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Transition Metal Complexes as Catalysts of the Synthesis of Hydrocarbons from Carbon Oxides and Hydrogen

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The results of studies on the synthesis of hydrocarbons from carbon oxides and hydrogen in the presence of metal complex catalysts are considered and the characteristic features of the activation of CO and CO_2 by transition metal complexes and the mechanisms of the reduction of carbon oxides by hydrogen are discussed.
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I. INTRODUCTION

The synthesis of hydrocarbons from carbon oxides and hydrogen has currently acquired renewed great practical importance as a method for the preparation of motor fuels and valuable chemical products based on coal[1-3]. The inadequate yield of the existing synthetic processes, the lack of catalysts for the specific synthesis of individual hydrocarbons and their narrow fractions, the considerable energy consumption, and also certain technological difficulties due to the need to remove considerable amounts of heat as a consequence of the highly exothermic nature of the reactions must be included among their deficiencies[4]. Both in our country and abroad, a vigorous search is being prosecuted for metal complex catalysts of the synthetic reactions, possessing high activity and selectivity under mild conditions[4,5].

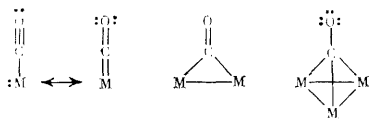
The synthesis of hydrocarbons from carbon oxides and hydrogen in the presence of metal complex catalysts is a comparatively new branch of metal complex catalysis. The first studies in this field were published as late as 1976. The number of publications having a direct bearing on the synthesis of hydrocarbons from CO and H_2 in the presence of transition metal complexes is small —it does not exceed several tens of communications dealing with the modelling of individual stages of the process and proposing reaction mechanisms. A series of reviews have considered the activation of CO [6,7] and CO_2 [7-9] by transition metal complexes, the reduction of CO [6,7] and CO_2 [7,9] to organic compounds, and the synthesis of hydrocarbons from CO and H_2 in the presence of metal complex catalysts[6,7].

The present review deals with methods for the activation of carbon monoxide and with its reactions in the presence of transition metal complexes, including the synthesis of hydrocarbons from CO and H_2; it also discusses the problem of the activation of CO_2 by transition metal complexes. The activation of hydrogen by transition metal complexes has been considered in a monograph[10].

II. THE REDUCTION OF CARBON MONOXIDE IN THE PRESENCE OF TRANSITION METAL COMPLEXES

1. The Ways in which Carbon Monoxide is Coordination to Transition Metals

Examination of various ways in which the CO molecule is coordinated to transition metals makes it possible to infer the degree of activation of the carbonyl ligand and hence to outline procedures for the reduction of carbon monoxide to hydrocarbons or other organic compounds. These procedures are represented below[7]:



(Ia) (Ib) (II) (III)

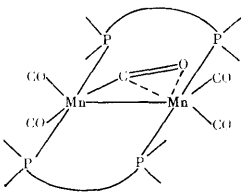
It is well known[11] that in metal carbonyls there is a simultaneous transfer of electrons from the σ orbital of the CO group to the metal atom and from the metal to the π orbital of CO. The transfer of electrons from the *d* orbitals of M to the π orbitals of CO entails a decrease of the C–O bond order and an increase of the metal–carbon bond order; this has been confirmed by infrared spectroscopic data. The stretching vibration frequency in free carbon monoxide is in the range 2146–2170 cm^{-1} and the corresponding vibration frequencies of the terminal CO group of metal carbonyls [structure (I)] have lower values (2000–2100 cm^{-1}).[11] With some approximation, the decrease of the stretching vibration frequency reflects the decrease of the C–O bond force constant and also the bond order. The increase of electron density at the transition metal atoms leads to an increase of the reverse supply of electrons to the π orbitals of CO and to a decrease of the C–O bond order. For example, the stretching vibration frequencies of the CO groups in the isoelectronic and isostructural complexes $[Mn(CO)_6]^+$, $Cr(CO)_6$, and $[V(CO)_6]^-$ are 2096, 2000, and 1859 cm^{-1} respectively[12]. Thus the contribution of the resonance structure (Ib) increases in the sequence Mn, Cr, V. However, the decrease of the bond order for the terminal CO groups of metal carbonyls is insignificant and an appreciable charge in the C–O bond length has not been observed[13].

The stretching vibration frequencies of the bridging carbonyl groups [structure (II)] are in the range 1700–1850 cm^{-1} and the C–O bond order is two and in some cases even less. Despite the outward analogy of the bridging carbonyl groups and organic carbonyl compounds (ketones, aldehydes, etc.), the character of the C–O bond in these compounds differs appreciably. Firstly, the transition metal atom is less electronegative than the carbon atom, which leads to a greater polarisation of the M–C bond compared with the C–C bond. Secondly, the MCM angle is much smaller than that at carbon in the sp^2-hybridised state and amounts to, for example, 83° for $Co_2(CO)_8$ and 77° for $Fe_2(CO)_9$.[14,15] Furthermore, the metal–metal bond shields the carbon atom of the bridging carbonyl ligand. For the reasons indicated above, the bridging carbonyl group is less reactive with

respect to nucleophilic attack on the carbon atom than the carbonyl groups in organic compounds.

The bridging carbonyl groups bound to three metal atoms [structure (III)] are inadequately described by the valence bond method. However, it is evident that an appreciable decrease of the C–O bond order is attained in this case because the stretching vibration frequencies in μ^3-CO are in the region of 1600 cm^{-1}. At the same time the bridging carbonyl groups bounds to three metal atoms are characterised by longer C–O bonds. For example, the C–O distance in $Rh_6(CO)_{16}$ is 1.155 ± 0.015 Å for the terminal groups and 1.201 ± 0.022 Å for the bridging groups[16].

Thus, depending on the nature of the complex and on the mode of coordination of the carbonyl ligand, the latter exhibits different reactivities, which are determined by the redistribution of electron density in the M_nCO system. An extremely unusual mode of coordination of the CO group has been observed comparatively recently. The complex $Mn_2(CO)_5(dppe)_2$, where dppe = bis(diphenylphosphino)-ethane[17], coordinates the CO molecule in accordance with the scheme below:

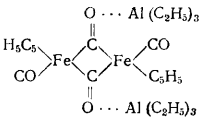


In this case the carbonyl ligand forms a σ-bond with one Mn atom and a π-bond with the other, which leads to an unexpectedly low stretching vibration frequency of CO (1645 cm^{-1}).

2. The Reactivity of the Carbonyl Ligand

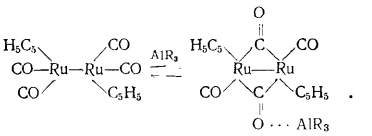
When a CO molecule is coordinated to two or more transition metal atoms, as indicated above, the C–O bond order is appreciably reduced. Thus the bridging carbonyl groups are activated to a greater extent by the transition metal than the terminal groups[18]. This type of coordination of CO obtains in carbonyl clusters and has much in common with the dissociative adsorption of CO on metal surfaces, including metals forming part of the composition of heterogeneous catalysts. Presumably the bridging carbonyl ligands bound to three carbon atoms are activated to the greatest extent. However, convincing evidence confirming their enhanced reactivity has not so far been obtained.

An appreciable increase of the reactivity of the carbon ligand is achieved when it interacts with Lewis acids[19,20]. Such interaction is characteristic of the strongest Lewis acids—derivatives of boron and aluminium. The possibility of adding a Lewis acid to the oxygen atom of the carbony ligand was observed for the first time by Schriver and co-workers[21,22] for the bridging CO groups in the complex $[(C_5H_5)Fe(CO)_2]_2$, which forms an adduct with two $Al(C_2H_5)_3$ molecules:



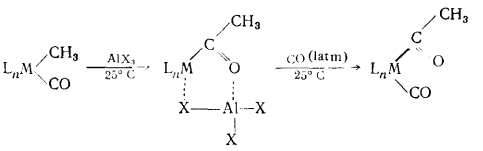
The structure of the adduct was established by X-ray diffraction[21]. Its formation reduces greatly the stretching vibration frequencies of the bridging CO groups involved in the interaction with the Al atom and some increase of the stretching vibration frequencies of the terminal carbonyl ligand. The decrease of the stretching vibration frequencies of the CO groups bound to Al is induced by the weakening of the C–O bonds as a consequence of the shift of electron density towards the electron acceptor molecule, which entails a decreased electron density at the transition metal atom and hence increased stretching vibration frequencies of the terminal CO groups.

The study of the interactions of complexes containing both bridging and terminal CO groups with Lewis acids has shown that the bridging CO groups are more basic. The basicity of the oxygen atom of the CO group increases in the sequence terminal groups < doubly bridging groups < triply bridging groups[19]. The differences between the basicities can be used to shift the equilibrium and to convert terminal groups into bridging groups; for example[23]:



Thus the action of the Lewis acid alters the structural parameters of the carbonyl ligand and leads to a redistribution of electron density, which favours nucleophilic attack on the carbon atom of the coordinated CO molecule.

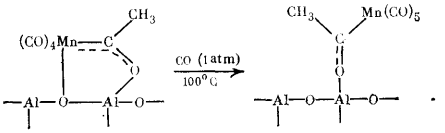
It has been shown[24,25] that the Lewis acids BX_3 (X = F, Cl, or Br) and AlX_3 (X = Cl, Br, CH_3, or iso-C_4H_9) catalyse the insertion of CO into the M–C bond:



$L_nM(CH_3)(CO)$ = $(CO)_5MnCH_3$, $(CO)_5MoCH_3$, $(C_5H_5)(CO)_3MoCH_3$ and $(C_5H_5)(CO)_2FeCH_3$.

The rate of insertion of CO increases by several orders of magnitude under these conditions. In certain cases, this reaction does not occur in the absence of the Lewis acid at a CO pressure of 1 atm and 25 °C. For example, the insertion of CO in the Fe–C bond of $(C_5H_5)(CO)_2FeCH_3$ occurs only at a CO pressure of 136 atm and 125 °C in the absence of AlX_3. The structure of the intermediate acyl complexes bound to the Lewis acid was established by X-ray diffraction[25].

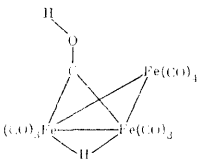
It is of very great interest that the above reaction is catalysed also by Al_2O_3.[26] It was found that, when $(CO)_5MnCH_3$ is deposited from pentane onto an Al_2O_3 film which had been heated to 500° or 1000 °C, the CO is inserted to the Mn–C bond at 25 °C. On the basis of the analysis of the infrared spectra, the authors[26] propose the following structure of the adducts:



In contrast to the adducts with molecular Lewis acids (AlX_3 and BX_3), in this case the successive addition of CO molecules takes place at higher temperatures (100 °C).

Thus the data presented above permit the conclusion that the Lewis acid significantly activates the carbonyl ligand in relation to nucleophilic attack on the carbon atom. The insertion of CO in the Mn–C bond on the Al_2O_3 surface is of fundamental importance because it is directly related to the mechanisms of the Fischer–Tropsch reaction in the presence of heterogeneous catalysts.

Reports of the activation of the carbonyl ligand by protic acids have appeared recently. It has been shown[27] that treatment of $[HFe_3(CO)_{11}]^-$ with a solution of HSO_3F in anhydrous CD_2Cl_2 leads to the formation of the compound $H_2Fe_3(CO)_{11}$, which has an extremely unusual structure according to ^1H NMR data and contains a protonated carbonyl ligand:



The same group of investigators were then able to show[28,29] that the carbonyl ligand activated in this way is capable of being reduced to CH_4 under mild conditions:

$$[Fe_3(CO)_{13}]^{2-} + HSO_3CF_3 \xrightarrow{25^\circ C} CH_4 + H_2 + CO + Fe^{2+} + SO_3CF_3^- .$$

The yield of CH_4 was 0.56 mole per mole of the cluster in three days. The presence of even trace amounts of water greatly reduced the rate of reaction.

3. The Reduction of the Carbonyl Ligand

The possibility of reducing the carbonyl ligand to the formyl ligand was first demonstrated in 1976.[30] It was found that, when various carbonyl complexes in tetrahydrofuran (THF) are treated with $Na[HB(OCH_3)_3]$ at 25 °C, the formyl derivatives are formed:

$$M(CO)_n + [HB(OCH_3)_3]^- \rightarrow \left[(CO)_{n-1}M-C\begin{matrix}O\\H\end{matrix}\right]^- + B(OCH_3)_3 .$$

The formation of the formyl ligand was detected by ^1H NMR, ^{13}C NMR, and infrared spectroscopic methods. On reduction of $Fe(CO)_5$, the formyl ligand was activated in the form of $[(Ph_3P)_2N][(CO)_4FeCHO]$ in 39% yield. A series of communications[31–44] on the synthesis of formyl complexes were published in subsequent years. It was shown[31,32] that the reduction of $[(C_5H_5)Re(CO)_2(NO)]BF_4$ with $Li[HB(C_2H_5)_3]$ in THF at 0–25 °C leads to the formation of mono- and di-formyl complexes, while BH_3 reduces the formyl ligand to the methyl ligand under the same conditions:

$$[(C_5H_5)Re(CO)_2NO]^+ \xrightarrow{HB(C_2H_5)_3^-} (C_5H_5)Re(CO)(NO)(CHO) \rightarrow \begin{cases} \xrightarrow{BH_3\cdot THF} (C_5H_5)Re(CO)(NO)(CH_3) \\ \xrightarrow{HB(C_2H_5)_3^-} (C_5H_5)Re(NO)(CHO)_2 \end{cases} .$$

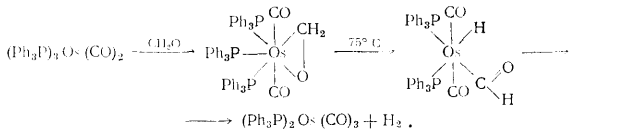
Another groups of investigators[33,34] were able to demonstrate the formation of the hydroxymethyl complex on reduction of the carbonyl ligand with $NaBH_4$ in THF at 0–25 °C:

$$[(C_5H_5)Re(CO)_2NO]^+ \xrightarrow{NaBH_4} (C_5H_5)Re(CO)(NO)X ;$$
$$X = CHO, CH_2OH, CH_3 .$$

Depending on the reaction conditions, it is possible to isolate formyl, hydroxymethyl, or methyl complexes.

Treatment of $Os_3(CO)_{12}$ or $Ir_4(CO)_{12}$ with $Li[HB(C_2H_5)_3]$ leads to the reduction of one of the carbonyl ligands to the formyl ligand[35,36] and the formation of the cluster anions $[Os_3(CO)_{11}(CHO)]^-$ or $[Ir_4(CO)_{11}(CHO)]^-$. The latter anion decomposes with formation of the hydride complex $[Ir_4(CO)_{11}H]^-$.

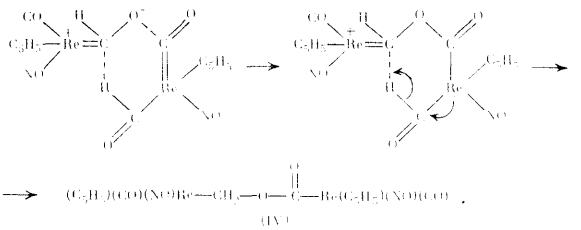
An osmium complex[27] containing coordinated formaldehyde, which is a tautomer of the hydroxymethylene ligand $-C\begin{matrix}H\\OH\end{matrix}$ has been synthesised:[37]



On heating, the complex decomposes with evolution of H_2 and formation of $(Ph_3P)_2Os(CO)_3$.

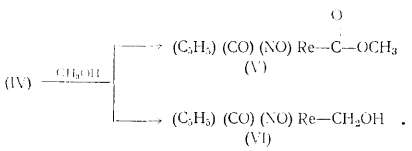
Studies have shown[38–40] that the formyl complexes behave as donors of the hydride ion. For example, when $[(C_2H_5)_4N]\cdot[(PhO)_3PFe(CO)_3(CHO)]$ reacts with $Re_2(CO)_{10}$, a formyl complex of rhenium is formed: in the case of acetone, isopropyl alcohol is produced and in the case of alkyl halides, the products are alkanes.

A hydride ion need not be transferred only to another transition metal complex. The disproportionation of formyl complexes with transfer of a hydride ion to the formyl ligand in accordance with the following scheme has been described[41,42]:



(IV)

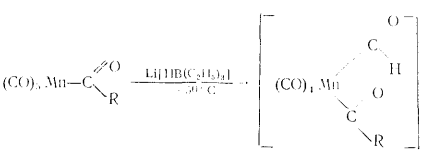
The metalloester (IV) has been isolated and characterised by ^1H NMR and infrared spectroscopy. Its methanolysis leads to the formation of the methyl ester of the metalcarboxylic acid (V) and to the hydroxymethyl complex (VI):

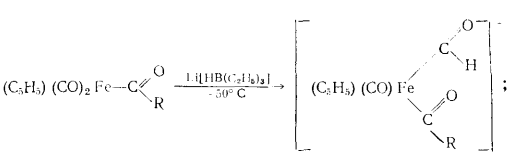


(V) (VI)

Dinuclear formyl complexes[43] of the type $Li[(CO)_5MM'(CO)_4\cdot(CHO)]$, where M = M' = Re or M = Re and M' = Mn, were first obtained from $Li[HB(C_2H_5)_3]$ and $ReMn(CO)_{10}$ or $Re_2(CO)_{10}$ at 25 °C.[43] Treatment of these complexes with an excess of $K[HB(t\text{-}C_4H_9)_3]$ leads to the formation of formaldehyde and methanol in yields of 21 and 38% respectively.

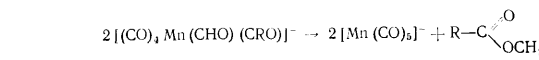
Formyl complexes of Mn and Fe containing an acyl ligand have been recently synthesised and characterised[45]:





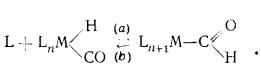
R = Ph, CH_2OCH_3, $COOCH_3$, CF_3, CH_3 .

These complexes decompose at room temperature in accordance with the scheme



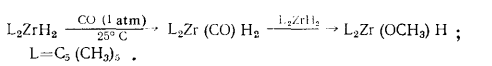
It has been suggested that the decomposition of these complexes entails a transfer of the hydride ion from the formyl to the acyl ligand[45].

Thus it has now been reliably demonstrated that formyl complexes of transition metals exist. It has been established that the reduction of the carbonyl ligand by an active donor of the hydride ion leads to the formyl ligand and in certain cases the latter is reduced with formation of the hydroxymethyl or methyl groups. The study of the properties of the formyl complexes showed that they are capable of transferring the hydride ion to the carbonyl[38–40], formyl[41,42], or acyl[45] ligand and also to ketones and alkyl halides[38–40]. It is noteworthy that in the cases indicated above it is suggested that the formyl ligand is formed on treatment with a hydride ion donor, namely BH_3, $NaBH_4$, $Li[HB(C_2H_5)_3]$, etc., i.e. as a result of the nucleophilic attack by the hydride ion on the carbonyl ligand. There has been only one communication[46] on the synthesis of a formyl complex as a result of the insertion of the CO group in the Rh–H bond [reaction (*a*)]. Furthermore, all the formyl complexes synthesised hitherto are coordination-saturated and reaction (b) is therefore hindered, although at elevated temperatures the ligand is split off and a carbonyl hydride complex is formed[35]:

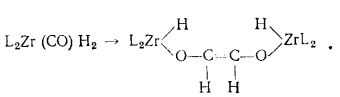


On the other hand, there exist many instances of the insertion of CO in a transition metal–carbon bond with formation of acyl complexes[47]. The formation of formyl complexes from hydrocarbonyls is thermodynamically less favourable than the formation of acyl complexes from alkyl carbonyls.

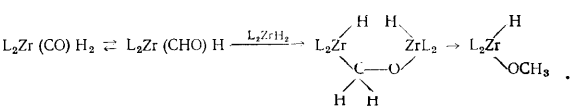
In 1976 the reduction of the carbonyl ligand to the methoxy-group was reported[48]:



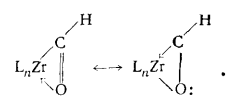
Hydrolysis of the resulting complex leads to the formation of methanol. In the absence of an excess of L_2ZrH_3, the carbonyl hydride complex $L_2Zr(CO)H_2$ dimerises according to the scheme



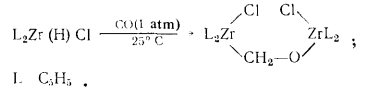
The authors[48] proposed a reaction mechanism with the intermediate formation of a formyl complex:



Subsequent investigations of this reaction led the authors[49] to the conclusion that the formyl complex formed on insertion of CO in the Zr–H bond can be stabilised as a consequence of the formation of a π-bond, as in the stabilisation of an acyl ligand[50]:



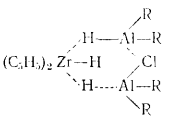
When CO interacts with zirconium halide hydride, a dinuclear complex is also formed and hydrolyses with formation of CH_3OH: [51]



L C_5H_5 .

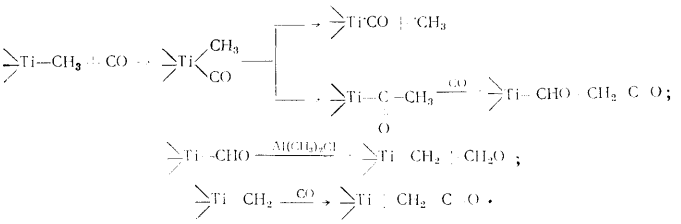
Thus zirconium hydride complexes reduce carbon monoxide under mild conditions. In this case the formation of the coordination-unsaturated formyl complex $L_2Zr(CHO)H$ as a result of the insertion of CO in the Zr–H bond has been postulated. The complex is stabilised by the additional π-binding of the formyl ligand.

In the presence of $HAlR_2$ (R = iso-C_4H_9) and $(C_5H_5)ZrCl_2$, it has been possible to reduce CO to linear alcohols[52]. The reaction proceeds at 25 °C and a carbon monoxide pressure of 1–4 atm in benzene. The formation of a zirconium hydride complex during the course of the reaction has been postulated:



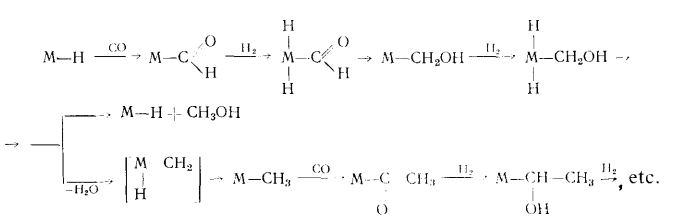
As a result of the interaction of this complex with CO and subsequent hydrolysis, a mixture of normal alcohols in the molar proportions $C_1 : C_2 : C_3 : C_4 = 1 : 0.12 : 0.15 : 0.03$ is formed. An excess of $HAlR_2$ inhibits the reaction but up to ten $HAlR_2$ addition cycles can be carried out without an appreciable decrease of activity. The use of ^{13}CO leads to the formation of $^{13}CH_3OH$.

Enikolopyan and co-workers observed that, in the presence of $Al(CH_3)_2Cl$, $(C_5H_5)_2TiCl_2$ catalyses the reduction of CO at 20–50 °C and atmospheric pressure to formaldehyde and keten. The introduction of $LiAlH_4$ into this catalytic system increases its activity (three moles of CH_2O per gramme-atom of Ti are formed in 1 h at 50 °C under 1 atm CO pressure). The authors[53] suggested the following reaction mechanism:



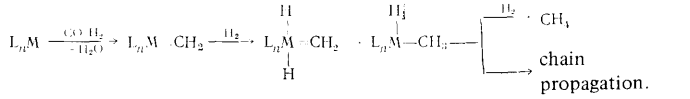
The study of model reactions involving the reduction of the carbonyl ligand and also the formation of complexes containing the formyl, hydroxymethyl, and methyl ligands on reduction of the coordinated CO molecule suggested a number of mechanisms of the CO hydrogenation reaction catalysed by transition metal complexes.

The following mechanism has been proposed for the process[54]:

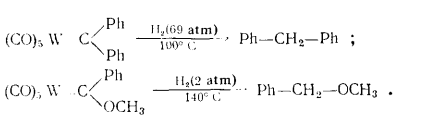


The authors were unable to confirm it experimentally because most of the studies on the CO reduction reaction were published subsequently.

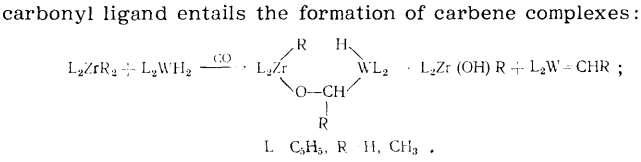
In 1976 it was suggested[30] that the reduction of the carbonyl ligand should lead to the formation of a carbene complex:



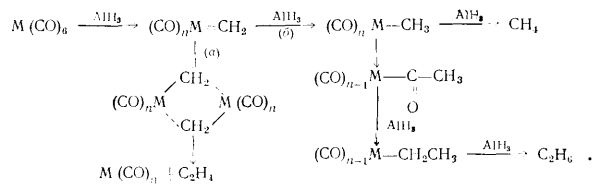
It has been shown that the carbene complexes are reduced with formation of alkanes:



Subsequent studies[55,56] confirmed that the reduction of the carbonyl ligand entails the formation of carbene complexes:

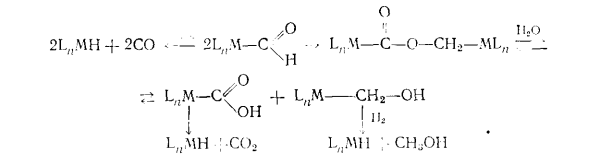


Treatment of $Ru_3(CO)_{12}$, $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ with aluminium hydride in THF at 22 °C leads to a rapid evolution of C_1–C_3 hydrocarbons[57]. The ethylene content in the reaction product is 95% for chromium, molybdenum, and tungsten carbonyls. Not more than two carbonyl groups of the complex are reduced during the reaction and the solution remains homogeneous. The activity of $LiAlH_4$ is somewhat lower if BH_3 is inactive. A mechanism involving the formation of a carbene complex has been postulated[57]:



The selective formation of C_2H_4 has been explained by the preferential occurrence of the process via pathway (*a*). It may be that the carbonyl ligand is activated as a result of the binary coordination of the CO group: M–CO...AlH_3.

A mechanism for the reduction of CO involving a stage in which formyl complexes disproportionate has also been proposed[41]:

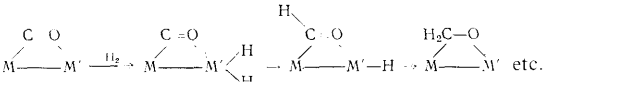


The authors observed[58] that the decomposition of the carbonyls $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Os_6(CO)_{16}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$ on the surfaces of Al_2O_3, SiO_2, or MgO at 250° to 400 °C in argon leads to the formation of C_1–C_3 alkanes and CO_2. The selectivity in the formation of CH_4 is 59–100%, depending on the nature of the complex. When the reaction is carried out in an atmosphere of CO, 5–13 moles of CH_4 and 40–90 moles of CO_2 are formed per mole of the complex. The authors suggest that the carbonyl ligand initially reacts with H_2O or surface OH groups of the oxide with formation of CO_2, after which the carbonyl ligand is reduced with hydrogen.

A more detailed study of this reaction showed[59] that hydrocarbons are formed from both polynuclear and mononuclear carbonyls and that in the case of the latter [$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and $Fe(CO)_5$] the maximum yield of CH_4 per gramme-atom of the metal is achieved. The authors[59] concluded that the synthesis of hydrocarbons in this instance does not require a catalyst of the cluster type and proposed a mechanism of the formation of methane in which H_2 plays an unusual role:

$$4OH(ads) + M(CO) \rightarrow MO_3 + 2O^-(ads) + CH_4 ;$$
$$3H_2 + MO_3 \rightarrow M + 3H_2O ;$$
$$\underline{2H_2O + 2O^-(ads) \rightarrow 4OH^-(ads)} \quad ;$$
$$CO + H_2 \rightarrow CH_4 + H_2O .$$

Inspection of the mechanisms presented above as well as the mechanisms of the model reactions involving the reduction of the carbonyl ligand permits the conclusion that the process can proceed with participation of a mononuclear complex rather than a cluster. On the other hand, it has been suggested[18,60] that carbon monoxide is reduced most readily in the presence of cluster catalysts because in the latter there is a possibility of the formation of active intermediates of the type M–CO–M', where M and M' are transition metal atoms:



Experimental confirmation of the existence of such structures has not so far been obtained, although they are known for transition metal complexes containing molecules with triple bonds (N_2 and C_2H_2).[60] It is believed[18,60] that the formation of intermediates of the type M–CO–M' and their hydrogenation may be energetically more favourable than the reduction of the CO molecule coordinated to one transition metal atom. Unfortunately both the possibility of the formation of such structures in carbonyl clusters and the possibility of the hydrogenation of CO with their intermediate formation have not so far been rigorously demonstrated[60–62].

We may note that, as stated above, the binary coordination of the carbon monoxide molecule (M–CO...M') is achieved in the adducts of metal carbonyls with Lewis acids. It has also been suggested that dinuclear complexes of the type L_nZr–CO–ZrL_n (L is the ligand) are formed on reduction of the carbonyl ligand to $-OCH_3$.

Thus examination of the above mechanisms of the reduction of CO with participation of transition metal complexes permits the conclusion that the most active catalytic system for the activation of CO is obtained on binary coordination of carbon monoxide of the type M–CO...M' or M–CO–M'.

4. The Synthesis of Hydrocarbons from CO and H_2

In 1976 Muetterties and co-workers[63] demonstrated for the first time that the synthesis of hydrocarbons from CO and H_2 can be catalysed by transition metal complexes. Methane is formed in the presence of $Ir_4(CO)_{12}$ or $Os_3(CO)_{12}$ in toluene at 140 °C and atmospheric pressure of the 1 : 4 CO–H_2 mixture. However, the rate of reaction is low and the degree of conversion of CO amounted to 1% after 3–5 days. The addition of Ph_3P or $(CH_3O)_3P$ increases slightly the activity of the catalyst.

The non-catalytic reduction of the carbonyl ligand occurs in the presence of niobium hydride complexes[64,65]. Treatment of $(C_5H_5)_2Nb(CO)H$ with hydrogen at 140 °C and a pressure of 1 atm in organic solvents leads to the formation of methane[64]. However, only the carbonyl ligand is then

reduced, which was demonstrated using $(C_5H_5)_2Nb(^{13}CO)H$. The introduction of a mixture of CO and H_2 into the system did not increase the yield of CH_4. The hydride complex $(C_5H_5)_2NbH_3$ reduces the carbonyl ligand to $Cr(CO)_6$ at 45 °C in benzene and an H_2 pressure of 1 atm;[65] this involves the formation of CH_4 and C_2H_6 (10% per gramme-atom of niobium). The yield does not increase when CO is introduced into the system and Cr_2O_3 and $(C_5H_5)_2Nb(CO)H$ are formed at the end of the reaction.

Another example of the non-catalytic reduction of CO by hydrogen to CH_4 is the reaction of $(C_5H_5)_2Ti(CO)_2$ with H_2 at 150 °C in toluene[66]. When D_2 is employed, CD_4 is formed. The authors[66] do not present quantitative data for the yield of CH_4, but state that the reaction is non-catalytic and that the introduction of CO into the system does not increase that the introduction of CO into the system does not increase the yield of CH_4. At the end of the reaction, a cluster having the composition $Ti_6O_8(C_5H_5)_6$ was isolated and its structure was determined. Apparently the formation of $Ti_6O_8.(C_5H_5)_6$ is caused by the interaction of the titanium complex with water formed in the course of the synthesis of CH_4 from CO and H_2.

The most active catalytic system at atmospheric pressure has been proposed by Demitras and Muetterties[67]. It includes iridium, rhodium, or ruthenium carbonyls and the Lewis acids $AlCl_3$, $AlBr_3$, and BBr_3.[67,69] When the reaction is carried out in a Lewis acid melt without solvent with the ratio $CO : H_2 = 1 : 3$ at 180 °C and 1 atm, C_1–C_4 alkanes are formed. The complexes can then be arranged in the following activity series: $Ir_4(CO)_{12} \cong Rh_6(CO)_{16} \cong Rh_4(CO)_{12} > Ru_3(CO)_{12} \gg H_2PtCl_6 > PdCl_2$. The complexes $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, $NiCl_2$, and $Co_4(CO)_{12}$ showed no activity. It is noteworthy that the activity series for the complex catalysts differs significantly from that for deposited heterogeneous catalysts in the methane formation reaction[70]. The catalytic activity of $Ir_4(CO)_{12}$ is such that 5 moles of CO enter into the reaction per mole of the complex in 1 h. During the reaction, the system remains homogeneous and the formation of metallic iridium is not observed. Furthermore, kinetic calculations based on the activity data for heterogeneous iridium catalysts showed that, even if the entire iridium from the initial $Ir_4(CO)_{12}$ catalyst were reduced to the metal and each metal atom functioned as an active centre for the methane formation reaction, then the calculated rate of reaction would have been lower by several orders of magnitude than the observed rate in the $Ir_4(CO)_{12}$–$AlCl_3$ system.[67] The introduction of metallic aluminium into the given catalytic system resulted in a sharp increase of the yield of hydrocarbons under the same conditions[71–73]. An appreciable alteration of the reaction products and an increase of the degree of conversion of CO are then observed[72].

Similarly the introduction of metallic aluminium into the "transition metal complex–$AlBr_3$" system led to a sharp increase of the yield of hydrocarbons when iridium, ruthenium, and particularly osmium and nickel carbonyls were employed under the same conditions[74]. The complex-forming metals used can be arranged in the following series in terms of their activities: Rh > Ir > Ru > Os > Ni (Table 1). This activity series differs from the analogous series for the M_nL_m–$AlCl_3$ systems presented above. The composition of the reaction products depends on the nature of the catalyst; in the presence of $Ir_4(CO)_{12}$ the main product is CH_4, while in the presence of $Rh_4(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$, appreciable amounts of C_4H_{10} and less C_2H_6 and C_3H_8 are formed together with CH_4. The degree of conversion of CO into hydrocarbons during the experiment then reaches 89% or 22 moles of CO per gramme-atom of rhodium. For the most active systems based on rhodium complexes, a study was made of the influence of the structure of the rhodium complex on the properties of the Rh_nL_m–$AlBr_3$–Al system[72] (Table 1). It was found that both mononuclear complexes and clusters exhibit virtually identical activities per gramme-atom of rhodium.

Table 1. The degrees of conversion of carbon monoxide (K_{CO}, mol CO/g-atom M) and the composition of the reaction products (vol.%) in the synthesis of alkanes from CO and H_2 in the presence of transition metal complexes.

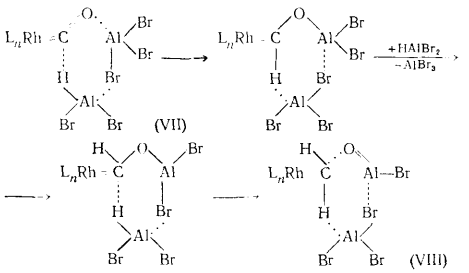
Complex	K_{CO}	CH_4	C_2H_6	C_3H_8	iso-C_4H_{10}	n-C_4H_{10}
$Rh_4(CO)_{12}$	22	47	8	14	30	1
$[Rh(CO)_2Cl]_2$	22	47	8	14	29	2
$Na_3[Rh_{12}(CO)_{30}]$	22	46	9	15	29	1
$(Ph_3P)_3RhCl$	21	50	6	13	30	1
$RhCl_3 \cdot 3H_2O$	3	37	13	12	35	3
$Ir_4(CO)_{12}$	12	73	9	8	9	1
$Ru_3(CO)_{12}$	7	50	5	9	35	1
$Os_3(CO)_{12}$	6	33	11	12	43	1
$NiCl_2$	3	33	16	13	36	2

Note: Conditions: 150°, 10 h, $CO : H_2 = 1 : 4$, molar ratios $M : AlBr_3 : Al : Co = 1 : 200 : 40 : 25$; the following catalysts showed no activity: $Fe(CO)_5$, $Co_2(CO)_8$, $(Ph_3P)_2PdCl_2$, $Mn_2(CO)_{10}$, $Mo(CO)_6$, $W(CO)_6$, and $TiCl_4$.

It was demonstrated by infrared spectroscopy[74] that in the course of the synthesis from CO and H_2 the initial rhodium complexes are converted into a mononuclear anion of the type $[Rh(CO)_2Br_2]^-$. Thus the data presented show that the synthesis of alkanes from CO and H_2 in the presence of the Rh_nL_m–$AlBr_3$–Al catalytic system proceeds on a mononuclear rhodium complex.

The study of the influence of the amount of metallic aluminium in the $Rh_4(CO)_{12}$–$AlBr_3$–Al system[72] showed that an increase of the ratio $Al : AlBr_3$ increases K_{CO} and the C_4H_{10} content in the products of the synthesis; at the same time there is a sharp decrease of the amount of CO_2. The authors[74] suggested the formation of $HAlBr_2$ from H_2, $AlBr_3$, and Al during the synthesis of alkanes from CO and H_2. The presence of $HAlBr_2$ was confirmed by the reduction of acetone to isopropyl alcohol. It was found that, when the $AlBr_3$–Al system was dissolved in THF and treated with a $1 : 4$ CO–H_2 mixture at 150 °C, solutions capable of reducing acetone were formed. The reaction with solutions known beforehand to contain $HAlBr_2$, obtained from $LiAlH_4$ and $AlBr_3$, proceeded analogously. In addition, the amount of isopropyl alcohol formed and hence of $HAlBr_2$ was directly proportional to the aluminium content in the $Rh_4(CO)_{12}$–$AlBr_3$–Al system. Thus an increase of the content of aluminium in the $Rh_4(CO)_{12}$–$AlBr_3$–Al system entails an increase of K_{CO} and at the same time also an increase of the amount of $HAlBr_2$ formed during synthesis.

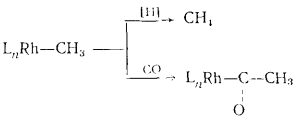
On the basis of the data obtained, the authors[74] proposed the following mechanism of the synthesis of hydrocarbons from CO and H_2 in the presence of the "rhodium complex–$AlBr_3$–Al" catalytic system:



The carbene complex formed and incorporated in the intermediate (VIII) can then be reduced to the methyl complex:

$$L_nRh{=}CH_2 \xrightarrow{[H]} L_nRh{-}CH_3 .$$

On further hydrogenation, this complex gives rise to an alkane or CO is inserted in the Rh–C bond and the resulting acyl complex is reduced in accordance with the mechanism presented above to the ethyl complex of rhodium:

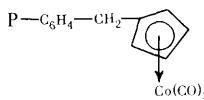


It has been observed[75] that in the presence of the $W(CO)_6$–$AlCl_3$ catalytic system at 200 °C and a pressure of the CO–H_2 mixture of 120 atm, alkylbenzenes are formed from benzene:

$$C_6H_6 + CO + H_2 \rightarrow Ph{-}(CH_2)_n{-}H .$$

The length of the aliphatic chain of alkylbenzenes is consistent with the Schulz–Flory distribution characteristic of heterogeneous catalysts of the Fischer–Tropsch synthesis[76]. The molar ratios of the products were $PhCH_3 : PhC_2H_5 : PhC_3H_7 : PhC_4H_9 : PhC_5H_{11} = 25 : 39 : 1 : 0.1 : 0.1$.[75]

A catalyst containing the cobalt carbonyl complex grafted to a polymer (P) has been proposed for the synthesis of hydrocarbons from CO and H_2:[77]



At 190–200 °C and a pressure of the 1 : 3 CO–H_2 mixture of 30 atm and using n-octane as the solvent, a mixture of C_1–C_{20} hydrocarbons was obtained. The content of hydrocarbons in the products of the synthesis decreases uniformly with increase of their molecular weight. The catalyst exhibits a fairly low activity: 1×10^{-5} mole of CO is consumed per gramme-atom of cobalt in 1 h. The catalytic system containing $Al(C_2H_5)_3$ and the nickel salt of a carboxylic acid with 8–10 carbon atoms, dissolved in a hydrocarbon solvent, proved to be more active[78]. At 330 °C and a pressure of the mixture ($CO : H_2 = 1 : 4$) of 8 atm, the formation of C_1–C_4 hydrocarbons was observed (91% CH_4, 6% C_2H_6, 2% C_3H_8, and 1% C_4H_{10}). After 8 h, the degree of conversion of CO was 62%; a gaseous mixture containing 31 vol.% of the hydrocarbon was formed.

In the presence of cobalt acetylacetonate and $Al(C_2H_5)_3$ dissolved in alkylterphenyl, the formation of C_1–C_6 hydrocarbons from a 1 : 1 CO–H_2 mixture was observed at 190 °C and 1 atm.[79] The rate of formation of the hydrocarbons was 4.4×10^{-4} mole C/h g CO.

The use of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Ir_4(CO)_{12}$ as catalysts of the Fischer–Tropsch synthesis in THF or n-heptane as the solvent has been described[80]. At 300 °C and a pressure of the mixture ($CO : H_2 = 1 : 1$) of 200 atm, a mixture of C_1–C_{30} hydrocarbons was obtained after 20 h (1.9 moles of C_{10}–C_{20} and 0.6 mole of C_{20}–C_{30} per mole of the catalyst). However, the study of the kinetics of the reaction and the infrared spectra of the reaction mixture under the conditions of the synthesis showed[81,82] that the true catalyst of the synthesis of hydrocarbons in this case was metallic ruthenium formed from $Ru_3(CO)_{12}$. Apparently reports of the metal complex catalysis of the Fischer–Tropsch reaction at temperatures above 200 °C should be treated with some caution, because the majority of the transition metal complexes are unstable under these conditions.

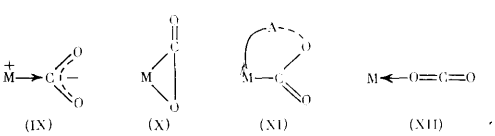
Layer compounds of graphite with transition metals occupy a position intermediate between homogeneous metal complex systems and heterogeneous catalysts of the Fischer–Tropsch reaction. It has been shown that at 300–350 °C the layer compounds of graphite with Group IV–VIII transition metals and potassium catalyse the synthesis of C_1–C_5 hydrocarbons from a mixture of CO and H_2 at 1 atm;[83,84] the main product of the synthesis is CH_4. The activity of layer compounds of graphite with $FeCl_2$ in the synthesis of hydrocarbons from CO and H_2 has been reported recently[85]. This catalyst is active in the synthesis of C_1–C_4 hydrocarbons from CO and H_2 at 300–500 °C and 1–20 atm; the main product of the synthesis is methane (70–90%).

Thus the survey of the literature dealing with the application of metal complex catalysts in the Fischer–Tropsch reaction permits the conclusion that homogeneous systems superior in their activity to traditional heterogeneous catalysts can be developed in principle. This problem has attracted many investigators both in our country and abroad as shown by the constant growth of the number of publications devoted to the application of metal complex catalysts in the reduction of CO to hydrocarbons. The development of studies in this field permits the hope that significant advances will be made in the immediate future.

III. THE REDUCTION OF CARBON DIOXIDE

1. The Ways in which Carbon Dioxide is Coordinated to Transition Metals

The activation of carbon dioxide by transition metals is directly related to the mode of formation of the bond between CO_2 and the transition metal. The coordination chemistry of CO_2 is a comparatively new field of the chemistry of organometallic compounds. The first complex containing the CO_2 molecule was synthesised by Vol'pin and Kolomnikov in 1969.[86] However, to date only a few complexes with CO_2 have been obtained when the structure has been established reliably. In principle the bond between CO_2 and the metal can be formed in accordance with the following schemes[8,9]:

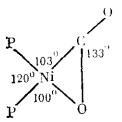


The interaction of the carbon atom of the CO_2 molecule, which exhibits Lewis acidity, with the transition metal [structure (IX)] is possible for metals in low oxidation states, which have an enhanced electron density. The adducts of transition metal complexes with Lewis acids containing the

"metal–Lewis acid" bond have a similar structure[20]. For example, the interaction of $(Ph_3P)_2Ir(CO)Cl$ with BF_3 leads to an adduct with a donor–acceptor Ir–BF_3 bond[87].

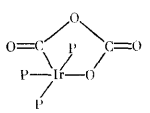
The complexes of transition metals in the lowest oxidation states, containing CO_2, can have the structure (X), which presupposes the interaction of the metal with the π-bond in CO_2. A third type of coordination is possible in the presence of a Lewis acidity centre in the coordination sphere or outside it [structure (XI)], where A is a Lewis acidity centre, which interacts with one of the oxygen atoms of the coordinated CO_2. Such interaction usually leads to the irreversible coordination of CO_2 in the form of carbonate, acetate, etc. Structure (XII) illustrates the interaction of the transition metal in the highest oxidation states, which is electron-deficient, with the weakly basic oxygen atom in CO_2. Such interaction between the transition metal and CO_2 is the least probable.

To date, X-ray diffraction studies have been carried out on only a few complexes containing CO_2 as the ligand. The structure of a complex containing CO_2 was first investigated by Aresta et al.[88] It was found that the P_2NiCO_2 fragment of the complex $[L_2Ni(CO_2)].0.75C_6H_5CH_3$, where $L = P(C_6H_{11})_3$, is located in a single plane:

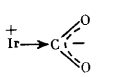


while CO_2 is linked to the nickel atom by a π-bond [see structure (X)]. The non-coordinated C–O bond has a length of 1.17 Å, which differs little from the length of the C–O bond in the free CO_2 molecule (1.16 Å), while the coordinated C–O bond has a length of 1.22 Å, which is much less than the length of a single C–O bond (1.45 Å); the OCO angle is 133°. Carbon dioxide is weakly bound in this complex and can be readily removed on passing argon through a solution of the complex in toluene at 25 °C; the initial complex is reformed on saturation of the solution with CO_2.

The structure of the complex $L_3Ir(CO_2)_2Cl$, where $L = P(CH_3)_3$, has also been established by X-ray diffraction[89]. Iridium has an octahedral coordination and the Ir–C and Ir–O bonds as well as a five-membered chelate ring formed by two CO_2 molecule were identified in the complex:



Thus CO_2 is coordinated in the given instance to the transition metal and the Lewis acid centre [see structure (XI)]. It has been suggested[89] that the complex is formed following the electrophilic attack by the carbon of the CO_2 group on the iridium atom with the subsequent analogous electrophilic attack by a second CO_2 molecule on the oxygen atom of the coordinated CO_2 and the closure of the organometallic ring. The replacement of the $P(CH_3)_3$ ligands by the chelating ligands $(CH_3)_2PCH_2CH_2P(CH_3)_2$(dmpe) in the above complex hinders the coordination of two CO_2 molecules. This results in the formation of the complex $(dmpe)_2Ir(CO_2)Cl$, for which the following mode of coordination of CO_2 has been proposed [see structure (IX)]:[90]



The structure of the complex $[Co(pr\text{-}Salen)K(CO_2)THF]_n$, where pr-Salen is *N,N'*-di(7-propylsalicylidene)ethylenediamine, has been studied recently[91]. In this polymeric complex CO_2 is coordinated to Co via the carbon atom, and one oxygen atom is linked to two potassium atoms, the other oxygen atom being linked to one potassium atom. Thus, in this instance CO_2 is bound to the transition metal via the carbon atom and there is additional coordination to the Lewis acidity centre (K^+) via the oxygen atoms. The lengths of the C–O bonds in the coordinated CO_2 molecule are 1.22 and 1.24 Å, while the OCO angle is 135 °C.

CO_2 is coordinated in an unusual manner in the $[HOs_3.(CO)_{10}(\mu\text{-}CO_2)Os_6(CO)_{17}]^-$ cluster[92]. The carbon atom of the CO_2 ligand is bound to the Os_6 cluster and the two oxygen atoms are found to the Os_3 cluster. The lengths of the C–O bonds in the CO_2 bridging ligand are 1.28 and 1.36 Å. It has been suggested[92] that the Os_6–C fragment can be regarded as a coordinated carbene and the coordination of the two oxygen atoms of the CO_2 ligand with the Os_3 cluster resembles that of a carboxylate ligand.

Thus the structures of only four complexes containing a coordinated CO_2 molecule have been reliably established by X-ray diffraction, CO_2 being coordinated in the complex in accordance with Schemes (IX)–(XI). The coordination of carbon dioxide to the transition metal alters its configuration. In all cases the OCO angle of the CO_2 ligand differs appreciably from 180° characteristic of the free CO_2 molecule. In certain cases the length of the C–O bond increases significantly. Evidently such marked changes in the structure of the CO_2 molecule as well as the redistribution of electron density induced by the interaction with the transition metal are associated with the activation of carbon dioxide. Since CO_2 is a fairly labile ligand, the preparation of the transition metal complexes of CO_2 must be based on initial coordination-unsaturated complexes.

2. The Reduction of Carbon Dioxide in the Presence of Transition Metal Complexes

The reactions involving the insertion of carbon dioxide in M–H or M–C bonds are apparently intermediate reactions in catalytic cycles leading to the reduction of CO_2. Unfortunately the mechanisms of these processes have not been investigated. The following schemes can therefore be proposed for the given reactions[8,9]:

$$LM{-}CO_2 \xrightarrow{X} LM{-}(CO_2){-}X\,, \qquad (1)$$

$$X{-}CO_2 \xrightarrow{LM} LM{-}(CO_2){-}X\,, \qquad (2)$$

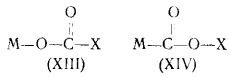
$$LM{-}X \xrightarrow{CO_2} LM\begin{matrix}X\\ \diagdown\\ \diagup\\ CO_2\end{matrix} \rightarrow LM{-}(CO_2){-}X\,, \qquad (3)$$

$$LM{-}X \xrightarrow{CO_2} LM{-}X{-}CO_2 \rightarrow LM\ CO_2X^{\ominus} \rightarrow LM{-}(CO_2){-}X\,, \qquad (4)$$

where LM is the transition metal complex and X = H or alkyl. The reaction involves three reactants: the transition metal complex, the ligand (H or R), and CO_2. Two of these can initially react with one another and then with a third reactant. Scheme (1) corresponds to attack by the free ligand on the coordinated carbon dioxide. Scheme (2) leads to an insertion product via the formation of an adduct of CO_2 with the ligand and its stabilisation on the transition metal. Both these schemes presuppose the presence of the free ligand in the reaction mixture. If the metal–ligand bond (M–H or M–R) is formed, the CO_2 molecule can be either coordinated to the coordination-unsaturated metal centre with subsequent migration of the ligand to the bound CO_2 [Scheme (3)] or can

attack directly the bound ligand with the intermediate formation of an ion pair [Scheme (4)].

There are two possible variants of the structure of the insertion product depending on the polarity of the M–X bond[8,9]:



(XIII) (XIV)

This entails the formation of a formate complex (XIII) or metal-carboxylic acids or their esters (XIV). The first of these reactions can serve as a basis for the catalytic reduction of CO_2 by hydrogen with formation of formic acid, methanol, and other products. In most of the known reactions involving the insertion of CO_2 in an M–H or M–C bond, formate complexes are formed. The insertion of CO_2 in a transition metal–hydrogen bond was observed for the first time in relation to the cobalt complex $(Ph_3P)_3Co(N_2)H$;[93] the cobalt formate complex $(Ph_3P)_nCoOOCH$ is formed in benzene at 25 °C and a CO_2 pressure of 1 atm. A similar formate complex has been obtained also from $(Ph_3P)_3CoH_3$.[94] The presence of the formate group in the complex has been confirmed by treatment with methyl iodide, which leads to the formation of methyl formate. In addition, treatment of the complexes with concentrated sulphuric acid leads to the evolution of CO; complexes of carbon dioxide evolve CO_2 under these conditions.

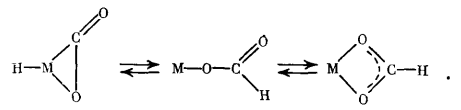
It is noteworthy that the reactions with sulphuric acid or methyl iodide constitute a kind of test and help to distinguish formate complexes from complexes with CO_2, which have very similar infrared spectra. As for the transition metal complexes with CO_2, the structure of the formate complexes has been established reliably by X-ray diffraction only in isolated cases. The structure of the ruthenium complex $(Ph_3P)_3$. .Ru(H)OOCH has been described[95]. In the crystalline form, the compound contains a formate group in which hydrogen is located in the *trans*-position relative to this group. This complex was obtained by the reaction of CO_2 with a solution of $(Ph_3P)_4RuH_2$ in toluene at 25 °C at 1 atm [96] or with solutions of $(Ph_3P)_3RuH_4$ and $(Ph_3P)_3Ru(N_2)H_2$.[97] The reactions of the above complex in solution are extremely unusual for formate complexes and are more consistent with the complex of ruthenium hydride and CO_2 of the type $(Ph_3P)_3Ru(CO_2)H_2$. For example, the reactions with Ph_3P, N_2, H_2, or CO are accompanied by the elimination of CO_2 under mild conditions[97]:

$$(Ph_3P)_3\,Ru\,(H)\,OOCH \xrightarrow{L} (Ph_3P)_3Ru\,(L)\,H_2 + CO_2\ ;$$
$$L = Ph_3P,\ N_2,\ H_2,\ CO\ .$$

The hypothesis of the formation of the ruthenium hydride complex with CO_2 has been confirmed by ^1H NMR study of a solution in the ruthenium formate complex $[Ph(CH_3)_2P]_4$. .Ru(OOCH)$^+$.[98]

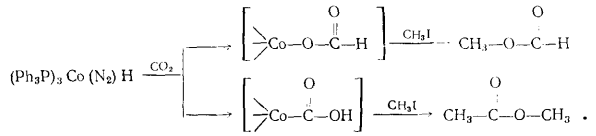
The iron formate complex $L_2Fe(OOCH)_2$, where $L = Ph(C_2H_5)_2P$ or $Ph_2(C_2H_5)P$, is formed when the solid complexes L_3FeH_4 or $L_3Fe(N_2)H_2$ are irradiated with visible light in an atmosphere of CO_2;[99] the formation of the formate complex is not observed in the absence of irradiation. The authors[99] suggest that the reaction is induced by the photochemical dissociation of the H_2 or N_2 ligand.

In all cases of the formation of formate complexes, it has been suggested that the first stage of the reaction is coordination of CO_2 to the transition metal atom, which requires the presence of a coordination-unsaturated complex with an enhanced electron density at the transition metal atom. Like the complexes containing CO_2, formate complexes can therefore be obtained only when the molecule of the initial complex containing labile ligands (N_2, H_2, Ph_3P), whose dissociation leads to coordination-unsaturated complexes. The formate complexes are apparently formed from the hydride complex with CO_2 as a result of the migration of the hydride to the carbon atom of the CO_2 molecule:



This reaction is in most cases reversible. For example, the ruthenium complex $(Ph_3P)_3Ru(H)OOCH$ contains the formate ligand in the solid state[95], while on its dissolution in CH_2Cl_2 a complex containing carbon dioxide is formed: $(Ph_3P)_3Ru$. .$(H_2)CO_2$.[97,98]

Together with the formation of formate complexes following the insertion of CO_2 in an M–H bond, a metal-carboxylic acid can also be produced. The interaction of CO_2 with $(Ph_3P)_3Co(N_2)H$ and subsequent methylation of the reaction products with CH_3I entail the formation of both methyl formate and methyl acetate (approximately 17%):[100]



Thus the interaction of carbon dioxide with transition metal hydride complexes leads to its reduction. This reaction is apparently the key stage in the reduction of CO_2 by hydrogen to give organic compounds.

Instances of the conversion of the formate complexes into carbonyl hydride complexes are known. For example, $(Ph_3P)_3Rh(OOCH)H$ is converted into $(Ph_3P)_3Ru(CO)H_2$ on heating[95]. In the presence of silicon or aluminium hydrides and ruthenium and rhodium complexes, CO_2 is reduced in benzene to CO:[101]

$$(Ph_3P)_3\,MCl + HSi\,(OC_2H_5)_3 \xrightarrow{CO_2\,(1\,atm)} (Ph_3P)_2\,M\,(CO)\,Cl\ ;$$
$$M = Rh,\ Ru\ .$$

The yield of CO is one mole per mole of the complex. HSi. .$(C_2H_5)_3$, $H_2Si(C_3H_7)_2$, and $LiAlH_4$ can be used as the reductants. It has been suggested[8,101] that in the first stage the silane adds to the complex via the oxidative addition mechanism with formation of a metal–hydrogen bond, after which CO_2 is inserted in this bond with formation of a formate ligand, whose decomposition leads to the formation of carbonyl complexes. The interaction of CO_2 with transition metal hydrides complexes also leads to carbonyl complexes[97,102]. The ruthenium complex $(Ph_3P)_4RuH_2$ reacts with CO_2 at 130 °C and a pressure of 20 atm to form $(Ph_3P)_3Ru(CO)H_2$.[97] The reaction with $[Ph_2(CH_3)P]_4WH_4$ takes place under milder conditions. The refluxing of a solution of this complex in toluene in a CO_2 atmosphere results in the formation of $[Ph_2(CH_3)P]_3W(CO)_3$ (yield 60%).[102] The reduction of CO_2 to CO can be achieved using H_2 as the reductant,[103] i.e.

$$(Ph_3P)_3\,RhCl + CO_2 + H_2 \xrightarrow[100^\circ C]{(40\ atm)} (Ph_3P)_2\,Rh\,(CO)\,Cl + H_2O + Ph_3P\ ,$$

and hexamethylphosphoramide as the solvent. The reaction is appreciably accelerated by the addition of water. It has been suggested[103] that formic acid is formed initially and then decomposes to CO and H_2O.

The disproportionation and deoxygenation of CO_2 in the presence of titanium and zirconium complexes have been described[104]:

$$[(C_5H_5)_2\,TiCl]_2 + CO_2 \xrightarrow[90^\circ C]{10\ atm} [(C_5H_5)_2\,TiCl]_2O + CO\ ,$$
$$4\,(C_5H_5)_2\,Ti\,(CO)_2 + 4^{13}CO_2 \xrightarrow[50^\circ C]{1\ atm} [[(C_5H_5)_2\,Ti]_2\,(^{13}CO_3)]_2 + 2^{13}CO + 8CO\ ,$$
$$3\,(C_5H_5)_2\,Zr\,(CO)_2 + 3CO_2 \xrightarrow[70^\circ C]{1\ atm} [(C_5H_5)_2\,ZrO]_3 + 9CO\ .$$

The disproportionation of CO_2 in the presence of carbonylmetallate anions has been investigated[105]:

$$2Na[(C_5H_5)Fe(CO)_2] + CO_2 \rightarrow [(C_5H_5)Fe(CO)_2]_2 + Na_2CO_3 + CO .$$

The use of $^{13}CO_2$ made it possible to demonstrate that the disproportionation of CO_2 proceeds in accordance with the mechanism

$$2CO_2 + 2e \rightarrow CO_3^{2-} + CO .$$

The authors[105] suggest that two CO_2 molecules are coordinated to the initial complex $Na[(C_5H_5)Fe(CO)_2]$ in the first stage of the reaction with the subsequent formation of Na_2CO_3 and $[(C_5H_5)Fe(CO)_3]^+$; the latter reacts rapidly with the excess of $[(C_5H_5)Fe(CO)_2]^-$ anions to form a dimer.

The example of the non-catalytic reduction of CO_2 to a formate ligand or to CO presented above can be regarded as models of the individual stages of catalytic processes involving CO_2. It is noteworthy that the reduction of carbon dioxide to CO or HCOOH is thermodynamically unfavourable at low temperatures and pressures. It therefore occurs only when the product can bind strongly to the transition metal.

3. Catalytic Reduction of Carbon Dioxide

Catalytic reactions based on CO_2 constitute a field of organic chemistry which has been little studied. Several investigations have been devoted to the synthesis of alkyl formates or formamides from CO_2, H_2, an alcohol, or an amine[106,107]. It has been shown[100] that methyl formate is formed from CO_2, H_2, and CH_3OH at 60 atm and 100 °C:

$$CO_2 + H_2 + CH_3OH \rightarrow HCOOCH_3 + H_2O .$$

Since the reaction involving the formation of HCOOH from CO_2 and H_2 is thermodynamically unfavourable under mild conditions, the authors added alkylating agents (CH_3I and a solution of BF_3 in CH_3OH) to the reaction mixture in order to shift the equilibrium. $(Ph_3P)_3IrH_3$ and $(Ph_3P)_3Ru(H)Cl$ showed the highest catalytic activity. Subsequently Japanese investigators obtained alkyl formates from CO_2, H_2 and alcohols (CH_3OH, C_2H_5OH, and C_3H_7OH) at 50 atm and 140 °C in the presence of $(Ph_2PCH_2CH_2PPh_2)_2Pd$ and $(Ph_3P)_4RuH_2$ and added amines $[(C_2H_5)_3N$, etc.].[107] The yield of alkyl formate reached 50 moles per mole of the catalyst. At a pressure of the CO_2–H_2 mixture of 50 atm and at room temperature, the formation of HCOOH in an amount up to 40 moles per mole of the catalyst was observed in the presence of $(Ph_2PCH_2CH_2.PPh_2)_2Pd$ and $(C_2H_5)_3N$. The addition of water to the reaction mixture increases significantly the yield of formic acid[108]. It has been shown[109] that the carbonylmetallate anions $[HFe.(CO)_4]^-$ and $[HFe_3(CO)_{11}]^-$ also catalyse the synthesis of alkyl formates from CO_2, H_2, and an alcohol.

Secondary amines interact with CO_2 and H_2 at 50–60 atm and 100–125 °C to form dialkylformamides[9]:

$$CO_2 + H_2 + R_2NH \rightarrow HCONR_2 + H_2O .$$

The most active catalysts are $(Ph_2PCH_2CH_2PPh_2)_2Pd$, $(Ph_3P)_2.Ir(CO)Cl$, and $(Ph_3P)_3CuCl$, in the presence of which the yield reaches 800–1200 moles of dimethylformamide per mole of the catalyst.

In protic media, vanadium, titanium, molybdenum, and tungsten complexes catalyse the reduction of CO_2 by zinc and aluminium amalgams to HCOOH, HCOH, CH_3OH and in certain cases also to CH_4 at a CO_2 pressure of 1–5 atm and 20 °C;[110,111] the yields amount to several moles per mole of the catalyst.

At 150 °C and 1 atm the L_nRh_m–$AlBr_3$ system, where $L_nRh_m = Rh_4(CO)_{12}$, $[Rh(CO)_2Cl]_2$, or $(Ph_3P)_3RhCl$, catalyses the reduction of CO_2 by hydrogen to carbon monoxide[112]. The yield of CO ranged from 9 to 11 moles of CO per gramme-atom of rhodium. In addition, traces of C_1–C_3 alkanes were detected in the gas phase and the dissolution of the solid phase in THF led to solutions whose infrared spectra (absorption bands at 1981 and 2059 cm^{-1}) corresponded to the anions $[Rh(CO)_2X_2]^-$, where X = Cl or Br. In the absence of the rhodium complex or H_2, there was no reduction of CO_2. It has been suggested[112] that a hydride-containing rhodium complex with CO_2 is formed in the given instance and that $AlBr_3$ apparently activates the coordinated CO_2 molecule. The introduction of metallic aluminium into the given system has resulted in a sharp increase in the yields of hydrocarbons under the same conditions (see Table 2).[73]

An increased content of aluminium in the $Rh_4(CO)_{12}$–$AlBr_3$–Al system gives results analogous to those in the synthesis of alkanes from CO and H_2 in the presence of the same system[73]. In the range of Al : $AlBr_3$ ratios from 0 to 0.1, the content of C_1–C_4 alkanes increases and there is a sharp decrease of the CO concentrations in the products of the synthesis. In the absence of metallic aluminium, CO_2 is reduced only to CO and the yields of alkanes are low (Table 2). The introduction of aluminium accelerates the reduction of CO to alkanes[72], which leads in its turn to a decrease of the CO concentration in the products of the synthesis.

Table 2. The degrees of conversion of carbon dioxide (K_{CO_2}, mol CO_2/g-atom Rh) and the compositions of the reaction products (vol.%) in the synthesis of alkanes from CO_2 and H_2 in the presence of rhodium complexes.

L_nRh_m	K_{CO_2}	Reaction products, vol.%					
		CO	CH_4	C_2H_6	C_3H_8	iso-C_4H_{10}	n-C_4H_{10}
$Rh_4(CO)_{12}$	9	0	64	9	5	21	1
$[Rh(CO)_2Cl]_2$	8	0	68	7	4	20	1
$(Ph_3P)_2Rh(CO)Cl$	6	0	73	8	4	15	0
$(Ph_3P)_3RhCl$	6	0	73	11	4	12	0
$RhCl_3 \cdot 3H_2O$	2	14	60	9	5	12	0
$Rh_4(CO)_{12}$	8	98	1	0.5	0.5	0	0

Note: Reaction time 20 h; the remaining conditions were the same as in Table 1. The last row presents data obtained in the absence of metallic aluminium.

The catalytic properties of the L_nRh_m–$AlBr_3$–Al system are significantly influenced by the structure of the rhodium compound (Table 2).[73] The compositions of the reaction products are extremely similar for all the rhodium complexes investigated but they are different from those obtained in the presence of $RhCl_3$. Thus the presence of ligands (CO and Ph_3P) in the molecule of the initial complex results, as in the reduction of CO (Table 1), in the formation of systems exhibiting a higher catalytic activity in the reduction of CO_2 than that of the $RhCl_3$–$AlBr_3$–Al system.

The synthesis of C_1–C_2 hydrocarbons and dimethyl ether from CO_2 and H_2 at 1 atm and 300–400 °C in the presence of graphite layer compounds with a transition metal (Mo, W, Co, Ni, Pd, Pt, Fe) and an alkali metal (K, Na), has been described[113].

Methanol has been obtained from CO_2 and H_2 in the presence of $SnCl_4$ at 200 °C and a pressure of 100 atm (1 : 3 CO_2–H_2 mixture).[114] The yield of methanol was 8.2% for a degree of conversion of CO_2 of 8.8%. Together with the synthesis of methanol, the authors[114] observed the formation of small amounts of CO at 200–300 °C.

These few examples exhaust the number of catalytic reactions involving the reduction of CO_2 in the presence of transition metal complexes. In most cases the mechanisms of the reactions of CO_2 with a transition metal and of the activation of the coordinated carbon dioxide molecule have not so far been established.

The data examined permit the conclusion that the development of metal complex catalysts for the synthesis of hydrocarbons from carbon oxides and hydrogen is so far feasible on a purely laboratory scale. The systems obtained cannot serve as a basis for the creation of catalysts of practical importance. On the other hand, the mechanisms of processes involving transition metal complexes and those in the presence of heterogeneous catalysts have much in common in many instances. The study of metal complex catalysts for the reduction of carbon oxides can therefore prove useful both for the development of new industrial catalysts for the synthesis of hydrocarbons from mixtures of carbon oxides and hydrogen and for the improvement of the existing ones.

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