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Carbon dioxide in coordination chemistry and catalysis

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ABSTRACT. **All aspects of the fixation of carbon dioxide in the presence of catalytic systems based on transition metals have been reviewed. The results of calculations to determine the nature of the complexes of the CO_2 molecule with transition metal atoms and complexes have been described. The progress made in new fields such as the electrocatalytic, photoelectrocatalytic, photocatalytic, and radiation-catalytic fixation of carbon dioxide has been examined.**

The bibliography contains 252 references.

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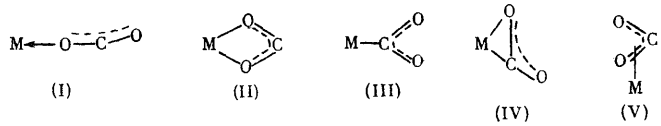
I. Introduction

The problem of the utilisation of carbon dioxide, that is its use as a source of carbon for organic synthesis, is extremely important.[1–8] The solution of this problem is closely related to the solution of the fuel problem (the use of CO_2 to prepare hydrocarbons, methanol, and other compounds), and also to the production of synthetic food. Here it should be borne in mind that carbon dioxide, which is a waste product from various industries, can provide a practically unlimited source of carbon. The fixation of carbon dioxide is of practical interest in connection with the development of waste-free technology and the accumulation of CO_2 in isolated systems such as submarines, spacecraft, etc. The utilisation of carbon dioxide is also of considerable importance for understanding the nature of photosynthetic and chemical synthetic processes. The most important stage in the transformation of carbon dioxide in catalytic processes is the activation of the CO_2 molecule, brought about by its coordination to transition metal compounds acting as catalysts. The most promising method of utilising carbon dioxide involves the use of systems in which the CO_2 molecule can be activated by the combined use of physical (radiation of different kinds, electrolytic reduction, etc.) and catalytic (catalysis by transition metal compounds with cocatalysts of different types) methods. Of particular interest is the fixation of carbon dioxide in aqueous solutions, when water acts as a source of hydrogen; this is related to problems of bioinorganic chemistry.

About 20 years have passed since the publication of the first papers on the preparation of stable complexes of transition metals with carbon dioxide, which have led to the achievements associated with the introduction of this molecule into catalytic processes. In this time, considerable progress has been made in the development of catalytic systems for obtaining organic compounds using carbon dioxide as the source of carbon, and this work has been fairly fully reviewed.[1–8] The present review differs from earlier reviews in its complete coverage of all aspects of CO_2 fixation.

II. Estimation of the stability of the complexes of transition metals with carbon dioxide

As noted in early reviews,[1,2] the coordination of a CO_2 molecule to a transition metal atom (M) can give not only M–O bonds but also M–C bonds. The preparation and determination of the structure of stable complexes of transition metals with CO_2 stimulated the development of methods for calculating the coordination of the CO_2 molecule to metals. In principle, when one CO_2 molecule is coordinated to a metal atom, the following structures may be produced:



(I) (II) (III) (IV) (V)

A virial-statistical method has been used to calculate the stability of structures (I)–(V) for the adducts $M.CO_2$, where M = Cu, Hg, and Tl.[9–14] Adducts of this type have been observed (as ions) in mass-spectrometric studies of the corresponding carboxylates (see the references in the paper by Nekrasov and co-workers[13]). According to the data obtained by mass-spectrometry and calculation, the thallium adducts are the most stable. In the series of structures (I)–(IV), the most stable for all the metals was found to be structure (IV), in which the CO_2 molecule is coordinated through oxygen and carbon atoms simultaneously;[12] the stability of the structures decreases in the order (IV) $\geqslant$ (III) $\gg$ (I) > (II) for copper and (IV) > (III) $\gg$ (I) > (II) for thallium. The results of calculations on these structures made it possible to put forward a mechanism for the fragmentation of copper and thallium carboxylates in the gas phase under the influence of electron impact; the mechanism suggests that the rupture of the C–C bond of the carboxylate gives adducts $M.CO_2$ in which the CO_2 molecule is coordinated to the metal with the formation of a metal–carbon bond.[5,10–12] According to later calculations, the formation of structure (V) is not excluded.[14] In this case, however, difficulties arise, associated with the destabilisation of the adduct as a result of the repulsion of the lone pairs of electrons of the oxygen atoms with the bending of the CO_2 molecule.

It was found by the CNDO-2 method that the stability of the copper adducts $M.CO_2$ decreases in the order (II), (IV) ≫ (III) ≫ (I).[15,16] In the opinion of the authors cited,[15,16] the coordination of a CO_2 molecule to give structure (IV) is favourable because the formation of an M—C bond leads to an increase in the strength of the M—O bond, and vice versa. In the case of titanium (in contrast to copper), the highest stability is shown by the adduct with structure (III), due, in the opinion of the authors cited,[16] to the increase in the separation between the donor levels of the atom of this metal and the unoccupied $2\pi_u$-orbital of the CO_2 molecule on formation of the complex. When there is a high charge on the metal, structure (IV) becomes unfavourable, and coordination of type (I), when the electron density is displaced from the $1\pi_g$-level to an unoccupied *d*-orbital of the metal, is preferred.

The *ab initio* method has been used to determine the nature of the coordination of CO_2 to the metal in the hypothetical complexes $(H_3P)_2Ni(CO_2)$ and $(H_3P)_2Cu(CO_2)^+$.[17] According to the data obtained by the authors cited,[17] who examined only structures of types (I) and (IV), the positively charged copper atom forms structure (I) preferentially, whereas for zerovalent nickel, the formation of structure (IV) is more probable. It is suggested that the coordination of carbon dioxide to nickel to give structure (IV) is brought about by the reverse displacement of electron density from the metal to the ligand, whereas the fact that structure (I) is preferred for copper(I) is due to the strong electrostatic interaction of the metal with the negatively charged oxygen atom. The authors cited do not exclude the possible formation of structure (III) for nickel, if for some reason (the non-availability of a coordination position, etc.) structure (IV) cannot be produced.

Calculation of the stability of the hypothetical complexes $(H_3P)_2Ni(CO_2)$ and $(H_3P)_2Cu(CO_2)^+$ by the extended Hückel method confirmed that structure (IV) is fairly stable for nickel, although its energy advantage over structure (I) is small.[18] The CNDO method was previously used to calculate the stability of the complex $(H_3P)_2Pt(CO_2)$, for which the coordination of CO_2 to the metal to give structure (IV) was found to be most favourable.[19]

The results of a calculation by the CNINDO method indicate that the adduct $Ag.CO_2$, obtained by the co-condensation of the products of the reaction of silver atoms with carbon dioxide, is stable in form (IV).[20] According to data obtained by various authers,[17—20] the CO_2 molecule coordinated to the metal is bent (problems related to the bending of CO_2 on excitation have been examined[1,2]).

Overall, the results of calculations of the stability of the complexes of transition metals with carbon dioxide by different methods indicate that the CO_2 molecule tends to coordinate to a metal atom through oxygen and carbon atoms simultaneously. Coordination to give structure (I) is most probable, however, for a positively charged metal, when the formation of the complex is essentially the result of the first stage of the reaction of the metal of the complex, acting as a Lewis acid, with carbon dioxide. Thus according to a calculation of the stability of the adducts of Zn^{2+} with carbon dioxide, the preferred structure is structure (I) with an equilibrium M—O distance of 1.85 Å.[21] According to calculations and spectral data, the adducts of CO_2 with the alkali metals have structures (I) (C_s) or (II) (C_{2v}) [22,23] (see also the next section).

Structure (I) tends to undergo conversion into structures (III) and (IV) containing an M—C bond, whose formation in existing complexes has been confirmed by X-ray diffraction (see next section). This tendency in turn is the result of the transition from the primary act of activation of the CO_2 molecule in its reaction with the metal atom to give structure (I) to the formation of more stable adducts in which CO_2 is coordinated to the metal not only through an oxygen atom but also through the carbon atom [structures (III) and (IV)].

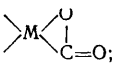
III. Complexes of transition metals with carbon dioxide

1. Stable complexes

Since carbon dioxide is a better acceptor than donor of electron density, it has been suggested that for this molecule, the formation of coordination compounds with the complexes of metals in a low oxidation stable is most characteristic.[2—4] In fact, compounds of this type have now been obtained by the direct action of carbon dioxide on complexes of metals with a low oxidation number, M^0 (Ni, Pt, Rh) or M^+ (Cu, Ag, Rh, Ir). Stable complexes have also been obtained by indirect methods.

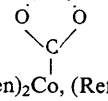
a. Direct method

The direct preparation of complexes of transition metals with CO_2 is of fundamental importance, since it is by this means that the CO_2 molecule can be introduced into catalytic processes. The first stable complex of CO_2 with rhodium(I) was obtained in 1969.[24] Since then, new complexes of various metals have been synthesised, fundamental problems associated with the use of CO_2 as a source of carbon for obtaining organic compounds have been solved, and the principal directions of study in the field of CO_2 fixation have been clearly defined. The number of complexes obtained by the direct method is small, since various side reactions take place. The difficulties associated with the preparation and identification of complexes of metals with CO_2 have been reviewed.[25] X-Ray diffraction has shown that a CO_2 molecule coordinated to a transition metal atom forms an M—C bond:

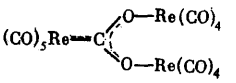


The following complexes have been obtained by the direct method:

$[(C_6H_{11})_3P]_2NiCO_2$ (Ref.26); $(\eta\text{-}C_5H_4Me)_2Nb(CH_2SiMe_3)(\eta^2\text{-}CO_2)$ (Ref.27);

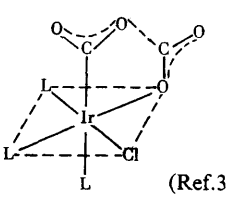


(n-Pr-Salen)$_2$Co, (Ref.28) where Salen = salicylidene-ethylenediamine;



(Ref.29)

$[HOs_3(CO)_{10}CO_2Os_6(CO)_{17}]^-$ (Ref.30);



L = PMe_3

(Ref.31).

A recently prepared complex of rhodium with carbon dioxide is $(diars)_2Rh(\eta^1\text{-}CO_2)Cl$, where diars = $Me_2AsCH_2CH_2AsMe_2$, in which, as shown by X-ray diffraction, the CO_2 molecule is

coordinated to the metal atom only through an oxygen atom, that is to give structure (I) (see previous section).[7] Since X-ray diffraction data are not available, it is impossible to reach an unambiguous conclusion about the mode of coordination of CO_2 in the complex $(dppe)_2RhCl.CO_2$, where dppe = $Ph_2PCH_2CH_2PPh_2$.[32] In the opinion of Areste and Nobile,[33] the action of the phosphines $EtPPh_2$ and $n\text{-}Bu_3P$ on the complex $[Rh(C_2H_4)_2Cl]_2$ and CO_2 gives adducts of two types: $L_3RhCl.CO_2$ and $L_2RhCl.CO_2$. The formation of these adducts was confirmed only by infrared spectroscopy.

According to the same authors,[34] for the nickel complexes $L_2Ni.CO_2$, where L = Et_3P and $n\text{-}Bu_3P$, the bands in the infrared spectrum corresponding to the antisymmetric and symmetric stretches and deformations of the coordinated CO_2 molecule are displaced from 1740 (br., s), 1150 (v.s), 1094 (v.s), 845 (s), and 730 (med) [for $(C_6H_{11})_3P$] to 1660, 1203, 1009, 823, and 750 (for Et_3P) and 1660, 1003, 825, and 750 (for $n\text{-}Bu_3P$).

The reaction of carbon dioxide with the anionic complexes $[(Salen)_2Co]^-$ gives adducts of cobalt with CO_2.[28] From X-ray diffraction data it was concluded that these compounds are complexes of carbon dioxide with cobalt, and that the K^+ cation brings about additional specific coordination of the CO_2 molecule as a result of its reaction with two oxygen atoms of carbon dioxide. Without X-ray diffraction data it is difficult to determine whether the products of the reaction of CO_2 with $NaRe(CO)_5$ or $CpFe(CO)_2MgBr$ are complexes of the metals with carbon dioxide or salts of the metal-carboxylic acids.[34–36] For example, the insertion product obtained by the reaction of CO_2 with $CpFe(CO)_2MgBr$ (an organometallic analogue of the Grignard reagent) is readily alkylated by methyl iodide to give the ester of the iron-carboxylic acid:[35]

$$CpFe(CO)_2MgBr + CO_2 \rightarrow \{CpFe(CO)_2(CO_2MgBr)\} \xrightarrow{MeI} \longrightarrow CpFe(CO)_2CO_2Me.$$

The problems associated with complex formation of this type have been examined in detail[36] (see also the next section). At the present time, because of the lack of X-ray diffraction data, it is difficult to determine the nature of the coordination of the CO_2 molecule in these compounds. Moreover, although in the complexes $[(Salen)_2Co]K$ the insertion of CO_2 is reversible,[28] the insertion of CO_2 into the rhenium and iron complexes[35,36] is irreversible.

The reaction of carbon dioxide with the complex $(dmpe)_2IrCl$, where dmpe = $Me_2PCH_2CH_2PMe_2$, gives the adduct $(dmpe)_2IrCl.CO_2$, which on heating is readily converted into a carboxylate complex of iridium:[37]

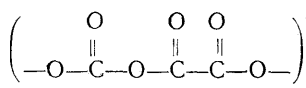
$$(dmpe)_2IrCl \cdot CO_2 \rightleftarrows Me_2PCH_2CH_2P(Me)CH_2CO_2(dmpe)IrCl.$$

If the ligand is not dmpe but diars (diars = $Me_2AsCH_2CH_2.AsMe_2$), the only product is $(diars)_2IrCl.CO_2$, whose infrared spectrum contains bands at 1550 cm^{-1} and 1220 cm^{-1}. The reaction of CO_2 with $(Me_3P)_3IrCl$, however, gives a complex containing two carbon dioxide molecules per metallic centre;[31] one CO_2 molecule is coordinated to the metal through an oxygen atom [structure (I)], and the other through the carbon atom [structure (III)], and the two CO_2 molecules are joined to one another by a C–O bond. It has also been suggested[38] that in the unstable adduct of molybdenum with carbon dioxide $(Me_3P)_3Mo.(CO_2)_2$, the two CO_2 molecules form a similar ring (the infrared spectrum of the adduct of iridium with two CO_2 molecules contains bands at 1725, 1680, 1648, 1605, 1280, 1008, and 790 cm^{-1}). The molybdenum complex readily disproportionates according to the scheme

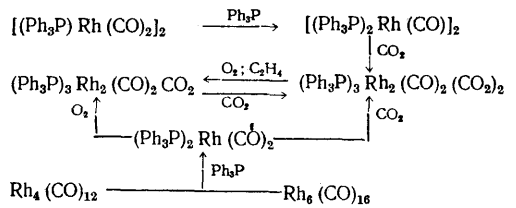
$$2(Me_3P)_3Mo(CO_2)_2 \rightarrow [(Me_3P)_3Mo(CO_3)(CO)]_2,$$

(see also the next section).

The reaction of CO_2 ligands at a metallic centre is an important process for the activation of this molecule, and it determines to a large extent the nature of the final products. The study of the nature of the coordination of several molecules at a metallic centre is of considerable interest for an understanding of the processes involved in the chemisorption of carbon dioxide on the surface of heterogeneous catalysts or on the electrode surface in the electrocatalytic reduction of CO_2. An interesting result is the preparation of an adduct containing three CO_2 molecules per metallic centre, $Mg(CO_2)_3^{2-}$.[39] The adduct was obtained in an inert-gas matrix by the co-condensation of Mg vapour with carbon dioxide. Analysis of the chemical reactions and the infrared spectroscopic data indicates that oxalate and carbonate units are combined in its structure:



The synthesis of the paramagnetic rhodium complex $(Ph_3P)_3Rh_2.(CO)_2(CO_2)_2.C_6H_6$ has been described.[40,41] This complex can be obtained by different methods:



b. Indirect methods

The first complex of a transition metal with CO_2 to be obtained by an indirect method was $(Ph_3P)_3Rh_2(CO)_2.CO_2.C_6H_6$.[42] It was obtained by oxidising a carbonyl group on the metal with oxygen. Reactions of this type have been reviewed.[8] The same complex was synthesised by another method, via an unstable rhodium-carboxylic acid:[41]

$$L_2Rh(CO)OH + CO \rightarrow L_2Rh(CO)CO_2H,$$

$$L_2Rh(CO)CO_2H + L_2Rh(CO)OH \rightarrow L_3Rh_2(CO)_2CO_2 + H_2O + L,$$

$$L = Ph_3P.$$

This complex can be regarded as the rhodium salt of a rhodium-carboxylic acid. The role of metal-carboxylic acids in the preparation of complexes with CO_2 by this method has been examined.[36] In particular, the reaction of a platinum-carboxylic acid with a phosphine complex of zerovalent platinum gives polynuclear complexes with carbon dioxide:[43]

$$2L_2Pt(Cl)CO_2H + L_3Pt \rightarrow [L_2Pt(Cl)CO_2]_2PtL_2 + 2H^+ + L,$$

$$L = Ph_3P.$$

The polynuclear complexes of rhenium[29] and osmium[30] are also probably formed via metal-carboxylic acids. Thus the rhenium complex is formed via the intermediate $(CO)_5ReOH$, which may be present in equilibrium with $(CO)_4ReCO_2H$. In connection with the

preparation of complexes of metals with carbon dioxide via metal-carboxylic acids, mention may be made of the formation of an ester of an iridium-carboxylic acid from a complex with CO_2:[44]

$$dmpe_2\,IrCl\cdot CO_2 + MeSO_3F \rightarrow [dmpe_2Ir(Cl)\,CO_2Me]^+\,SO_3F^-.$$

The existence of the stable rhenium-, iron-, and iridium-carboxylic acids described in the literature extends considerably the possibilities for obtaining transition metal complexes.[36] The use of metal-carboxylic acids is also important because it gives complexes with carbon dioxide in which the M–C bond is fixed on a definite metal.

2. Unstable complexes

The formation of unstable adducts of carbon dioxide with transition metals takes place in the solid, liquid, and gas phases. Thus the co-condensation of silver atoms with CO_2 in a matrix gives the adduct $Ag.CO_2$.[20] From the similarity in the infrared and ultraviolet spectra of this adduct and the corresponding spectra of the complex of nickel with CO_2, whose structure has been determined,[26] it was concluded that the CO_2 molecule is π-coordinated to Ag. Adducts of CO_2 with other metals have been obtained in matrices.[45] It has been suggested that the formation of CO_3 by the ultraviolet irradiation of mercury in a carbon dioxide atmosphere involves the intermediate $Hg.CO_2$.[2] The formation of the adduct $Tl.CO_2$ in the solid phase during the thermal decomposition of thallium(I) carboxylates has been reported.[46]

The formation of unstable adducts $M.CO_2$ in solution has been examined.[1,2] In the formation of the complexes of carbon dioxide with hydride complexes of cobalt and iron, the initial stage of the reaction is the insertion of CO_2 at an M–H bond.[47,48] The existence of the equilibrium

$$(Ph_3P)_3\,Ru\,(H)\,O_2\,CH \rightleftarrows (Ph_3P)_3\,Ru\,(CO_2)\,H_2,$$

and the formation of an intermediate adduct of ruthenium with CO_2 were discussed in a study of the kinetics of the reduction of alkenes by formic acid in the presence of phosphine complexes of ruthenium.[1,8,49] ^1H NMR has been used to study the transformation of ruthenium formates into a complex of ruthenium with carbon dioxide in solution.[50,51] The formation of unstable complexes with CO_2 may take place in the decarboxylation of the fragment $[Ir]O_2CR$,[37] and also copper carboxylates.[52,53] Carbonate and hydrogen carbonate complexes are also formed via unstable intermediates formed by the metals with CO_2 (see next section). The formation of an adduct of cobalt with CO_2 has been noted in the electrolytic reduction of Co^{3+} complexes.[36]

Adducts with CO_2 are formed in the reaction of N-bases with metal-carboxylic acids:[36]

$$[M]\,CO_2H + R_3N \rightleftarrows [M]\,CO_2^- + R_3NH^+.$$

The study of the behaviour of transition metal formates and metal-carboxylic acids in solution is extremely important for an understanding of the mechanism of the preparation of "synthetic gas":[7,36]

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

Different groups of workers have observed the formation of the following unstable adducts of metals with CO_2 in the gas phase (mass-spectrometric data): $Cu(CO_2)^+$,[54–57] $Cu_2O(CO_2)^+$,[55] $Cu(CO_2)_2^+$,[56] $Cu(O_2CR)(CO_2)^-$,[55] $Cu_2(CO_2)(O_2CR)^+$,[55] $Cu_4(CO_2).(CO)^+$, $Cu_4(CO_2)_2(CO)_2^+$,[55] $Cu_4O_2(CO_2)_2^+$,[55] $Re(CO_2)^+$,[58] $(CO)_5Re(CO_2)Re(CO)_4^+$,[29] and $Tl(CO_2)^+$.[11–14,59,60]

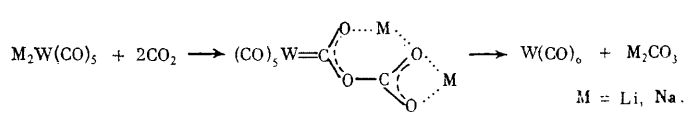
A noteworthy feature is the selective formation of the adduct $Tl.CO_2^+$ from Tl^I carboxylates, which opens up the possibility of studying the mode of coordination of the CO_2 molecule to the metal in the gas phase and its behaviour in chemical reactions.[11–14] The reaction of nickel vapour with CO_2 gives Ni(CO).[61]

3. The formation of carbonate and hydrogen carbonate complexes in the reaction of CO_2 with transition metal compounds

The formation of carbonate and hydrogen carbonate complexes by the reaction of carbon dioxide with transition metal compounds is a side reaction in the preparation of complexes with CO_2, and in most cases takes place under mild conditions.[1,2,26] The formation of the carbonate ion and carbon monoxide can be represented as the result of the reaction of two radical-anions $CO_2^{\cdot-}$ at a metallic centre:[2]

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

Thus the final product of the reaction of $(Me_3P)_4Fe$ with CO_2 is $(Me_3P)_3Fe(CO_3)(CO)$.[62] According to the data obtained,[62] this reaction involves the formation of an intermediate unstable adduct of iron with carbon dioxide. The formation of molybdenum carbonate from an adduct containing two CO_2 molecules per metallic centre was noted in section 1. Carbonates are readily formed by the reaction of CO_2 with hydride complexes of ruthenium, cobalt,[1,26] and rhodium,[26,63] and with alkyl derivatives of cobalt and palladium.[26] In the reaction of CO_2 with anionic complexes of transition metals under mild conditions, disproportionation of carbon dioxide to CO_3^{2-} and CO takes place.[26,64–70] Na_2CO_3 and CO were identified in the reaction of CO_2 with $CpFe(CO)_2Na$.[64] The rate of the reaction of carbon dioxide with anionic complexes of iron, nickel, tungsten, and manganese changes in the same sense as the relative nucleophilic character of the metals. The reaction of CO_2 with the complexes formed by the action of organic derivatives of Li, Mg, and Al on the hydrides $CpMH_2$, where M = Mo or W, has been studied.[65–67] The formation of the carbonate ion and CO involves the insertion of CO_2 at the M–Li, M–Mg, or M–Al bonds respectively. It has been suggested that in the reaction of the tungsten dianion with CO_2, an adduct with two CO_2 molecules is formed as an intermediate:[70]



The unstable adduct $[Ir]CO_2[Al]$ is probably liberated in the hydrolysis of an ester of an iridium-carboxylic acid in the presence of $AlCl_3$.[71]

The CO_2 molecule, which is a heterocumulene, contains nucleophilic and electrophilic centres, so that it can be activated extremely effectively by coordination to metals with different electron-donor and electron-acceptor properties (bifunctional catalysis). Catalysis of this type reveals most clearly the role of the catalytic centre containing the transition metal, to which carbon dioxide is able to coordinate to give an M–C bond, and also the role of metals of groups I–III, capable of forming M–O bonds (see next section).

IV. The insertion of carbon dioxide at an M–X bond

1. The insertion of carbon dioxide at an M–H bond

The problems associated with the insertion of a CO_2 molecule at an M–H bond have been reviewed in detail.[1,7,47,48] The insertion can take place in two ways:[1,7]

$$[M]-H + CO_2 \begin{cases} \longrightarrow [M]O_2CH \\ \longrightarrow [M]CO_2H \end{cases}.$$

The insertion products may be formed at an intermediate stage in the reduction of carbon dioxide to HCO_2H, etc. For example, the reaction of carbon dioxide with $(Ph_3P)_2Cu.BH_4$ [72] or with $(dppe)ReH_3$ [73] gives $L_2Cu(\eta^2\text{-}O_2CH)$ and $(dppe)ReO_2CH$ respectively. The reaction of the cluster $(Ph_3PCuH)_6$ with CO_2 has been studied.[74] The main product is formate, but the authors cited suggest that an unstable copper-carboxylic acid is formed in one of the stages. Carbon dioxide can be selectively reduced to MeO^- by treatment with the hydride complex of zirconium $Cp_2Zr(H)Cl$.[75] In the $TiCl_4-Mg-CO_2-THF$ system, the formate complex $Ti(O_2CH)_2.MgCl_{1.5}.THF$ is formed.[76] The source of hydrogen (moisture or the solvent) is not indicated, but it is stated that in the reaction of $TiCl_4$ with Mg in THF it is possible to isolate a complex which gives titanium formate when treated with CO_2:

$$2TiCl_4.2THF + 6Mg + 2THF \xrightarrow{Ar} (TiMg_2Cl_2.THF)_2 + 2MgCl_2.THF \xrightarrow{CO_2} \rightarrow Ti(O_2CH)_2MgCl_{1.5}.THF.$$

The presence of traces of moisture in the solvent or the addition of water may have a significant influence on the nature of the catalytic processes involving carbon dioxide.[1,7,8] Thus the reduction of CO_2 by molecular hydrogen in $C_6H_6-H_2O$ solution in the presence of basic additives and phosphine complexes of palladium, rhodium, ruthenium, and iridium gives formic acid.[77] A significant feature is that when these systems contain hydrogen carbonate, HCO_2H is also formed in the absence of CO_2. In this connection it should be noted that transition metal compounds are able to activate water with the formation of hydride complexes. In the presence of phosphine complexes of palladium and copper as catalysts, and of alcohols and amines as additives, methane is formed in addition to derivatives of formic and oxalic acids.[78] The formation of CH_4 from CO_2 and H_2 has also been observed in the presence of ruthenium compounds deposited on an Al_2O_3 surface.[79]

A phosphine complex of ruthenium or its hydride cluster have been used for the hydrosilylation of carbon dioxide.[80,81] This reaction takes place with the intermediate formation of ruthenium formates.

2. The insertion of carbon dioxide at an M–C bond

The solution of the fundamental problems associated with the insertion of CO_2 at a transition metal–carbon bond[1] stimulated the appearance of a large number of publications on this topic. From the wide range of studies it is necessary to distinguish those involving the investigation of the mechanism of the reactions leading to the formation of the M–C bond and the preparation of organic products by the carboxylation of intermediates produced, for example, by the oligomerisation or polymerisation of unsaturated compounds in the presence of catalysts. Of particular importance is the formation of organic products as a result of the carboxylation, by carbon dioxide, of organometallic compounds produced by the activation of C–H bonds by transition metal complexes. Thus acetonitrile, acrylonitrile, and phenylacetylene are carboxylated in the presence of phosphine complexes of rhodium and iridium ML_4^+, where L = a trialkyl- or triarylphosphine:[82]

$$L_4M^+ + RH \rightleftarrows L_4M(R)H \underset{-CO_2}{\overset{+CO_2}{\rightleftharpoons}} L_4M(O_2CR)(H).$$

It has also been shown that it is possible in principle to carry out the carboxylation of cyclohexene in the presence of H_2 and of amines to the corresponding acid amides on complexes of iridium, rhodium, platinum , and palladium.[83]

Since the insertion of CO_2 at an M–C bond has been fairly fully reviewed,[1,3,5,7] only the principal results obtained in the last ten years will be presented here.

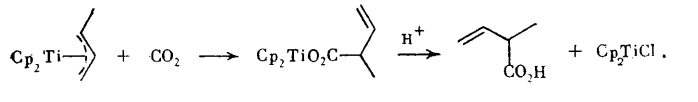
Elements of group I (copper, silver). The insertion of CO_2 at an M–C bond in the copper complex $(Ph_3P)_2CuMe$ and the organometallic derivatives of silver RAg, where R = n-tolyl, etc., gives in the first case the compound $(Ph_3P)_2CuO_2CMe.CO_2$, and in the second case the silver complexes $RAgCO_2Ag$, which can be regarded as the silver salts of silver-carboxylic acids.[1] The reversible insertion of CO_2 at a Cu–C bond has been studied in detail (see the review of Kolomnikov and Grigoryan[1] and section III.2 of the present review).

The reaction of carbon dioxide with the compounds RM, where R = fluorenyl or phenylacetylenyl, and M = Cu or Ag, in the presence of different ligands (BuNC, R_3P, Py, etc.) in a number of cases gives the corresponding acids, identified as the esters.[84] Carbon dioxide can be inserted at the M–C bond in the compound $(CF_3)_2CFAg$, to give the corresponding carboxylate.[92] It has been reported that CO_2 is not inserted at the M–C bond in the complex Ph_3PAuMe, even under severe conditions.[1]

Elements of group II (zinc). The insertion of carbon dioxide at the zinc–carbon bond in the compounds ZnR_2, where R = Alk, has been reported in connection with the use of organometallic compounds of zinc as catalysts of the co-condensation of oxiranes with CO_2.[1,85]

Elements of group IV (titanium, zirconium). The titanium and zirconium compounds R_4M, where R = CH_2Ph, react readily with carbon dioxide to form unstable carboxylates.[1] The reaction of CO_2 with diphenyltitanocene to give the cyclic carboxylate $Cp_2TiO_2CC_6H_4$ has been studied in detail.[1] The mechanism of the thermal decomposition of the compounds Cp_2TiR_2, where R = *m*- or *p*-tolyl, in a carbon dioxide atmosphere has been studied.[86] The detection, among the products of this reaction, of the cyclic titanium carboxylates $Cp_2TiO_2C[m(p)\text{-}C_6H_4Me]$, similar to that noted above, made it possible to determine the nature of the reaction taking place and to establish fairly reliably the appearance of a dehydrobenzene intermediate of titanium in this reaction.

The reaction of carbon dioxide with the organometallic compounds of titanium(III) Cp_2TiR, where R = allyl or methallyl, has been studied.[87–90] The insertion of CO_2 at the M–C bond gives the corresponding carboxylates Cp_2TiO_2CR. In the case of the alkylallyl ligand, asymmetric insertion takes place:[90]

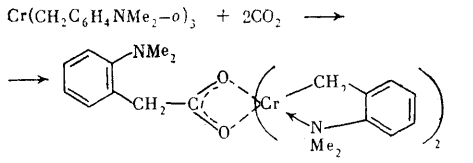


The zirconium compounds $Cp_2Zr(R)Cl$, where R = Me or C_6H_{11}, do not react with carbon dioxide.[83] The reaction of Ph_2ZrEt_2O with CO_2, however, readily gives a zirconium carboxylate.

Elements of group V (vanadium). The reaction of the vanadium(III) compounds R_3V, where R = C_6H_5 or CH_2SiMe_3, with CO_2 gives vanadium(II) carboxylates:[91]

$$2R_3V.THF + CO_2 \rightarrow V(O_2CR)_2 + R_4V.THF.$$

Elements of group VI (chromium, molybdenum, tungsten). Carbon dioxide is not inserted at an M–C bond of the complex $(PhCH_2)_3Cr.H_2O$,[1] but this reaction can take place with the complex $Cr(CH_2C_6H_4NMe_2\text{-}o)_3$:[92]



The reaction of CO_2 with $MeCr(CO)_5^-$ anions has been reported.[7,93] The rate of formation of the carboxylates $MeCO_2Cr(CO)_5^-$ increases considerably when alkali metal salts are added. A similar reaction takes place with $MeW(CO)_5^-$.[94]

Carboxylates are also formed in the reaction of carbon dioxide with bis(ethylene)-complexes of molybdenum and tungsten:[95]

$$trans\text{-}[M(C_2H_4)_2(PMe_3)_4] \xrightarrow{CO_2} \tfrac{1}{2}[M(H_2CCHCO_2H)(C_2H_4)(PMe_3)_2]_2.$$

The reaction of $CpW(CO)_3Me$ with carbon dioxide gives the corresponding carboxylate.[96] The rate of this reaction is increased when Lewis acids are added.

The addition of transition metal salts to the $C_6H_6-AlX_3-CO_2$ system increases the yield of benzoic acid.[97] The highest yield was observed when $MoCl_5$ was added, and this may be due to the formation of an intermediate containing an Mo–C bond.

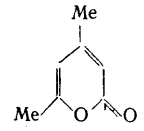
Elements of group VII (manganese). Carbon dioxide reacts readily with $(PhCH_2)_2Mn$ to give an unstable carboxylate.[98]

Elements of group VIII. The reversible insertion of CO_2 at the Fe–C bond formed by the rupture of the P–C bond in the complex $(Me_3P)_4Fe$ has been noted.[62] The intermediate formed in the reaction of a phosphine complex of iron with acetonitrile reacts with CO_2 to give cyanoacetic acid:[99]

$$(dmpe)_2Fe(H)(CH_2CN) \xrightarrow{CO_2;\ H^+} NCCH_2CO_2H.$$

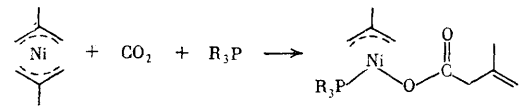
For organometallic derivatives of cobalt it has been shown that, in addition to the usual insertion of carbon dioxide at a Co–C bond to give a carboxylate, "anomalous" insertion to give the ester of a cobalt-carboxylic acid is possible.[1,7] Carbon dioxide can be inserted at the Co–Me bond of a complex of cobalt with salicylidene-ethylenediamine.[1] This reaction is promoted by the addition of dithiols, and does not take place in their absence.

The reaction of carbon dioxide with the rhodium complexes $(Ph_3P)_3RhR$, where R = Me or Ph, gives the carboxylates $(Ph_3P)_3RhO_2CR$.[1] In the oligomerisation of methylacetylene in the presence of *cis*-$(dppe)Rh(CO)_2^+$, 4,6-dimethyl-2-pyrone is formed as the product of the oligomerisation of the alkene and the insertion of CO_2 at a rhodium–carbon bond:[100]

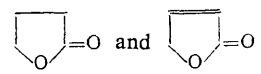


The CO_2 molecule undergoes reversible insertion at an Ir–C bond with the rupture of a P–C bond formed by the phosphine ligand in the complex $(dmpe)_2IrCl$.[37] The insertion of CO_2 at Ir–C and Rh–C bonds has been discussed.[82]

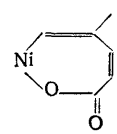
Carbon dioxide is readily inserted at an Ni–C bond in its reaction with bis(methylallyl)nickel in the presence of phosphines:[101]



The author cited also described the formation of cyclic derivatives of nickel as the products of the cyclodimerisation of butadiene on a nickel complex and the insertion of CO_2 at an Ni–C bond. The reaction of CO_2 with bis(allyl)nickel in dimethylformamide gives lactones:[102]

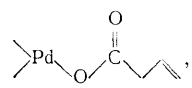


The reactions of carbon dioxide with intermediates formed in the oligomerisation of hex-1-yne and but-2-yne in the presence of phosphine complexes of zerovalent nickel have been studied.[103,104] The final products are substituted pyrones,[103] and a complex of the following type[104]

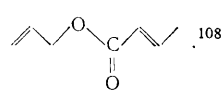


is formed in the reaction. The insertion of a CO_2 molecule at an Ni–C bond has also been described by Yamamoto and Yamamoto.[105]

A wide range of reactions involving the insertion of CO_2 at a Pd–C bond are now known. The telomerisation of butadiene in a CO_2 atmosphere readily gives lactones and octadienyl esters.[106,107] An interesting feature is that the rate of the dimerisation of butadiene and isoprene is increased in the presence of carbon dioxide. The action of carbon dioxide on bis(η^1,η^3-allyl)Pd.R_3P gives the fragment



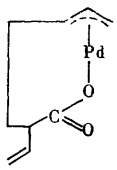
which subsequently reacts with carbon monoxide to give



[108]

The similar insertion of CO_2 at a Pd–C(η-allyl) bond has been reported.[109] In the carboxylation of bis(η^3-butenyl)palladium, but-1-ene-3-carboxylic acid is formed selectively after acidification.[110]

This reaction takes place with the formation of the intermediate



In a CO_2 atmosphere in the presence of the catalytic system bis(allyl)Pd$-PR_3$, allene undergoes copolymerisation to give a mixture of esters and lactones.[111] The corresponding lactone is formed smoothly from methylcyclopropane and CO_2 in the presence of $(dppe)_2Pd$.[112] The reversible insertion of carbon dioxide at a Pd$-$C bond to give cyclic adducts has been observed.[113]

Finally, carbon dioxide can also be inserted at an M$-$C bond in reactions involving lanthanides and actinides.[114,115]

3. The insertion of carbon dioxide at M$-$O and M$-$N bonds

The insertion of CO_2 at an M$-$OH bond can give a stable hydrogen carbonate complex or an unstable adduct with carbon dioxide:[1,2]

$$[M]{-}OH + CO_2 \rightleftarrows [M](CO_2)OH \rightarrow [M]O_2COH.$$

In the absence of X-ray diffraction data, the determination of the nature of the complexes formed is extremely difficult.[25] The ease of formation of hydroxo-complexes of transition metals in catalytic systems in the presence of traces of water makes it possible to regard this reaction in the case of reversible addition as a stage in the activation of the CO_2 molecule.

Copper(I) alkoxides readily undergo the following reversible reaction:[25]

$$CuOR + CO_2 \rightleftarrows CuO_2COR.$$

Zinc-containing complexes and enzymes such as carbanhydrase, containing a Zn$-$OH bond, can catalyse the reaction of CO_2 and H_2O to give carbonic acid.[1] The ready formation of hydrogen carbonates and alkyl carbonates has also been observed in reactions involving hydroxo-complexes and alkoxides of ruthenium, rhodium, iridium, palladium, etc.[25]

The insertion of CO_2 at an M$-$N bond is similar to its insertion at an M$-$O bond. The addition of carbon dioxide again may be reversible, or may give stable carbamates. The structure of various carbamates obtained in this way has been established by X-ray diffraction.[2] The insertion of a CO_2 molecule at an M$-$N bond has been studied in detail (see for example the papers of Chisholm and co-workers,[116,117] and references therein). The formation of carbamates by the insertion of CO_2 at an M$-$N bond has been observed for compounds of titanium,[118] tungsten,[2,119] and uranium.[120]

The insertion of CO_2 at a Cu$-$N bond is reversible.[121] EPR has shown unambiguously that the reaction of copper(II) ephedrinate with carbon dioxide gives an unstable carbamate,[122,123] and not a complex of copper with CO_2, as suggested in early studies.

Finally, it may be noted that the insertion of CO_2 at M$-$O and M$-$N bonds, like its insertion at an M$-$C bond, provides a new method for obtaining the hydrogen carbonates, carbamates, and carboxylates of transition metals, lanthanides, and actinides. It is well known that the addition of amines to catalytic systems facilitates the insertion of carbon dioxide at an M$-$C bond, that is the activation of the latter.[1] It is also possible that carbon dioxide is activated in these systems as a result of simultaneous reaction with the atoms of the transition metal and nitrogen (bifunctional catalysis). This indicates the importance of the study of the mechanism of the insertion of carbon dioxide at an M$-$N bond for the solution of the problem of involving this molecule in catalytic processes to give organic products.

V. Reduction of carbon dioxide

1. Chemical reduction of carbon dioxide

The reduction of carbon dioxide by alkali metal amalgams gives oxalate ion in the absence of moisture, and formic acid in the presence of moisture.[2] In addition to oxalic acid, the products of the reaction of CO_2 with alkali metal amalgams in aprotic media, after hydrolysis, contain acetic, malonic, glycollic, tartaric, and other acids.[2]

The coordination of CO_2 to the alkali metals, and the reaction products, have been studied.[22,23] An interesting feature is that the adduct $LiCO_2CO_2$ was detected among the products of the reaction of CO_2 with lithium vapour in a matrix. The published[22] reaction scheme explains, on the one hand, the formation of the oxalate ion, and on the other hand the formation of the carbonate ion and carbon monoxide.

An example of bifunctional catalysis is provided by the reduction of carbon dioxide in the presence of the Cp_2TiCl + Al system in tetrahydrofuran.[124] $Cp_2Ti(CO)_2$ is formed in this system as the main product, in 80% yield. The influence of the Lewis acids VCl_4, $HgCl_2$, and $GaCl_3$ on the yield of dicarbonyltitanocene has been studied. The carbonate $(Cp_2Ti)_2CO_3$ was detected in addition to the titanium carbonyl.

The reduction of carbon dioxide by molecular hydrogen to methanol and methane in the presence of bifunctional catalysts has been examined.[125]

The reduction of CO_2 in aqueous media, when the water molecules act as hydrogen donors, are of particular interest. An extremely important feature of these systems is the ability of the transition metal to activate a water molecule with the formation of a hydride complex. Thus the splitting of water by cobalt complexes takes place under mild conditions according to the scheme[126]

$$2[Co] + H_2O \rightarrow [Co]H + [Co]OH,$$

and its splitting by phosphine complexes of platinum takes place according to the scheme[127]

$$[Pt] + H_2O \rightarrow H[Pt]OH.$$

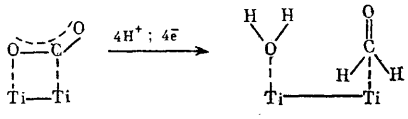
The hydrogenating power of the cobalt complex increases when reducing agents (Zn/Hg etc.) are introduced into the system.[126]

In the reduction of salts and oxides of vanadium by amalgamated zinc in aqueous solutions in a CO_2 atmosphere, the chief reaction product is HCO_2H, whereas malic acid is formed preferentially under the same conditions in the presence of molybdenum derivatives, and malic and tartaric acids in the presence of $TiCl_4$.[128] In aqueous solutions in the presence of the $Ti(SO_4)_2-Al/Hg$ system, formaldehyde and formic acid are produced (10% of the yield of H_2CO).[129] HCO_2H, H_2CO, MeOH, and CH_4 have been detected in the reduction of carbon dioxide in acidic solutions in the presence of sodium amalgam and compounds of manganese, tungsten, and molybdenum. The main product is methanol in the absence of oxygen, and H_2CO and MeOH in the presence of oxygen.

In the presence of the $Ti^{2+}-Al/Hg$ system at pH 1.7 and a CO_2 pressure of 5 atm, the main product of the reduction of CO_2 is H_2CO, whereas in the $Cr^{3+}-Al/Hg$ system, HCO_2H is formed preferentially. The selective reduction of carbon dioxide to formaldehyde in aqueous solution was observed in the presence of the $TiCl_3-Al/Hg$ system.[130] The competing reaction of molecular hydrogen liberation takes place in parallel. The highest yield of H_2CO is achieved at pH 3.5. An interesting feature is that at pH 3.8 in aqueous solutions, the following equilibrium is established[2]

$$CO_2^{\cdot-} + H^+ \rightleftarrows \dot{C}O_2H.$$

It has been shown using $^{14}CO_2$ that the reduction of CO_2 in the presence of the $Ti^{3+}-Al/Hg$ system is a four-electron process taking place according to the scheme



2. The electrochemical and electrocatalytic reduction of CO_2

a. Electrochemical reduction

Considerable attention has been paid to the electrolytic reduction of carbon dioxide in aprotic and proton-containing electrolytes.[2,131-136] The interest in this problem is due largely to the utilisation of CO_2 in isolated systems,[135] and also in relation to the production of organic compounds of interest as future sources of energy (HCO_2H), MeOH, CH_4, etc.) or as foodstuffs.[136-138]

The principal reactions in the electrolytic reduction of carbon dioxide are the formation of oxalate or carbonate ions and carbon monoxide in aprotic media, and the formation of formic acid in aqueous media and in general in the presence of proton donors.[2,131-134] In all cases, the radical-anion $CO_2^{\cdot-}$ is formed in the first stage as the product of electron transfer from the electrode surface to an adsorbed CO_2 molecule:

$$CO_2 + e^- \rightarrow CO_2^{\cdot-} \begin{cases} \xrightarrow{+(CO_2)} CO_3^{2-} + CO \\ \xrightarrow{+(CO_2^{\cdot-})} C_2O_4^{2-} \\ \xrightarrow{+H^+(+e^-)} HCO_2^- \end{cases}$$

The formation of the radical-anion $CO_2^{\cdot-}$ requires a fairly high potential. Thus according to Eggins and McNeill,[139] the direct reduction of carbon dioxide takes place with great difficulty at a potential of -2.0 V (normal hydrogen electrode). In aqueous solutions, this high potential lowers the yield of organic products as a consequence of the competing process of molecular hydrogen liberation.

In a study of the mechanism of oxalate formation, two radical species were detected in the reaction mixture:[134,140]

$$CO_2 + e^- \rightarrow CO_2^{\cdot-},$$
$$CO_2^{\cdot-} + CO_2 \rightarrow CO_2CO_2^{\cdot-},$$
$$(CO_2)_2^{\cdot-} + e^- \rightarrow C_2O_4^{2-}.$$

According to Kafafi and co-workers,[141] the oxalate ion is formed by the dimerisation of two $CO_2^{\cdot-}$ radical-ions. An interesting feature is that the formation of dimers $M(CO_2CO_2)^-$ was suggested as one of the stages in the reaction of alkali metal vapour with CO_2 [141,142] or in the insertion of this molecule at an Fe–Na bond[64] (see also section III). When the adsorption of the dimer $CO_2CO_2^{\cdot-}$ on the electrode is weak, the oxalate ion is formed, and when its adsorption is strong, the carbonate ion and CO are formed.[143] On Pt, Au, and Ag electrodes in DMSO and other aprotic solvents, carbon monoxide is formed,[144-146] whereas on Hg and Pb electrodes in DMF and DMSO, $C_2O_4^{2-}$ is liberated in addition to CO.[131] The lead electrode is preferred for the preparation of oxalate, and the mercury electrode for the preparation of CO. On In, Sn, and Zn electrodes in DMSO at an increased CO_2 pressure, the main product is carbon monoxide.[147] A systematic study of the influence of the electrode material, the carbon dioxide pressure, and other parameters on the yield of oxalic acid in aprotic solvents has been carried out.[139,148] The cathode materials studied were Pb, Pb/Hg, stainless steel, Cr, Cd, Al, Cu, Zn,[139] glass carbon, Hg, Pt, Pb, and Au.[148]

In aprotic media, other organic products are formed in addition to oxalate and carbonate ions and carbon monoxide. Thus at a lead cathode in DMSO, in addition to oxalate, another ten products were detected, including propionic, maleic, tartaric, and other acids.[147] The formation of various organic products in the synthesis of oxalic acid in aprotic solvents has been reported.[131,150] In the presence of moisture in an aprotic solvent, hydroxyacids are formed in addition to oxalate and HCO_2H.[2,147,149] Thus in the presence of water, glycollic acid is liberated at a Pb electrode,[131,151] and malic acid at an Hg electrode.[152]

As noted above, in aqueous solutions the main product of the reduction of carbon dioxide is formic acid. HCO_2H is formed via the radical-anion $CO_2^{\cdot-}$. The electrolytic reduction can take place by a one-electron or by a two-electron mechanism:[2,133]

$$CO_2 + e^- \rightarrow CO_2^{\cdot-},$$
$$CO_2^{\cdot-}(ads) + H_2O \rightarrow CO_2^{\cdot-}(H_2O),$$
$$2\,CO_2^{\cdot-}(H_2O) \rightarrow CO_2 + HCO_2^- + OH^-,$$

or

$$CO_2 + e^- \rightarrow CO_2^{\cdot-}(ads),$$
$$CO_2^{\cdot-}(ads) + e^- \xrightarrow{H_2O} HCO_2^- + OH^-.$$

A mechanism for the electrolytic reduction of carbon dioxide with the simultaneous transfer of two electrons in the CO_2 molecule has been proposed:[153]

$$CO_2 + 2e^- \rightarrow CO_2^{2-},$$
$$CO_2^{2-} + H_2O \rightarrow HCO_2^- + OH^-.$$

The formation of CO_2^{2-} in the reaction of carbon dioxide with alkali metals has been reported.[154] The CO_2 pressure has a significant influence on the order of the reaction.[155]

The $CO_2^{\cdot-}$ radical-anion is extremely unstable, making it difficult to study the mechanism of the electrolytic reduction of carbon dioxide by the methods of electrochemical kinetics.[131] From known thermodynamic quantities, the electron affinity of CO_2 in aqueous solution has been estimated as ~ 0.5 eV.[155,156] The highest current efficiency under optimum conditions was observed at -1.9 V (silver chloride reference electrode) at Zn, Pb, and In cathodes, and at -1.7 V at an Sn electrode.[157] The study of cathode materials with medium and high hydrogen overvoltages showed that in the electrolytic reduction of carbon dioxide, the overvoltage increases in the order Sn < Cu < Zn < Cd < Pb < Au [158] (see also the paper by Vasil'ev and co-workers[133]). The highest efficiency in this process is shown by metals with a medium overvoltage. The high overvoltage at the Sn electrode also ensures high rates of the

electrolytic reduction of CO_2.[159] In the electrolytic reduction of carbon dioxide in aqueous solutions, the formation of propionic[160] and butyric[161] acids in addition to HCO_2H has been noted.

The more extensive reduction of carbon dioxide to formaldehyde, methanol, and methane is accompanied by the transfer of four, six, and eight electrons respectively, that is it requires a much greater expenditure of energy:[162]

$$CO_2(gas) + 2H_2O(liquid) = HCO_2H(solv.) + \tfrac{1}{2}O_2 \quad (E^0 = 1.428 \text{ eV});$$

$$CO_2(gas) + H_2O(liquid) = H_2CO(solv.) + O_2(gas) \quad (E^0 = 1.350 \text{ eV});$$

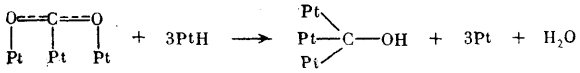
$$CO_2(gas) + 2H_2O(liquid) = MeOH(solv.) + \tfrac{1}{2}O_2 \quad (E^0 = 1.119 \text{ eV});$$

$$CO_2(gas) + 2H_2O(liquid) = CH_4(gas) + 2O_2(gas) \quad (E^0 = 1.037 \text{ eV}).$$

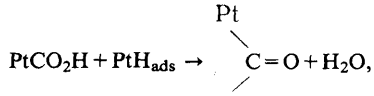
Cyclic voltammetry, preparative electrolysis, and other methods have been used to make a detailed study of the mechanism of the electrolytic reduction of CO_2 to H_2CO and HCO_2H at Hg, Pb, and Sn electrodes in the pH range 6.8–13.0.[137]

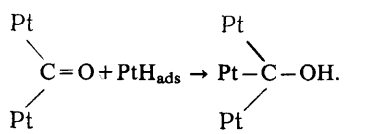
At a platinum electrode in a saturated carbonate solution in a cell with non-separated anode and cathode compartments, formaldehyde is formed in addition to HCO_2^-.[163,164] Fairly high methanol current efficiencies are achieved in the electrolytic reduction of carbon dioxide at an In cathode in lithium carbonate solution.[136] HCO_2H is reduced in acidic media at Pb and Sn to methanol.[137] At a dropping mercury electrode, the reduction of H_2CO to MeOH takes place by two different mechanisms, depending on the pH of the medium. The more extensive reduction of HCO_2H on Sn at comparatively low current densities, in the opinion of the authors cited,[137] is due to the formation of organotin compounds on the electrode surface. The formation of hydrocarbons in the electrochemical reduction of carbon dioxide at an Ag electrode has been reported.[165] In the opinion of the authors cited, the electrolytic reduction of CO_2 passes through a stage involving the formation of unstable silver formate on the electrode surface.

The mechanism of the chemisorption of carbon dioxide in its electrolytic reduction at smooth electrodes is of fundamental importance.[134,166,167] This problem is closely related to the chemisorption of carbon dioxide on the surface of heterogeneous catalysts,[2] and also to the coordination of CO_2 to metals in matrices or in various metallic centres. Of particular interest in this connection is the coordination of carbon dioxide to the surface of a platinum electrode through the carbon atom with the subsequent formation of organometallic adducts during the reduction:[166]



$$Pt_3(CO_2)_{ads} + PtH_{ads} \rightarrow Pt{-}CO_2H,$$





As already noted in section III, X-ray diffraction data show that the bent CO_2 molecule forms a complex with three metal atoms (rhenium and osmium). It is quite possible that a CO_2 molecule coordinated on the surface of a platinum electrode forms a π-allyl adduct. In this connection it should be noted that in the chemistry of coordination compounds there are known cases of the transfer of an allyl ligand from one metallic centre to another.[168,169] Transfer of this kind is particularly important in the electrocatalytic reduction of carbon dioxide.

Hydrogen chemisorbed on a Pt electrode can reduce carbon dioxide to formic acid.[170] The reaction of CO_2 with H_{ads} at the surface of a platinum electrode in 0.5 M sulphuric acid gives the fragment $[Pt]CO_2H$.[171] As noted in section III, the action of water on a cationic complex of platinum gives a stable platinum-carboxylic acid $(Et_3P)_2Pt(Cl)CO_2H$.[36] The formation of esters of a platinum-carboxylic acid of the type $[Pt]-CO_2R$ was detected in the electrocatalytic carboxylation of unsaturated compounds in the presence of platinum clusters.[172] To this it should be added that carbon dioxide can react with the hydride complexes of transition metals in two ways:[1,2,173]

$$[M]{-}H + CO_2 \rightarrow [M]O_2CH,$$
$$[M]{-}H + CO_2 \rightarrow [M]CO_2H,$$

that is with the formation of either formates or metal-carboxylic acids.

Fundamental difficulties in the electrolytic reduction of CO_2 at smooth electrodes are associated with increasing the current density. The low current density is a consequence of the low solubility of carbon dioxide in many solvents. This problem can be solved, in particular, by using porous electrodes, increasing the CO_2 pressure, introducing catalytic additives, etc.

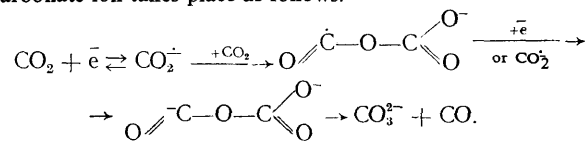
b. Electrocatalytic reduction

In the last ten years, a fairly large number of published papers have described the electrolytic reduction of carbon dioxide in the presence of transition metal compounds acting as catalysts. The introduction of transition metal compounds into the electrocatalytic circuit makes it possible to solve a number of fundamental problems, in particular to lower considerably the potential of the electrolytic reduction of CO_2, to create conditions for many-electron transfer, etc. The nature of the transition metals whose compounds are used as catalysts determines the specific features of the electrocatalytic stage and hence the organic reaction products formed. The way in which the metal compound is introduced into the catalytic circuit is extremely important: the coordination compound is either deposited on the electrode surface or dissolved in the electrolyte.

c. The reduction of CO_2 to CO_3^{2-} and CO

Carbon monoxide is a valuable raw material for the synthesis of organic compounds. For example, methanol can be obtained from carbon monoxide in good yield by electrocatalytic reduction under mild conditions.[174] Organic acids can be obtained by electrocatalytic reduction from unsaturated compounds, CO, and water in the presence of platinum complexes.[172] Finally, the electrocatalytic reduction of carbon monoxide in aqueous solution is of considerable importance for the production of "synthetic gas".[175]

The electrolytic reduction of carbon dioxide to carbon monoxide and carbonate ion takes place as follows:[150]



In the electrolytic reduction of carbon dioxide at a mercury electrode in acetonitrile containing KNO_3 or $LiClO_4$ as background, carbon monoxide is not formed in the absence of a catalyst at -1.6 V. When tetra-aza-macrocyclic derivatives of divalent cobalt and nickel complexes are added to the electrolyte, the reduction of CO_2 to CO takes place at -1.3 V with a current efficiency of up to 90%.[145] In the presence of a catalyst but in the absence of water, carbon monoxide is not formed. The electrocatalytic behaviour of the complex $Ni^{2+}L_2$, where L_2 = 1,4,8,11-tetra-azacyclotetradecane, has been studied.[176] At an Hg electrode in an electrolyte consisting of an MeCN + H_2O mixture, or in an aqueous medium in the presence of this complex, carbon monoxide is formed from CO_2. The authors cited[176] relate the formation of CO in aqueous solution to the geometry of the macrocyclic ligand, which creates round the metallic centre a hydrophobic space or "aprotic niche", which does not prevent the approach of CO_2 to the metal but which hinders the approach of moisture. Of the large number of divalent nickel complexes studied, only dicyclic compounds of nickel were found to be active, and complexes of nickel with unsaturated macrocyclic ligands or with open chains are inactive in this process. In the opinion of Pearce and Pletcher,[132] the fact that no formic or oxalic acid is formed in electrocatalytic processes involving nickel and cobalt chelates is due to the fact that this process takes place by the following mechanism:

$$[LM^{I}]^{n+} + \bar{e} \rightleftarrows [LM^{I}]^{(n-1)+},$$

$$[LM^{I}]^{(n-1)+} + CO_2 + Na^+ \rightleftarrows [LM^{III}CO_2^-Na^+]^{n+},$$

$$[LM^{III}CO_2^-Na^+]^{n+} + H_2O \xrightarrow{\text{rapidly}} [LM^{III}CO_2H]^{n+} + NaOH,$$

$$[LM^{III}CO_2H]^{n+} + \bar{e} \rightarrow [LM^{II}CO_2H]^{(n-1)+},$$

$$[LM^{II}CO_2H]^{(n-1)+} \xrightarrow{\text{slowly}} [LM^{II}]^{n+} + CO + OH^-,$$

$$2\,NaOH + 2\,CO_2 \rightarrow 2\,NaHCO_3,$$

where M = Co or Ni, and L represents the macrocyclic ligand.

According to the data of Tinnemans and co-workers,[177] the complexes of cobalt and nickel with tetra-aza-macrocyclic ligands are effective electron acceptors (first stage). The next stage, according to the above scheme, involves the formation of an adduct with carbon dioxide, in which an alkali metal atom also takes part (bifunctional catalysis). The products of the insertion of CO_2 at a transition metal–alkali metal etc. bond were examined in sections III and IV. The metal-carboxylic acid formed at the stage of protonation of the coordinated CO_2 molecule may be stable even in aqueous media.[36] Nickel-carboxylic and cobalt-carboxylic acids are unstable.[36]

The formation of a complex of carbon dioxide with a Co^{2+} complex obtained by the electrolytic reduction of a Co^{3+} chelate has been described.[178]

The reduction of carbon dioxide to the monoxide in aqueous media can be carried out at a graphite electrode modified by the deposition of cobalt phthalocyanine.[175] The electrocatalytic reduction of CO_2 on this electrode in a citrate buffer at pH 5 takes place at -1.0 V (standard calomel electrode). The efficiency of the electrolytic reduction of CO_2 is sufficiently high only when cobalt phthalocyanine is deposited on the electrode surface; when it is added to the electrolyte, the system has a low catalytic activity, and the results are not reproducible. The potential for the reduction of carbon dioxide is lowered considerably in the presence of complexes of metals with sulphonated phthalocyanines at an amalgamated platinum electrode.[179] In this case the reduction of CO_2 involves two stages; in the first, a complex of the metal with carbon dioxide is formed on the electrode surface, and in the second, an electron is transferred to the CO_2 molecule from the electrode via the transition metal complex.

The electrocatalytic reduction of carbon dioxide to CO also takes place in the presence of bipyridyl complexes of rhenium[180] and ruthenium.[181,182] Thus selective formation of carbon monoxide takes place in the electrolytic reduction of CO_2 in the presence of (bipy)$Re(CO)_3Cl$ in DMF–water (9:1) solution at a glass electrode at -1.25 V (normal hydrogen electrode).[180] The absence of other carbon-containing reduction products was confirmed by ^{13}C NMR. Carbon dioxide is reduced in the presence of the cationic complex of ruthenium $(bipy)_2Ru(CO)_2^{2+}$ in DMF–H_2O solution at -1.5 V (saturated calomel electrode) at an Hg electrode.[181] When the concentration of water in the electrolyte is high, formic acid is also produced. The processes taking place in the electrocatalytic reduction include the formation of an unstable adduct of ruthenium with carbon dioxide:[181]

$$(bipy)_2Ru(CO)_2^{2+} \underset{-OH^-}{\overset{+OH^-}{\rightleftharpoons}} [(bipy)_2Ru(CO)(CO_2H)]^+ \underset{-OH^-}{\overset{+OH^-}{\rightleftarrows}}$$

$$\rightleftarrows [(bipy)_2Ru(CO)(CO_2^-)]^+ + H_2O.$$

Carbon monoxide is liberated with a high current efficiency, together with methanol and methane, at a ruthenium electrode deposited on a carbon electrode at $-(0.35-0.65)$ V (normal hydrogen electrode).[183] CO is also formed in the electrolytic reduction of CO_2 in the presence of sulphur-containing iron clusters.[184] Carbon monoxide and carbonate ion are formed by the photoelectrocatalytic reduction of CO_2 in aqueous solutions at an electrode of the semiconducting *p*-GaAs at -1.2 ± 0.1 V (normal hydrogen electrode)[185] (see next section).

The preparation of CO by the reduction of the hydrogen carbonate ion by a bipyridyl complex of cobalt(I) in aqueous solution at pH 8.5–10.0 has been studied.[186] The carbon monoxide formed reacts with the bipyridyl complex of cobalt to give the stable complex (bipy)$Co(CO)_2$, which has been isolated. Small quantities of formate ion were also produced. The results indicate that the reaction of H_2O and HCO_3^- with $(bipy)_3Co^+$ involves the intermediate formation of the hydride complex of cobalt $(bipy)_2Co(H_2O)H^{2+}$.

Thus the electrocatalytic reduction of CO_2 to CO and CO_3^{2-} differs significantly from the electrolytic reduction of this molecule at smooth electrodes. The study of the electrocatalytic reduction of carbon dioxide in aqueous media involves considerable difficulties, due primarily to the fact that the stages involving the protonation of the coordinated CO_2 molecule, the formation of complexes with carbon dioxide from the metal-carboxylic acids, and the reaction of the hydroxo-complexes with CO_2 have been insufficiently studied, and also to the lack of detailed information on the behaviour of the hydrogen carbonate ligand at the metallic centre, etc.

d. The reduction of CO_2 to formic acid

Formic acid is a product of the reaction of the radical-anion CO_2^-, formed by the electrolytic reduction of carbon dioxide, with water or other proton sources in the electrolyte.[2] Among the methods for obtaining HCO_2H, a unique place is occupied by the electrocatalytic reduction of CO_2.

Formic acid is produced by the electrocatalytic reduction of carbon dioxide at a graphite electrode on which the phthalocyanines of cobalt, iron, or copper have been deposited.[187] The highest yields of HCO_2H are obtained when cobalt phthalocyanine is used. This result does not agree with earlier data, according to which oxalic and

glycollic acids, but not formic acid, are produced in the presence of metal phthalocyanines deposited on a graphite electrode.[188] A later study of the behaviour of metal phthalocyanines on an electrode surface showed that formic acid is produced at pH 3.7.[189] In less acidic solutions, the catalytic system in inactive. It was also found that the cathode current increases linearly with increase in the carbon dioxide concentration. The activity of the metals in this process decreases in the order Co^{2+}, $Ni^{2+} \gg Fe^{2+} \simeq Cu^{2+} > Cr^{3+}$.[189] In the electrocatalytic reduction of CO_2 in the presence of cobalt phthalocyanine, small quantities of methanol were detected.

The formate ion is produced in acetonitrile at a graphite electrode on which the complexes of rhodium or ruthenium with 2,6-bis-(2-pyridyl)pyridine have been deposited.[190] When the rhodium complex is used, the electrolytic reduction of CO_2 takes place at -1.55 V (saturated calomel electrode) and gives HCO_2^- (current efficiency 64%) and H_2 (current efficiency 12%), and in the case of ruthenium, formate ion and CO are produced at -1.4 V. It was suggested that an important role in the catalytic act is played by the polypyridyl ligand, acting as an "electron reservoir'. In the electrolytic reduction of CO_2 for a short time interval at a mercury electrode in acetonitrile containing the dissolved complex $(dppe)_2RhCl$, formate is produced with a current efficiency of 42%; with increase in the reduction time, the yield of formate decreases.[191] It is suggested that a complex of rhodium with carbon dioxide is formed during the reaction; this complex in turn reacts with the proton donor to form a hydride, which takes part in the transfer of hydrogen to the coordinated CO_2 molecule.

The electrocatalytic reduction of carbon dioxide has been carried out at a mercury electrode in DMF containing dissolved sulphur-containing iron clusters $[Fe_4S_4(SR)_4]^{2-}$, with R = $PhCH_2$ and Ph.[192] In the presence of these clusters, with a corresponding lowering of the potential, only formic acid is produced, whereas in the absence of the catalyst the main product is oxalate, formed with a current efficiency of 73% (formate ion and carbon monoxide are also obtained, with current efficiencies of 12% and 13% respectively). The authors cited[192] suggest that the source of hydrogen in the synthesis of HCO_2H is the organic radical Bu_4N^+, used as background.

Electrocatalytic reduction always occurs with the formation of a hydride complex, which takes part in the transfer of hydrogen to the CO_2 molecule coordinated to the metal.[191] In principle, the hydride complexes can be formed in two ways:

$$[M] + H_2O \rightleftarrows M(H)OH,$$
$$2[M] + H_2O \rightleftarrows [M]OH + [M]H.$$

Finally, it may be noted that the electrocatalytic reduction of carbon dioxide may involve a fairly complex chain of processes. Thus the preparation of sugars and aminoacids in aqueous solutions has been carried out by creating a catalytic chain in which the photosynthetic stage is replaced by the electrochemical reduction of $NADP^+$ (nicotinamide phosphate) in the presence of ferredoxin or methylviologen to bring about the electron transfer from the electrode to $NADP^+$.[138] The closure of the catalytic ring is achieved by the regeneration of NADPH by electrolytic reduction.

3. The photoelectrocatalytic reduction of carbon dioxide

a. Photoreduction at electrodes of semiconducting materials

The ability of various semiconductors (TiO_2, *p*-GaAs, etc.) to transform light energy into a photo-current has been used, in particular, to reduce carbon dioxide in aqueous solutions.[136] The photoreduction of CO_2 in these media is closely related to the photocatalytic decomposition of water.[193] The solution of the problems of transforming solar energy into electrochemical energy depends to a large extent on the development of studies in this field.[194–196] The efficiency of the transformation of solar into electrical energy on single crystals of *n*-GaAs and *p*-InP reaches 12%.[197]

The photo-process taking place when a quantum of light acts on a semiconductor reduces to the transfer of an excited electron from the valence band of the semiconductor to the substrate. Thus on the irradiation of electrodes to *p*-GaP [198] and *p*-GaTe [199] in the presence of CO_2, the radical-ions $CO_2^{\cdot-}$ are formed on the surface of the photo-cathodes. Carbon monoxide has been obtained from CO_2 at an *n*-CdTe photo-cathode in DMF or MeCN containing small quantities of water.[200] The replacement of Bu_4NClO_4 as electrolyte by NH_4ClO_4 has a marked influence on the magnitude of the photo-current.[201] In the mechanism proposed for the reaction, the ammonium ion transfers the electron to CO_2. CO is formed with a current efficiency of 80% from CO_2 at electrodes of CdTe, GaAs, GaP, and InP in DMSO, DMF, or propylene carbonate.[202] In contrast to the electrolytic reduction of CO on In, Pb, and Hg (see previous section), the reduction of CO_2 on photo-cathodes takes place at potentials between -0.7 V and $+1.0$ V.

In the photo-reduction of CO_2 in aqueous solutions at GaP and GaAs electrodes, the main product is HCO_2H with a small quantity of H_2CO and MeOH. The highest current efficiency of 80% is achieved at a CO_2 pressure of 8.5 atm and a potential of -1.0 V (silver reference electrode). The potential of the cathodic photo-current changes linearly with increase in the pressure. The formation of HCO_2H with a current efficiency of 1% has been observed in the photo-reduction of CO_2 at GaAs in an electrolyte containing the redox system V^{2+}/V^{3+} to prevent photo-corrosion.[204]

Carbon dioxide is reduced to H_2CO, MeOH, and HCO_2H when a *p*-GaP photo-cathode is irradiated with an Hg lamp at pH 6.8.[205] The accumulation of HCO_2H and MeOH at room temperature was observed for 18–90 h. The maximum efficiency of the formation of H_2CO and MeOH when monochromatic light (365 nm) is used has the values 5.6% and 3.6% respectively. For illumination with sunlight, the efficiency decreases to 0.97% and 0.61% respectively. Methanol, CO, and H_2 were detected on the irradiation of a solution of hydrogen carbonate at a GaP photo-cathode using Hg, Xe, and W halide lamps.[206] The addition of crown ethers to lithium carbonate solution in the photo-reduction of CO_2 on GaP increases both the photo-current and the current efficiency of H_2CO, HCO_2H, and MeOH. It has been suggested that the metallic lithium liberated in the presence of the crown ethers reacts with CO_2 to give $CO_2^{\cdot-}$.

Methanol is also formed in the photo-reduction of CO_2 on *p*-GaAs and *p*-InP in an electrolyte containing sodium sulphate.[198] The density of the photo-current and the current efficiency of MeOH depend significantly on the type of electrolyte. The irradiation of CO_2 with monochromatic light in 0.5 M H_2SO_4 on *p*-GaP at -1.5 V gives formaldehyde and methanol.[207] With a disc electrode in the form of a single crystal of *p*-GaAs (As 111) at pH 4.2, the current efficiency of MeOH in the reduction of CO_2 reaches 10% at a current density of 1.4×10^{-4} A cm^{-2}.[185] Increase in the current density leads to a decrease in the yield of MeOH. A study of the influence of the deposition on the *p*-GaP photo-cathode of films of metals with a high hydrogen liberation overvoltage (Pb, Zn, Au) showed that when a Pb film is used, the chief product of the reduction of CO_2 is HCO_2H with a current efficiency of 42%, and the yield of this product is ten times lower at a cathode without a

coating.[208] When the cathode is coated with a Zn film, the main product is CO with a current efficiency of 18%. In both cases, H_2CO and MeOH were not detected in the reaction products. Irradiation with an Xe lamp at a *p*-type silicon photo-cathode alloyed with boron gives HCO_2H (current efficiency 28%) and H_2CO (19%),[207] and the photo-irradiation of CO_2 on photo-electrodes of TiO_2 and titanates containing 0.05–0.5 wt.% added Mn, Fe, Co, and Nb gives H_2CO and MeOH.[208] An apparatus for the photo-initiation of the reaction of CO_2 with water, adsorbed on the [111] face of strontium titanate, on irradiation with an Hg lamp has been described.[209] The products of this reaction include not only methane but also other hydrocarbons, HCO_2H, H_2, and O_2. In the monochromatic (752 nm) irradiation of a *p*-GaP electrode in $MeCN-H_2O$ solution containing tetra-aza-macrocyclic metal complexes, the potential for the reduction of CO_2 is 0.6 V lower than that on metallic electrodes in the presence of the corresponding catalysts.[210]

A laboratory photocatalytic cell for the preparation of HCO_2H from CO_2 using solar energy has been proposed.[211] The efficiency of the cell depends markedly on its design, particularly if the anode and cathode compartments are separated.

Finally, it should be emphasised that an extremely important characteristic of semiconducting photo-electrodes is their ability to reduce CO_2 under "dark" conditions by the creation of a reserve of electrons on preliminary illumination of the photo-cathode.[205,212]

b. Photo-reduction in suspensions of semiconducting materials

The photoelectrocatalytic reduction of carbon dioxide can also be carried out using semiconducting materials in the form of suspensions and colloids. In these systems, the particles of the semiconductor can be regarded as microphoto-electrodes, since the action of light on the surface of the particles produces regions capable of acting as cathodes and anodes. A systematic study of the reduction of CO_2 in aqueous solutions in the presence of suspensions of S, C, CdS, GaP, ZnO, TiO_2, and WO_3 has been carried out.[213] H_2CO and MeOH are formed in the reduction. The yield of MeOH correlates with the potential of the conductivity band of the semiconducting material; catalysts for which the potential is more negative are more effective. Formaldehyde is produced in the presence of suspensions of TiO_2 and calcium and strontium titanates.[214,215] The addition of ruthenium dioxide to TiO_2 leads to the more complete transformation of solar into electrochemical energy, compared with the use of niobium and uranium oxides.[216] The reaction products are H_2CO, MeOH, and HCO_2H. Formaldehyde is produced on the irradiation with an Hg lamp of TiO_2 suspensions covered with films of Pt, Au, Ag, Hg, Co, or Pb.[217] The highest yield is achieved when Hg films are used. Although mercury is oxidised during the photo-reduction, the reverse reduction of mercury oxide to the metal takes place at $\lambda = 600$ nm. H_2CO, HCO_2H, MeOH, MeCHO, and EtOH were obtained from CO_2 and water by the irradiation with an Hg lamp of strontium titanate containing the added oxides of Rh, Ir, Pt, and Ru.[218] The addition of 0.5% $LaCrO_3$ to this system increased the yield of MeOH three-fold. HCO_2H is formed from CO_2 on the irradiation of a suspension of $BaTiO_3$ containing added lanthanide oxides.[219]

An assembly has been proposed[220] for obtaining organic products by irradiation of a CO_2-H_2O-photo-activator (titanates) system. When Li_2CO_3 is added to this system, the degree of transformation of solar energy reaches 0.011–0.016%. The reaction $CO + H_2O \rightleftarrows CO_2 + H_2$ taking place when a TiO_2 suspension is irradiated with an Hg lamp has been studied.[221,222] In particular, it was found that the rate of this reaction is proportional to the light intensity. The preliminary reduction of TiO_2 with molecular hydrogen leads to a marked increase in the photocatalytic activity of the oxide.[223]

4. The photochemical and photocatalytic fixation of carbon dioxide

The problem of obtaining organic products from CO_2 and water under the influence of different forms of radiation is directly related to the study of chemical evolution on the Earth.[2,224] The progress made in recent years in the activation of CO_2 and H_2O by systems based on transition metals has also made a significant contribution to the development of these studies. Early studies examined mainly the effect of ultraviolet irradiation on the CO_2-H_2O system,[2,225–234] to which compounds of transition metals or uranium were added in some cases. Systematic studies[230–234] showed that the ultraviolet irradiation of the CO_2-H_2O system gives CO, HCO_2, H_2CO, and MeCHO. The yield of the photolytic reaction products increases slightly in the presence of Fe^{2+} ions. When aqueous solutions containing CO_2 in the presence of Fe^{2+} were irradiated using a lamp with a power of 375 W (365.5 nm), the formation of oxalic, acetic, and malonic acids was observed. Fe^{2+} ions are usually added to the photolytic system to stabilise $^{\cdot}OH$ radicals.[2] It is possible that they also stabilise $CO_2^{\cdot-}$ radical-anions, which according to the data obtained[230–234] are formed in the photolytic system being considered. In the photolysis of CO_2 using light with arbitrary wavelength, the principal products are CO, O, and small quantities of ozone.[224] The photolysis of carbon dioxide in the presence of metallic mercury gives CO_3,[2] probably via the intermediate $Hg.CO_2$.

Since water and CO_2 do not absorb visible light, a photocatalytic process in this case is possible only when a photosensitiser capable of transferring its absorbed energy to CO_2 and H_2O is added to the system. If the lifetime of the photosensitiser in the excited state is insufficient for the transfer of a quantum of light, the photocatalytic act may be brought about by the introduction of a special agent to transfer an electron from the photosensitiser to the CO_2 molecule. Photocatalytic systems of this type containing a photosensitiser and electron-transfer agents have recently been detected and studied. Thus in the presence of bipyridyl complexes of ruthenium and cobalt, the photocatalytic decomposition of water by visible light can be brought about, with further transformation involving CO_2, by two different paths.[186] The first path can be represented as follows:

$$Ru^{2+} \xrightarrow{h\nu} {}^*Ru^{2+},$$

$$^*Ru^{2+} + AH^- \rightarrow Ru^+ \ (AH^- \text{ represents the ascorbate ion}),$$

$$Ru^+ + Co^{2+} \rightarrow Ru^{2+} + Co^+,$$

$$Co^+ + H_2O \rightarrow Co^{2+} + {}^1/_2H_2 + OH^-.$$

The Co^+ ion by itself undergoes practically no reaction with CO_2, but in the presence of bipyridyl it becomes a strong reducing agent:[186,235]

$$2(bipy)_3Co^+ + HCO_3^- + H_2O \rightarrow 2(bipy)_3Co^{2+} + CO + 3OH^-,$$

$$(bipy)_3Co^+ + CO \rightarrow {}^1/_4[(bipy)Co(CO)_2]_2 + {}^1/_2(bipy)_3Co^{2+} + bipy.$$

It can be seen from this scheme that the bipyridyl complex of ruthenium acts as the photosensitiser, and the bipyridyl complex of Co acts as the electron-transfer agent. The chief product is CO, but in the pH range 5–10, H_2 and small quantities of HCO_2H are formed.

The second path is represented by the scheme:

$$Ru^{2+} \xrightarrow{h\nu} {}^*Ru^{2+},$$
$${}^*Ru^{2+} + Co^{2+} \rightarrow Ru^{3+} + Co^{+},$$
$$Ru^{3+} + NTE \rightarrow Ru^{2+} + NTE^{\cdot+} + NTE \rightarrow NTE^{\cdot} + NTEH^{+},$$
$$NTE^{\cdot} + Co^{2+} \rightarrow \text{products} + Co^{+},$$
$$Co^{+} + H_2O \rightarrow Co^{2+} + {}^1/_2H_2 + OH^{-},$$

where NTE = 2,2′,2″-nitrilotri(ethanol).

The variety of functions which can be carried out by cobalt ions in catalytic systems was noted above; they bring about the decomposition of water,[76] form an adduct with CO_2 in electrolytic reduction,[36] are involved in the formation of cobalt-carboxylic acids,[1,36] etc.

HCO_2H is formed in the photocatalytic reduction of CO_2 in water on irradiation with an Hg lamp with a light filter (λ = 320 nm) in the presence of the system $(bipy)_3Ru^{2+}$ – methylviologen (MV) – triethanolamine (or ethylenediaminetetra-acetic acid).[236] The process involves the MV^+ radical-cation, which in turn is the product of electron transfer from the photo-excited ruthenium complex. The formation of HCO_2H was confirmed using labelled $^{13}CO_2$.[237] It was also shown that the photolysis involves the formation of ruthenium(I), which reacts with water to give a hydride involved in the formation of the complex with CO_2.

The influence of bipyridyl and 1,10-phenanthroline on the photocatalytic behaviour of M^{2+} ions (Ru, Fe, Co, Cr) on the ultraviolet irradiation (254 nm) of the CO_2-H_2O system has been studied.[238] MeOH and H_2CO are formed in the presence of Fe, Co, and Cr ions. The formaldehyde obtained can be further reduced to MeOH and CH_4.

CO_2 has been reduced to CO in visible light in the presence of $(bipy)Re(CO)_3Cl$ in NTE–DMF solution.[239] Depending on the amine, the photocatalytic system is capable of up to 50 cycles. An attempt has been made to use the photochemical reaction

$$Na_2Ru_3(CO)_{11} \xrightarrow{h\nu} Ru(CO)_5$$

to close the catalytic chain in the production of CO and CO_3^{2-} from CO_2:

$$Ru(CO)_5 \xrightarrow{h\nu} Ru_3(CO)_{12} \xrightarrow{2Na^+} Na_2Ru_3(CO)_{11} + CO_2,$$
$$\uparrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$
$$\leftarrow\!\!-\!\!-\!\!-

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