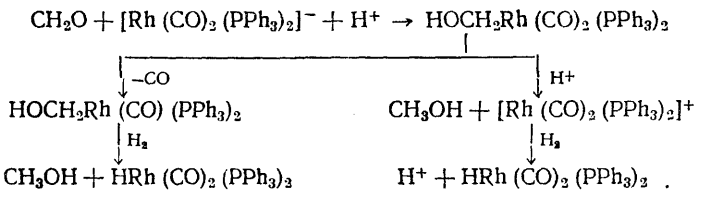
Being strong bases, the anionic rhodium complexes afford hydrides on interaction with weak acids (H_2, ROH).[65] The formation of the anionic rhodium complexes also in the absence of amine promoting agents can apparently be explained by the reversibility of this reaction:

$$[Rh(CO)_x(PPh_3)_{4-x}]^- + MeOH \rightleftarrows HRh(CO)_x(PPh_3)_{4-x} + [MeO]^-.$$

The activity of $[Rh(CO)_2(PPh_3)_2]^-$ and the inertness of $[Rh(CO)_4]^-$ have been demonstrated by special experiments.[27] However, it is still not understood at which stage the activity of PPh_3 is manifested.

According to the existing ideas, the anionic precursors of the catalyst react with formaldehyde to form a hydroxymethyl complex which catalyses in its turn the hydrogenation, via the elimination of methanol, after interaction with H_2 or H^+:

Scheme 1

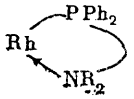


Experiment shows that both pathways can be followed, since the yield of methanol increases in the presence of an excess of the proton-donating reagent or with increase in the H_2:CO ratio.[27]

The effect of the amide in the presence of Spencer's catalyst is analogous to the effect of amines. The mechanism of its action is determined by its weak electron-donating properties.[27]

In the presence of both organic and inorganic basic promoting agents, the rate of hydroformylation of formaldehyde increases, but its condensation is at the same time accelerated sharply, which impairs the process selectivity (Table 4). Apart from methanol, trioses, tetroses, pentoses, and hexoses, have been identified among the side products, the rate of their formation increasing with increase in temperature and in the basicity of the medium. In addition, glyceraldehyde, 1,3-dihydroxypropanone, erythrose, 1,3-dihydroxybutanone, etc. have been detected in systems of this kind.[66]

In contrast to the above, the use of phosphineaminerhodium complexes with ligands of the type $PPh_2(CH_2)_2N(CH_3)_2$ [45] in acetone lowers the content of side products to 9%, which can be explained by the close proximity of the amino-group to the metal complex-forming atom and the chelate effect:



There is no information about the contribution of the condensation reaction of formaldehyde in its hydroformylation to glycolaldehyde. The only mention is in a communication[67] where the hydroformylation of $[^{13}C]$-CH_2O using a polynuclear rhodium complex in amide solvents in the presence of dimethylimidazole or *N*-methylpyrrolidinone is described. The results of the analysis of the positions of the labels in the products permitted the conclusion that under these conditions the dimerisation of formaldehyde to glycolaldehyde does not occur.

It has also been postulated that the catalytically active mononuclear species participating in the hydrogenation of CO to ethylene glycol are anionic in character. In tetraglyme, in the presence of the $Rh(acac)(CO)_2$ catalyst precursor promoted with *N*-methylimidazole (*N*-MI) (the latter is taken in a large excess),[68] whereupon the reaction is believed to proceed via the intermediate formation of formaldehyde and its hydroformylation, the catalyst is the mononuclear anionic rhodium complex formed when rhodium hydride is acted upon by a base:

$$HRh(CO)_3(N\text{-}MI) \rightarrow HRh(CO)_4 \rightarrow [N\text{-}MI]^+[Rh(CO)_4]^-.$$

The fact that the hydrogenation of CO to ethylene glycol, proceeding via the hydroformylation of formaldehyde, is catalysed by polynuclear complexes has been confirmed.[69] The anionic nature of such clusters is also determined, according to the authors, by the action of basic additives or solvents.

On the basis of the idea that the species active in the catalysis of the hydroformylation of formaldehyde are anionic in character and, as the function of the basic promoting agents and polar solvents consists in reducing the oxidised rhodium precursors to low-valence catalytically active anions, Marchionna and Longoni[70] used anionic rhodium carbonyl complexes as direct catalyst precursors. Because of this, they were able to exclude completely basic promoting agents and solvents from the composition of the catalytic system, ensuring nevertheless a high degree of conversion of formaldehyde and a high selectivity of the formation of glycolaldehyde. The $[Rh_5(CO)_{15}]^- - [Rh(CO)_2Cl_2]^- - PPh_3$ catalytic system (with a composition of 1:5:10) at 110 °C, 12 MPa, and with the ratio $CO:H_2 = 1:1$ makes it possible to obtain glycolaldehyde in 87.9% yield in acetone, while the yield of methanol is 9.4%.

It had been shown earlier[63] that selective hydroformylation is possible when one uses the $Rh_4(CO)_{12} - PPh_3 - HI$ catalytic system in which the postulated catalytically active species $[Rh_5(CO)_{15-x}(PPh_3)_x]^-$ with $x = 1,2$ and $[Rh(CO)_2Cl_2]^-$ were identified by IR spectroscopy. In the presence of PPh_3, the complex $[Rh_5(CO)_{15}]^-$ produces $[Rh_5(CO)_{15-x}(PPh_3)_x]^-$.[70] Its combination with $[Rh(CO)_2Cl_2]^-$ leads to the formation of a system analogous to that generated from $Rh_4(CO)_{12} - PPh_3 - HI$.

It has been suggested that each of the two anionic species $[Rh_5(CO)_{15-x}(PPh_3)_x]^-$ and $[Rh(CO)_2Cl_2]^-$ participates in the catalytic cycle, accelerating different hydroformylation stages.

The increased activity of the first of these complexes in the hydroformylation of formaldehyde to methanol provided grounds for the hypothesis that it has an activating effect on H_2 and CH_2O. According to the authors,[70] the anion $[Rh(CO_2)Cl_2]^-$, to which an enhanced activity is attributed in the migration insertion of carbon monoxide with formation of a hydroxyacyl intermediate,[71] is responsible for the high selectivity of the formation of glycolaldehyde. The combination of such or similar species in optimum proportions can ensure a fairly high rate of hydroformylation of formaldehyde with a satisfactory selectivity with respect to glycolaldehyde.

A two-component Co – Rh catalytic heterometallic anionic system has been described.[72] Using mixtures of $Rh_4(CO)_{12}$ and $CoCl_2.6H_2O$ or the mixed cluster $Co_2Rh_2(CO)_{12}$ as the catalyst precursors in DMF, it was possible to achieve a selectivity with respect to glycolaldehyde up to 65%. At the same time, the formation of ethylene glycol was observed. The experiments were performed at 110 °C and a pressure of 10–12 MPa. It was established that at least two types of catalytically active species are generated in the system: species of one type catalyse the formation of glycolaldehyde, while others catalyse its hydrogenation as well as the hydrogenation of CH_2O to ethylene glycol and methanol respectively. The identified structure of the carbonyl complexes before and after the

reaction indicates the reduction of the cobalt and rhodium carbonyls to $[Co(CO)_4]^-$ and $[Rh(CO)_4]^-$ respectively:

$$5Co_2Rh_2(CO)_{12} \rightarrow 2[Rh_5(CO)_{15}]^- + 4Co^{2+} + 6[Co(CO)_4]^- + 6CO,$$
$$5Rh_4(CO)_{12} + 2H_2O + 4DMF + 2CO \rightarrow 4[Rh_5(CO)_{15}]^- + 4DMFH^+ + 2CO_2,$$
$$[Rh_5(CO)_{15}]^- + Cl^- \rightleftarrows [Rh_5(CO)_{14}Cl]^{2-} + CO,$$
$$[Rh_5(CO)_{15}]^- + 10Cl^- + 2Co^{2+} + 3CO \rightarrow 5[Rh(CO)_2Cl_2]^- + 2[Co(CO)_4]^-.$$

The nature of the species active in hydroformylation was not established, but it has been suggested that the monometallic rhodium anion $[Rh(CO)_4]^-$ plays this role.

One should apparently not rule out also the possible activity of mixed Co–Rh carbonyls. The formation of an equilibrium mixture of the Co–Rh clusters $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ and the complexes $CoRh(CO)_8$ and $CoRh(CO)_7$ from $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ under CO pressure at 80–90 °C in solutions in dioxan has been reported.[73]

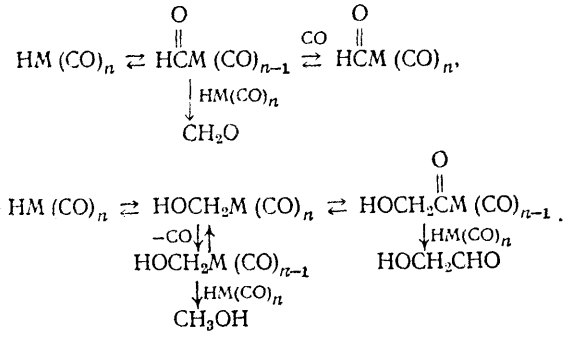
A gradual deactivation of the Co–Rh catalytic system is attributed to the reduction of $[Co(CO)_4]^-$ and $[Rh(CO)_4]^-$. The highest selectivity is observed in the system containing cobalt(II) compounds, which is attributed to their ability to oxidise rhodium complexes to anionic carbonyls and to serve as the buffer for the stabilisation of the active rhodium, the formal oxidation state of which is between +1 and −0.2.

An alternative explanation consists in the cooperative action of the cobalt and rhodium complexes in different oxidation states, analogous to the situation arising in the catalytic hydrogenation of CO to ethylene glycol in the presence of ruthenium carbonyls.[74,75]

V. The chemistry of coordinated formaldehyde and the hydroformylation mechanism

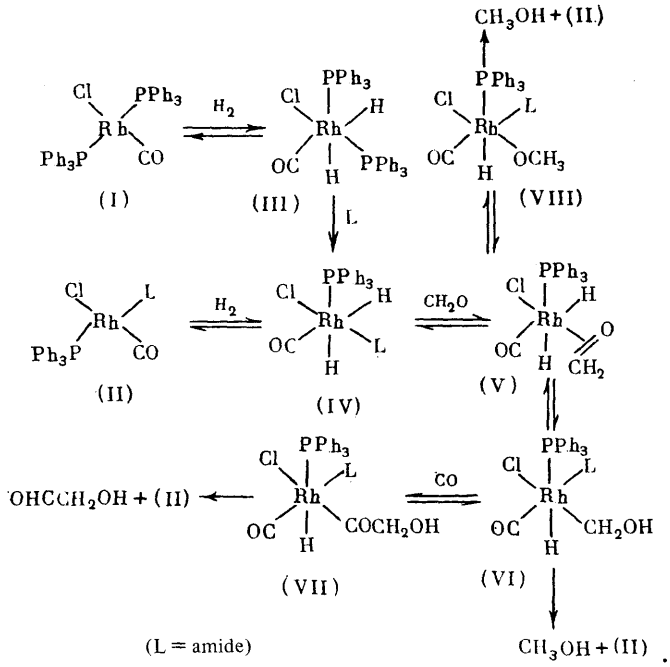
It is believed that the mechanism of the hydroformylation of formaldehyde is on the whole analogous to the known mechanism of the hydroformylation of olefins. In particular, the reaction is determined by the polar character of formaldehyde. It has been suggested that the formation of formaldehyde is an intermediate stage in the homogeneous-catalytic hydrogenation of CO to methanol, methyl formate, ethylene glycol, and other polyhydric alcohols in the presence of transition metal complexes (Scheme 2); the hydroformylation of CH_2O determines the content of ethylene glycol in the products:[4,76]

Scheme 2



Spencer[51] proposed a mechanism for the hydroformylation of formaldehyde in which provision is made for catalysis by a chlororhodium complex in the presence of an *NN*-dialkylamide:

Scheme 3



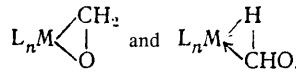
According to this Scheme, the dialkylamide should influence the stages involving the formation of the products (IV)–(VII). The absence of a directing effect of the amide is explained by its displacement by formaldehyde [the reaction (IV) ⇄ (V)]. Evidently this stage represents the interaction of formaldehyde with a solution of the metal complex. Such reactions are known for many neutral or cationic transition metal complexes.[77,78] The reactions of anionic complexes with CH_2O have not been described, which must be borne in mind in connection with the postulated mechanism of their catalytic action.[22,70]

Metal complexes are also capable of interacting with a suspension of paraformaldehyde,[77] gaseous formaldehyde,[52] or an aqueous formalin solution;[53] when trioxan is used, higher temperatures are required for its degradation.[24] In most cases, the complex with the η^2-CH_2O ligand (a π-complex) or a metal carbonyl are formed under very mild conditions.[79,80] It has been established that the complex with the η^2-CH_2O ligand is the most probable precursor in all subsequent reactions of the coordinated formaldehyde,[77] its formation being promoted by the presence of the PR_3 ligands, which are readily substituted in the interaction with CH_2O. As a result of the ligand exchange with CH_2O, stable complexes of this type have been obtained. The first such complex $(CO)_2(PPh_3)_2Os(CH_2O)$ was described in 1979.[81] The complexes $(CO)_2FeL_2(CH_2O)$,[80] $Cp_2V(CH_2O)$,[82] $CpRe(CO)_2(CH_2O)$,[83] $Cp_2Mn(CH_2O)$,[84] and the cationic complex $CpRe(NO)(PPh_3)(CH_2O)^+$ [85] have also been obtained. There are data concerning the bridge type coordination of the μ-CH_2O ligand, which are of interest in connection with the hypothesis that polynuclear and tetrametallic complexes of the type

$$(\eta^5\text{-}C_5H_5)_2Zr(Cl)(\mu\text{-}CH_2O)(Cl)Zr(\eta^5\text{-}C_5H_5)_2$$

are active.[76,86]

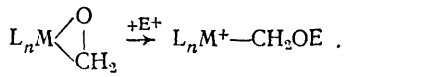
The interaction of formaldehyde with ML_n can lead to the bidentate binding of CH_2O of two types:[81,83,87,88]



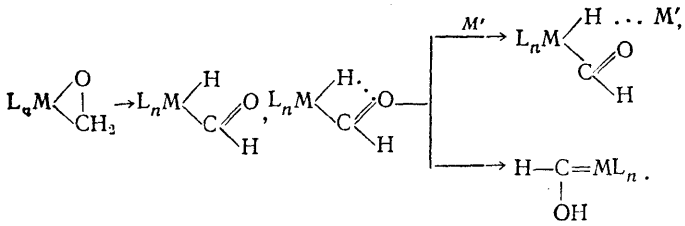
A characteristic feature is the weakening of the C=O bond in such compounds compared with the bond in the non-coordinated formaldehyde, which is manifested by the ν(CO) stretching vibration frequency.

The reactions of the coordinated formaldehyde η^2-CH_2O in the transition metal complex are summarised below:[77,89]

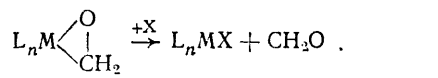
(1) attack on the oxygen atom of the coordinated formaldehyde:[80,82]



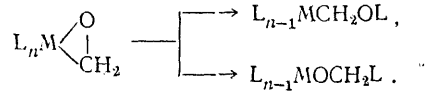
(2) Oxidative addition with formation of a formyl derivative:[81]



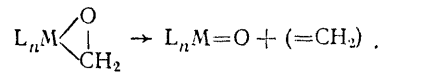
(3) Displacement of formaldehyde from the coordination sphere:[82]



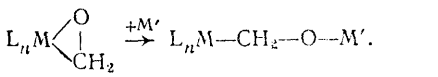
(4) Insertion of formaldehyde in an M–H [82] or M–C [90] bond:



(5) Dissociation of the C=O bond of formaldehyde with its deoxygenation:[89]



(6) Ditto with formation of the bridging μ-CH_2O form:[86,89]



The mode of reaction and its rate are determined by the nature of the metal, the ligand environment, and the reaction conditions.

Certain other, perhaps unexpected, reactions have also been described. Thus the interaction of the cation $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3).(\eta^2\text{-}CH_2O)]^+$ with PR_3 (R = Rh or Me) at 25 °C led to the formation of the adduct[91]

$$[(\eta^5\text{-}C_5H_5)\,Re\,(NO)\,(PPh_3)\,(OCH_2PR_3)]^+.$$

instead of the expected substitution of the coordinated CH_2O by PR_3.

Reactions (1)–(4) should apparently be assigned to the hydroformylation mechanism proper.

A metal characterised by appropriate oxophilic properties can combine with formaldehyde oxidatively with participation of the C=O or C–H bonds.

The last reaction, leading to the formation of the formyl complex, is of interest in connection with the mechanism, postulated by Keim et al.,[92] of the formation of ethylene glycol in the presence of solutions of cobalt carbonyls in the hydrogenation of CO:

$$(CO)_n\,Co{-}CHO \xrightarrow{HCo(CO)_n} (CO)_n\,Co{-}CH_2O{-}Co\,(CO)_n \xrightarrow{CO}$$
$$\rightarrow (CO)_n\,Co{-}CO{-}CH_2O{-}Co\,(CO)_n \xrightarrow{H_2} CH_2OH{-}CH_2OH.$$

The key stage is that of the interaction of the formyl complex, formed from CO and H_2, with the carbonyl hydride. In addition, it may prove to be the key stage in the formation of active carbonyl derivatives of the metal in the carbonylation of metal complexes by formaldehyde.

The decarbonylation of formaldehyde by metal complexes proceeds via an oxidative addition stage with formation of a formyl complex.[77,93] The equilibrium

$$H_yM\,(Co)_x \rightleftarrows H_{y-1}M\,(Co)_{x-1}\,(CHO)$$

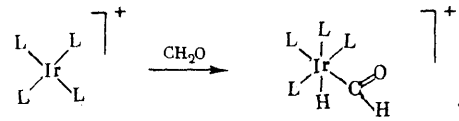
explains the relative instability of the formyl intermediates.[93]

It has recently been reported that nickel complexes are capable of rapidly decarbonylating formaldehyde via the stoichiometric reaction[89]

$$Ni\,(PR_3)_4 + CH_2O \rightarrow Ni\,(PR_3)_3\,(CO) + H_2.$$

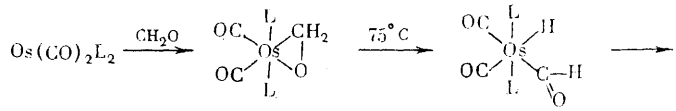
The presence of the rigid bulky np_3 ligand {np_3 = tris[2-diphenylphosphino)ethylamine]} in the coordination sphere makes it possible to alter the formaldehyde reaction pathway and the decarbonylation reaction may become catalytic.[79]

Relatively stable formyl complexes are obtained by the oxidative addition of formaldehyde to cationic or neutral square planar iridium(I) complexes:[80]



Many mono- and poly-nuclear, cationic, neutral, and anionic formyl complexes have been described.[77,78,94] It has been shown for some of them that the M–CHO fragment is an effective hydride donor[91,95] and that it can be stabilised by an electrophile.[96]

The rearrangement $(\eta^2\text{-}CH_2O)M \rightarrow HM{-}CHO \rightarrow MCO$ has been observed for the osmium carbonyl complex:[81]



The main reaction of the coordinated formaldehyde in the hydroformylation process is reaction (4) (L = H) with formation of a hydroxymethyl derivative, which is a precursor of glycolaldehyde: the methoxy-intermediate controls the formation of methyl formate, both affording methanol after reductive elimination.

The insertion of formaldehyde in the M–H bond in the hydroformylation process with formation of the M–O and M–C bonds should determine the ratio of the methyl formate and

glycolaldehyde formed. However, there also exists the view that the presence of a compound with the M–O bond is not an obligatory condition for the formation of formate, since it can be obtained via the reaction[97]

$$HO-CH_2M(CO)_n + RCH_2OH \rightarrow RCH_2O\overset{O}{\overset{\|}{C}}H + HM(CO)_n.$$

Examples of the methoxy-complexes described in the literature are fairly rare, one of them being $Cp_2W(CH_3)(OCH_3)$.[98]

The formation of the methoxy-derivative from the zirconium carbonyl complex has been observed in its reaction with hydrogen, which proceeds tentatively via the intermediate hydroformyl derivative $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH)_3$.[99] The hydride donating capacity of the formyl derivative of Re^+ made it possible to obtain a 52% yield of the methoxy-complex from the $\eta^2\text{-}CH_2O$ cation:[91]

$$[CpRe(NO)(PPh_3)(\eta^2\text{-}CH_2O)]^+ + CpRe(NO)(PPh_3)(CHO) \rightarrow$$
$$\rightarrow CpRe(NO)(PPh_3)(OCH_3) + [CpRe(NO)(PPh_3)(CO)]^+.$$

The interaction of this methoxy-complex with $[Ph_3C]^+[PF_6]^-$ in CH_2Cl_2 results in the reformation of the initial complex.

The insertion of formaldehyde in the M–H bond in octaethylporphyrinrhodium hydride led to the formation of a hydroxymethyl derivative:[100] $Rh-H + CH_2O \rightarrow Rh-CH_2-OH$.

There exist numerous examples of similar complexes with different metals.[77,78]

Apparently both types of insertion, with formation of both M–C and M–O bonds, are possible under the conditions of the catalytic reactions of the carbonyl group in solutions of metal complexes.

The stoichiometric hydroformylation of formaldehyde has been carried out using $HCo(CO)_4$ as the source of hydrogen under the conditions of an excess of CO (the reaction was carried out at 0 °C and a pressure of 1 atm in CH_2Cl_2):[101]

$$2\,HCo(CO)_4 + CH_2O \xrightarrow{CO} HOCH_2CHO + Co_2(CO)_8.$$

The yield with respect to the $HCo(CO)_4$ which reacted amounted to 60–90%. There was no methyl formate among the reaction products, which indicates the addition of formaldehyde to the carbonyl hydride complex with formation of a Co–C bond.

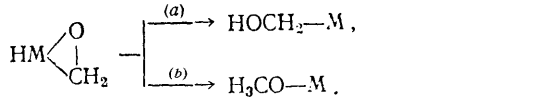
The possibility of the direct interaction of aldehydes with $HCo(CO)_4$ involving coordination via the oxygen atom of the carbonyl group has been noted;[97] the conversion of aldehydes into alcohols takes place in this way. The catalytic hydroformylation of epoxides presupposes the formation of the Co–C bond; both Co–C and Co–O bonds can participate in the reduction of CO.

The formation of methyl formates (Co–O) (yield up to 40%) in the complete absence of hydroxyaldehydes (Co–C) has been observed in the catalytic hydroformylation of aldehydes in the presence of cobalt carbonyls modified with PR_3.[102] Hydroxyaldehydes are also not formed under the conditions of the hydroformylation of olefins in the presence of cobalt or rhodium catalysts. The principal products of the secondary reactions of aldehydes in oxo synthesis are alkyl formates.[6,103]

In this connection one should note that, in contrast to other aliphatic aldehydes, formaldehyde is capable of undergoing π-type coordination ($\eta^2\text{-}CH_2O$). Coordination via the oxygen atom is characteristic of other aldehydes and π-type coordination is not observed.[104]

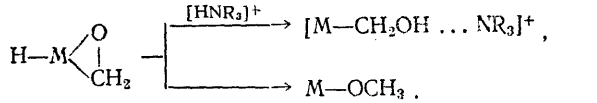
Methyl formate is formed in trace amounts in the catalytic hydroformylation of formaldehyde, the selectivity with respect to the target product (in the absence of condensation) being determined by the glycolaldehyde/methanol ratio and not by the glycolaldehyde/methyl formate ratio. The appreciable yield of methyl formate observed in the study of Marchionna and Longoni[72] can be explained by the interaction of formaldehyde with CO and the Cannizzaro–Tishchenko reaction.

It is apparently so far impossible to identify the precursor of methanol (the hydroxymethyl or methoxy-intermediate), but the majority of investigators incline to the view that the formation of methanol via a methoxy-derivative is unlikely, i.e. that pathway (*b*) does not play a significant role under the reaction conditions:



This can be accounted for by several causes. In particular, by thermodynamic control for certain metals. Thus it has been shown that the Ir–O bond in iridium complexes is weaker than the Ir–C bond.[105]

In addition it has been suggested[27] that the suppression of pathway (*b*) is due to the use of basic promoting agents and polar media which promote the hydroxymethyl hydrogen transfer:



and also to the nucleophilic character of the attack on the active anionic metal carbonyl species in their interaction with CH_2O:[27]

$$[Rh(CO)_2(PPh_3)_2]^- \overset{CH_2O,H^+}{\rightleftharpoons} HOCH_2Rh(CO)_2(PPh_3)_2.$$

The promotion of rhodium catalysts by acids also drives the reaction towards the formation of the M–C bond:[3,63]

$$CH_2O + HI \rightarrow ICH_2OH,$$
$$ICH_2OH + M \rightarrow HOCH_2MI.$$

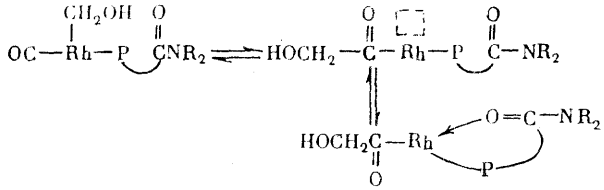
In most cases, it is impossible to state unambiguously how formaldehyde is converted into the hydroxymethyl intermediate: via insertion in the M–H bond, as a result of oxidative addition, or via a bimolecular mechanism.

The migration insertion of CO in hydroxymethylcarbonyl complexes leads to the formation of a hydroxyacyl intermediate (see Scheme 3). This reaction has been achieved recently for the octaethylporphyrin (OEP) complex of rhodium:[106]

$$(OEP)Rh(CH_2OH) \xrightarrow{CO} (OEP)RhCOCH_2OH.$$

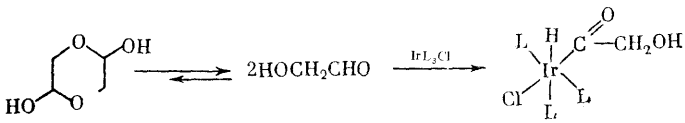
In contrast to alkylmetal carbonyl complexes, the carbonylation of the hydroxyalkyl derivatives proceeds with difficulty.[107,108] It has been suggested that this reaction is accelerated in the presence of electron-donating solvents, in particular amides, and in the presence of basic ligands. This hypothesis is based on the analogy with the migration insertion of CO in alkylmetal complexes with formation of acyl derivatives, which is promoted by alkali metal cations, amide solvents, basic promoting agents, and basic ligands.[4,76,109] For example, in the reaction involving the formation of acylmanganese complexes from the alkyl complexes, a significant increase in the rate was observed after the replacement of the solvent (mesitylene) by DMF.[76] The $HOCH_2CH_2OH$:CH_3OH ratio in the products must be determined by the ratio of the rates of insertion of CO and of the

reductive elimination of CH_3OH from the common intermediate for these compounds. It is believed that the rate of the migration insertion with formation of a hydroxyacyl complex can greatly exceed the rate of the irreversible stage involving the reductive elimination of ethanol only in highly electron-donating solvents;[76] the participation of an electron-donating ligand in the reactions of compounds (IV)–(VII) (see Scheme 3) has therefore been postulated. A characteristic feature of the phosphine amide ligand is, according to Jacobson,[45] the acceleration of the reaction (VI) → (VII) as a consequence of the nucleophilic attack on the coordinatively-unsaturated organometallic centre:



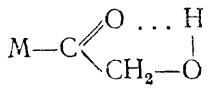
Whereas hydromethyl complexes are relatively well known, the hydroxyacyl complexes have been studied to a much smaller extent.

Apart from the octaethylporphyrinrhodium complex,[106] the hydroxyacyliron complex $Fe(COCH_2OH)[P(OMe)_3]_2$ has been described.[110] Data are available concerning the stabilisation of the hydroxyacyl complexes by chelating ligands.[111] The hydroxyacyl-iridium and hydroxyacylrhodium hydride complexes have been recently characterised. They were obtained by the oxidative addition of glycolaldehyde to square-planar iridium(I) and rhodium(I) complexes:[105]



The hydroxyacylrhodium complex is formed in 92% yield from the glycolaldehyde dimer (2,5-dihydroxy-1,4-dioxan) at 25 °C; it is stable in the solid state, decomposing slowly in solution.

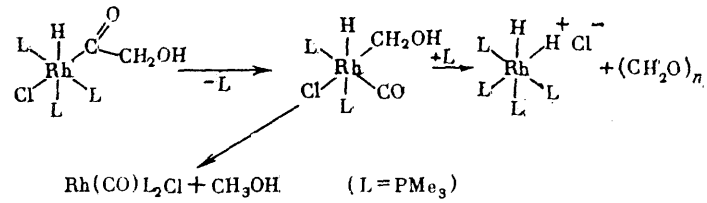
An important structural feature of such complexes proved to be the presence of an intramolecular hydrogen bond C=O...H–O, which leads to the formation of a five-membered ring:[105]



This was demonstrated by IR spectroscopy, showing a lack of dependence of ν_{OH} on the concentration of the complex in C_6D_6.

Since the $M-CH_2OH$ complexes show a greater tendency towards the migration insertion of CO than their analogues $M-CH_2OR$, it has been suggested that the presence of the intramolecular hydrogen bond is a general phenomenon for the α-hydroxyacyl complexes.

The reactions observed in the study of the thermal decomposition of the hydroxyacylrhodium complex[105] may serve as models of the reactions (V) → (IV), (VI) → CH_3OH + (II), and (VII) → (VI) (see Scheme 3). It has been established that the hydroxyacylrhodium complex undergoes on heating a reaction which is the reverse of the migration insertion of CO with formation of $Rh(CO)L_2Cl$ and CH_3OH from the hydroxymethyl intermediate. β-Elimination results in the formation of formaldehyde and a hydride, the reaction being the dominant one:

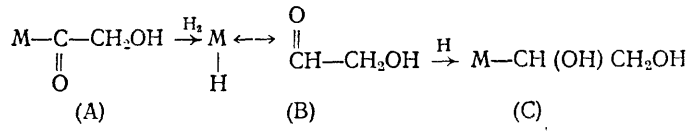


In addition, the elimination of glycolaldehyde was observed.

The fact that the introduction of the electron-donating ligand (PMe_3) inhibits the decomposition of the hydroxyacyl complex can apparently be associated with its activating effect in hydroformylation. The reversible formation of the hydroxyacyl complex via the oxidative addition of glycolaldehyde is consistent with Spencer's hypothesis of the reaction equilibrium (VII) ⇄ (II) (not shown in the Scheme), by means of which he explains the inhibition of the hydroformylation by the excess glycolaldehyde. A probable cause of this phenomenon may be the blocking of the coordination centres by the bidentate ligand $HOCH_2CHO$.[4] The reversibility of this stage distinguishes the mechanism considered from the mechanism of the hydroformylation of olefins, in which the reversible reductive elimination of the aldehyde has been demonstrated.

An alternative mechanism of the elimination of glycolaldehyde from the hydroxyacyl complex may involve intermolecular reductive elimination with participation of carbonyl hydride complexes. An analogous mechanism is known for the hydroformylation of olefins.[4,112,113]

The reactions



are of key importance in the formation of ethylene glycol.[114] The intermediate (C) may serve as a source of ethylene glycol or can enter into the chain propagation reaction under the influence of CO. The reduction of compound (B) can lead to the formation of ethylene glycol via the intermediate (C) or via the *O*-bonded alkoxy-complex. The latter does not participate in the chain propagation reaction.

The (A) → (B) → (C) chain of reactions has been investigated for the methoxyacetyliron complex $Cp(CO)_2Fe-C(O)-CH_2OCH_3$.[114]

As stated above, the selective hydrogenation of glycolaldehyde to ethylene glycol under the conditions of a homogeneous-catalytic reaction has been demonstrated in a solution of $Rh(acac)(CO)_2$.[50]

The intermediate transition metal complexes, which are believed to be formed in a hydroformylation of formaldehyde, can be distinguished by means of their spectral characteristics (Table 5).

VI. Conclusion

The formaldehyde hydroformylation reaction is of interest not only as a method of synthesis of glycolaldehyde and ethylene glycol but also as the postulated intermediate stage in the homogeneous-catalytic hydrogenation of CO to methyl formate, ethylene glycol, and other polyhydric alcohols. The formation of ethylene glycol from CO to H_2 requires severe conditions, probably because of the thermodynamic difficulties in the formaldehyde formation stage.

The absence of this energetically difficult stage in the synthesis of ethylene glycol by the hydroformylation of formaldehyde makes it possible to carry out the reaction under mild conditions: 8–10 MPa using mononuclear precursors of the rhodium catalyst and 1.5 MPa in the presence of the dinuclear rhodium complex.

Table 5. The stretching vibration frequencies in the spectra of the formaldehyde complexes of transition metals.

Complex	ν, cm^{-1}		Refs.
	ν_{CO} (η^2-CH_2O)		
CH_2O	1746		[24]
$Os(PPh_3)_2(CO)_2(\eta^2\text{-}CH_2O)$	1017		[81]
$Cp_2V(\eta^2\text{-}CH_2O)$	1160		[89]
$[(CH_3O)_3P]_3(CO)_2Fe(\eta^2\text{-}CH_2O)$	1220		[80]
$[CpZrCl]_2(\eta^2\text{-}CH_2O)$	1015		[86]
	ν_{CO} (CHO)		
$(np_3)Ni(CHO)$	1615		[79]
$OsH(CO)_3(PPh_3)(CHO)$	1601		[81]
$[Rh_{17}(CO)_{32-n}S_2(CHO)]^{(3+n)-}$	1585—1600		[94]
$(CO)_3Fe(\mu\text{-}PPh_2)_2Os(CO)_2(CHO)$	1545		[115]
$Co_2Fe_2(CO)_{10}(PPh_3)_2(CHO)$	1570		[116]
	ν_{OH} (CH_2OH)		
$OsCl(CO)_2(PPh_3)_2(CH_2OH)$	3540		[81]
	ν_{CO}	ν_{OH}($COCH_2OH$)	
$HRhCl(PMe_3)_3(COCH_2OH)$	1630	3395	[105]
$Rh(OEP)(COCH_2OH)$	1697	3424	[106]

The hydroformylation of formaldehyde differs from the analogous hydroformylation of olefins by a multiplicity of features due to the characteristics of the structure of the substrate molecule and the ability of formaldehyde to be coordinated in different ways to the transition metal complex. The formaldehyde hydroformylation mechanism postulated by analogy with the hydroformylation of olefins does not take into account all the experimentally observed features of this reaction and requires certain modifications.

References

1. P Chaumette, F Hugues *Rev. Inst. Franç. Petrole*, 1985, **40**(1) 91
2. A Aquilo, J S Alder, D N Freeman, R J H Voorhoeve *Neft', Gaz, Neftekhimiya za Rubezhom*, 1983, (3) 68
3. R A Sheldon *Catalysis by Metal Complexes*, Vol. 3, *Chemicals from Synthesis Gas* (Translated into Russian), Izd. Khimiya, Moscow, 1987, 248 pp
4. G Henrici-Olive, S Olive *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide* (Translated into Russian), Izd. Mir, Moscow, 1987, 245 pp
5. W Keim *Catalysis in C-Chemistry* (Translated into Russian), Izd. Khimiya, Leningrad, 1987, 296 pp
6. Y Falbe *New Synthesis with Carbon Monoxide* Springer Verlag, New York, 1980, 465 pp
7. M G Katsnel'son, V A Rybakov, M V Khokhlova *Okis' Ugleroda i Vodorod Vmesto Etilena v Neftekhimicheskikh Sintezakh* (The Replacement of Ethylene by Carbon Monoxide and Hydrogen in Petrochemical Syntheses), Izd. TsNIIteneftekhim, Moscow, 1986, 48 pp
8. J Kollar *Chem. Technol.*, 1984, 504
9. E V Anderson *Chem. Eng. News*, 1984, **62**(29) 9
10. H Izawa *Chem. Econ. Eng. Rev.*, 1980, **12**(3) 17
11. E M Ermolaeva, G L Avrekh, A E Ioffe *Khim. Prom.*, 1982, (7) 432
12. I I Moiseev *Zhur. Vses. Khim. Obshch. im Mendeleeva*, 1982, **27** 309
13. I I Moiseev *Khim. Prom.*, 1985, (4) 230
14. I Tkatchencho *Inf. Chim.*, 1984, **249** 115
15. J Gautier-Lafaye, R Perron *Methanol et Carbonylation* Rhone-Poulenc, Paris, 1986, 248 pp
16. A Weiss, S Trigerman, G Dunnells, et al. *Ind. Eng. Chem. Proc. Des. Develop.*, 1979, **18** 552
17. H Arakawa *Shokubai (Catalyst)* 1983, **25** 392
18. Japanese P. 57-81 422; *Chem. Abs.*, 1983, **97** 38 492
19. Japanese P. 58-81 423; *Chem. Abs.*, 1983, **97** 38 493
20. Japanese P. 53-73 506; *Chem. Abs.*, 1980, **88** 190 077
21. BRD P. 2 625 072; *Chem. Abs.*, 1981, **88** 89 114
22. Japanese P.57-118 527; *Chem. Abs.*, 1982, **97** 215 530
23. US P. 4 405 821; *Chem. Abs.*, 1983, **99** 194 433
24. S K Ogorodnikov *Formal'degid* (Formaldehyde), Izd. Khimiya, Leningrad, 1984, 279 pp
25. F Suzuki *Nippon Kagaku Kaishi*, 1982, (8) 1357
26. US P. 3 920 753; *Chem. Abs.*, 1975, **82** 124 761
27. A S C Chan, W E Carrol, D E Willis *J. Mol. Catal.*, 1983, **19** 377
28. Europ. P. 0 096 905; *Chem. Abs.*, 1987, **100** 191 374
29. Europ. P. 0 061 791; *Chem. Abs.*, 1983, **98** 34 242
30. Japanese P. 57-130 940; *Chem. Abs.*, 1982, **97** 215 527
31. K Wada, F Onoda *J. Synth. Org. Chem.*, 1983, **41** 515
32. US P. 4 358 411; *Chem. Abs.*, 1982, **94** 120 902
33. Japanese P. 57-165 337; *Chem. Abs.*, 1983, **98** 34 242
34. Japanese P. 58-88 333; *Chem. Abs.*, 1983, **98** 429
35. Europ. P. 0 072 051; *Chem. Abs.*, 1983, **99** 5209
36. US P. 4 405 821; *Chem. Abs.*, 1983, **99** 194 433
37. US P. 4 405 814; *Chem. Abs.*, 1985, **100** 5855
38. Japanese P. 76-128 903; *Chem. Abs.*, 1980, **92** 65 481
39. US P. 4 200 765; *Chem. Abs.*, 1981, **88** 190 089
40. L.Nawata, H Migazeki *J. Synth. Org. Chem.*, 1983, **41** 545
41. P E Garrow *Chem. Techn.*, 1985, **15** 123
42. T Sakakura, T A Kobayashi, T Hayashi, et al. *J. Organomet. Chem.*, 1984, **427** 171
43. W R Moser, C J Papile, S J Weininger *J. Mol. Catal.*, 1987, **41** 293
44. US P. 4 496 781; *Chem. Abs.*, 1987, **102** 203 599
45. S E Jacobson *J. Mol. Catal.*, 1987, **41** 163
46. Europ. P. 0 002 908; *Chem. Abs.*, 1982, **92** 6064
47. B. P. 2 085 426; *Chem. Abs.*, 1982, **94** 120 867
48. T Okano, M Marino, H Konishi *Chem. Lett.*, 1985, (12) 1793
49. French P. 2 363 538; *Chem. Abs.*, 1981, **93** 113 951
50. E Watanabe, J Hara, K Wada, et al. *Chem. Lett.*, 1986, (2) 285
51. A J Spencer *J. Organomet. Chem.*, 1980, **194** 113
52. F Suzuki *Bull. Chem. Soc. Jap.*, 1982, **55**(2) 169
53. D Evans, J A Osborn, G J Wilkinson *J. Chem. Soc.A*, 1968, 3133
54. A B Sanger *Can. J. Chem.*, 1985, **63** 571
55. Yu S Varshavskii, T G Cherkasova, N V Kiseleva, et al. *Zhur. Neorg. Khim.*, [*Russ. J. Inorg. Chem.*], 1986, **30** 152
56. Yu S Vashavskii *Kompleksy Metallov Platinovoi Gruppy v Sinteze i Katalize* (Platinum Group Metal Complexes in Synthesis and Catalysis), Chernogolovka, 1983, p. 52

57. R Y Mawby, F Bassolo, R G Pearson *J. Amer. Chem. Soc.*, 1966, **44** 1881
58. O S Roshchupkina, A V Bulatov, Ya Kh Samovarov, et al. *Koord. Khim.*, 1987, **13** 321
59. J E Parmeter, U Schwalke, W H Weinberg *J. Amer. Chem. Soc.*, 1987, **109** 5083
60. P Abley, F J McQuillin *J. Chem. Soc. Chem. Comm.*, 1969, 477
61. C Claver, J Fis, P Kalck *C1 Mol. Chem.*, 1987, **2** 25
62. A Dedieu, P Escaffre, J M France, et al. *Nouv. J. Chim.*, 1986, **10** 631
63. M Marchionna, G Longoni *Gazzetta*, 1986, **116** 453
64. US P. 4 477 685; *Chem. Abs.*, 1982, **96** 134 553
65. A S C Chan, H S Shieh, J P Hill *J. Organomet. Chem.*, 1985, **279** 171
66. US P. 4 238 418; *Chem. Abs.*, 1982, **94** 120 867
67. Y Ohgomori, S Mori, S Y Yoshida, Y Watanaba *J. Mol. Catal.*, 1987, **40** 223
68. Y Kiso, M Tanaka, T Hayashi, et al. *J. Organomet. Chem.*, 1987, **322** C32
69. G A Olah, L.Ohannesian, M Arvanghi *Chem. Rev.*, 1987, **87** 671
70. M Marchionna, G Longoni *Organometallics*, 1987, **6** 606
71. G D Vaughn, J A Gladysz *J. Amer. Chem. Soc.*, 1986, **108** 1473
72. M Machionna, G Longoni *J Mol. Catal.*, 1986, **35** 107
73. J Ojima *J. Mol. Catal.*, 1986, **37** 25
74. B D Dombeck *Adv. Catal.*, 1983, **32** 325
75. B D Dombeck *Organometallics*, 1985, **4** 1707
76. L C Costa *Catal. Rev.*, 1983, **25** 325
77. D L Thorn *J. Mol. Catal.*, 1982, **17** 279
78. J A Gladysz *Adv. Organomet. Chem.*, 1982, **20**(1) 1
79. C Bianchini, A Meli *Organometallics*, 1985, **4** 1537
80. H Berke, W Bankhardt, G Huttner, et al. *Chem. Ber.*, 1981, **114** 2754
81. K L Brown, G R Clark, C E L Headford, et al. *J. Amer. Chem. Soc.*, 1979, **101** 503
82. S Gambarotta, C Floriani, A Chiesi-Villa, et al. *J. Amer. Chem. Soc.*, 1982, **104** 2019
83. H Berke, R Birk, G Huttner, et al. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.*, 1984, **39B** 1380
84. S Gambarotta, C Floriani, A Chiesi-Villa, et al. *J. Amer. Chem. Soc.*, 1985, **107** 2985
85. W E Buhro, S Georgiou, J Fernandez, et al. *Organometallics*, 1986, **5** 956
86. S Gambarotta, C Floriani, A Chiesi-Villa, et al. *Organometallics*, 1983, **105** 1690
87. P T Barger, J E Bercaw *Organometallics*, 1984, **3** 278
88. D L Thorn *Organometallics*, 1982, **1** 197
89. S Gambarotta, C Floriani, A Chiesi-Villa, et al. *Organometallics*, 1986, **5** 2425
90. P Leoni, M Pasquali *J. Organomet. Chem.*, 1983, **255** C1
91. W E Buhro, S Georgiou, J M Fernandez, et al. *Organometallics*, 1986, **5** 956
92. W Keim, M Berger, A Eisenbeis, et al. *J. Mol. Catal.*, 1981, **13** 19
93. Yu N Kukushkin *Koord. Khim.*, 1986, **12** 147
94. R C Schoening, J L Vidal, R A Fiato *J. Mol. Catal.*, 1981, **13** 83
95. W Tam , G I Lin, W K Wong, et al. *J. Amer. Chem. Soc.*, 1982, **104** 14
96. I L C Freriks, P C de Jong-Versloot, A G T Kortbeek, et al. *J. Chem. Soc. Chem. Comm.*, 1986, 253
97. B R James *Homogeneous Hydrogenation* (Translated into Russian), Izd. Mir, Moscow, 1976, 570 pp
98. L Farrugia, M L H Green *J. Chem. Soc. Chem. Comm.*, 1975, 416
99. P T Wolczanski, J E Bercaw *Acc. Chem. Res.*, 1980, **13** 121
100. B B Wayland, B A Woods, V M Minda *J. Chem. Soc. Chem. Comm.*, 1982, 634
101. J A Roth, M Orchin *J. Organomet. Chem.*, 1979, **172** C27
102. C D Wood, P E Garrow *Organometallics*, 1984, **3** 170
103. V Yu Gankin, G S Gurevich *Tekhnologiya Oksosinteza* (The Technology of the Oxo Synthesis), Izd. Khimiya, Leningrad, 1981, 262 pp
104. I B Kim, C S Chin *Polyhedron*, 1984, **3** 1151
105. D Milstein, W C Fultz, J C Calabrese *J. Amer. Chem. Soc.*, 1986, **108** 1336
106. S L Van Voorheese, B B Wayland *Organometallics*, 1985, **4** 1887
107. G O Nelson *Organometallics*, 1983, **2** 1474
108. Y C Lin, D Milstein, S S Wreford *Organometallics*, 1983, **2** 1461
109. R J Mawby, F Bassolo, R G Pearson *J. Amer. Chem. Soc.*, 1964, **86** 3994
110. H Berke, G Huttner *J. Organomet. Chem.*, 1981, **219** 353
111. G D Vaughn, J A Gladysz *Organometallics*, 1984, **3** 1596
112. H Henrici-Olive, S Olive *Coordination and Catalysis* (Translated into Russian), Izd. Mir, Moscow, 1980, 421 pp
113. M E Mirbach *J. Organomet. Chem.*, 1984, **265** 205
114. E J Crauford, T W Bodnar, A R Cutler *J. Amer. Chem. Soc.*, 1986, **108** 6202
115. S Rosenberg, S P Lockledge, G L Geoffroy *Organometallics*, 1986, **5** 2517
116. M G Richmond, J K Kochi *J. Organomet. Chem.*, 1987, **323** 219