Translated from *Uspekhi Khimii*, 50, 111 - 136 (1981) U.D.C. 547.222

Organic Syntheses Based on Carbon Dioxide

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Organic syntheses based on carbon dioxide are examined. Together with syntheses of organic compounds, certain aspects of the mechanism of the coordination of CO_2 to transition metal complexes are considered. The review includes studies published up to 1977.
The bibliography includes 171 references.

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I. INTRODUCTION

The use of carbon dioxide as the starting material for organic syntheses constitutes one of the most important problems of modern organic chemistry. There has been a recent growth of interest in the chemistry of carbon dioxide, the reserves of which in nature are practically inexhaustible. The most promising of the natural sources of carbon dioxide are coal and carbonates. The interest in the chemistry of carbon dioxide is to a large extent associated with the latest advances in metal complex catalysis, which permits the activation of the CO_2 molecule. The advances in this field permit the hope for a successful achievement of catalytic syntheses on the basis of CO_2.

In recent years there has been a sharp increase of the amount of CO_2 released into the atmosphere by engines, industry, and electric power stations. The average increase of the CO_2 content in the Earth's atmosphere as a result of the combustion of fuels is 0.2% per annum, which is extremely undesirable from the ecological point of view[1].

In view of the rapid depletion of the reserves of petroleum and the development of coal-chemical industries, the synthesis of compounds of practical importance based on CO_2 has also become important. On the basis of carbon dioxide derived from coal, it is possible to synthesise products which are nowadays manufactured using petroleum as the raw material; this makes it timely to develop effective methods for the synthesis of important organic compounds from CO_2.

This review deals with the principal literature data published in 1971–1977 and concerning the syntheses of organic compounds with participation of CO_2 (electrochemical and photochemical processes are not included).

II. SOME ASPECTS OF THE MECHANISM OF THE FIXATION OF CO_2 BY TRANSITION METAL COMPLEXES

1. Coordination to Transition Metal Complexes

Carbon dioxide is the highest oxide of carbon, which is much more reactive than nitrogen. The CO_2 molecule has a linear structure with an ionisation potential of 13.7 eV and an electron affinity of 3.8 eV.

The bond between CO_2 and the metal in complexes can be formed in principle via the following mechanisms:

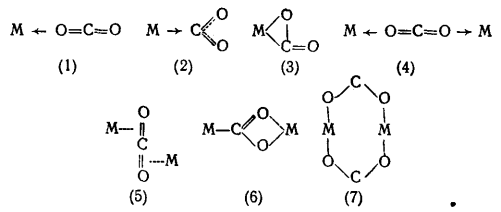


Table 1. Parameters of the infrared spectra of transition metal complexes of CO_2.

Complex	ν_{CO_2}, cm^{-1}	References
$Rh_2(CO_2)(CO)_2(PPh_3)_3$	1498,1368,813	2,3
$Rh_2Cl_2(CO_2)(PPh_3)_5$	1630	4,5
$Rh_2(CO_2)_2(CO)_2(PPh_3)_3C_6H_5$	1600,1355,800	3
$Rh(OH)(CO_2)(CO)(PPh_3)_2$	1602,1351,821	6
$RuH(OMe)(CO_2)(PPh_3)_3$	—	5,7
$Co(CO_2)(PPh_3)_3$	—	8
$Ni_2(CO_2)(PPh_3)_4$	1735	9
$Ni(CO_2)(PPh_3)_2$	1740,1698,1150	10
$Pt(CO_2)(PPh_3)_2$	1640,1370,1320	4
$C_6H_5AgCO_2Ag$	1496,1326,828	11
Cu(II)-ephedrine-CO_2	2350,2380	12
$Cu(OOCMe)(CO_2)(PPh_3)_2$	2620,1600,1302	13
$Cu(OOCMe)(CO_2)(PPh_3)_2$	821,1610,1420,1380, 830,650	14
$Ir(OH)(CO_2)(CO)(PPh_3)_2$	1636,1310,815	6
$Mo(CO_2)_2(PMe_2Ph)_4$	1760,1510,1335	15
$Cu_2(CO_2)(PPh_3)_4$	1475,1330,835	16

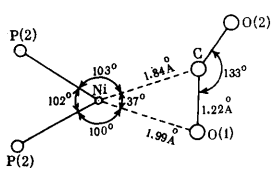
Evidently CO_2 interacts with the metal as an electron acceptor or as a powerful nucleophile via the carbon atom. The M–O bond formed via schemes (1) and (4) is less likely; the bond is most probably formed either via the carbon atom with transfer to the latter of electrons from the metal and the formation of organometallic compounds—derivatives of metal-carboxylates [scheme (2)]—or via a mechanism involving the formation of a π-complex with participation of the C=O double bond [schemes (5), (6), and (7)]. There are at present no data confirming unambiguously a particular structure. Some information is provided by the infrared spectra of transition metal complexes of CO_2, which are presented in Table 1. With

the exception of the complex $Rh_2(CO_2)(CO)(PPh_3)_3$, synthesised by oxidising with oxygen the compound $Rh_2(CO)_4(PPh_3)_3$, and also $Cu(CO_3)(PPh_3)_4$, all the complexes presented in Table 1 have been obtained by the direct interaction of the metal compounds with CO_2.

The presence of CO_2 in the rhodium complex obtained by passing CO_2 into a solution of triphenylphosphinerhodium chloride and containing one CO_2 molecule for two rhodium atoms has been confirmed by the isolation of carbon dioxide on heating, on reduction with $LiAlH_4$ with formation of methanol, and on quantitative substitution of CO_2 by carbon monoxide[17,18]. The alkylation reaction was used to detect the metal–carbon bond in this complex. If the complex contains only the metal–oxygen bond, alkylation should lead to the formation of a carbonate ester. On the other hand, if the complex is constructed in such a way that it contains a CO_2 fragment linked to the metal via the carbon atom, alkylation may be expected to lead to the formation of a derivative of an alkanecarboxylic acid. It was found that, when the rhodium complex is acted upon by methyl iodide, methyl acetate is formed. These data are satisfactorily consistent with structure (6) containing the fragment Rh–COO–Rh.

Pure gaseous carbon dioxide gives rise to two characteristic absorption bands in the infrared spectrum in the region of 2349 and 667 cm^{-1}. The appearance of three new absorption bands in the spectrum of the complex $Rh_2(CO_2)(CO)_2 \cdot (PPh_3)_3$ in the region of 1498, 1368, and 813 cm^{-1} is treated as a result of the coordination of CO_2 to the central metal atom and of the simultaneous formation of a bent configuration of the CO_2 molecule of type (II) and (III). Such a complex has also been obtained by the interaction of $Rh_2(CO)_4 \cdot (PPh_3)_4$ with $^{18}O_2$.[2] A polynuclear complex containing CO_2 gives rise to a single absorption band in the region of 1735 cm^{-1}, corresponding to the CO_2 group. This group is capable of coordinating with two nickel atoms with formation of a π-bond in a type (5) structure[9]. However, structure (6) has been attributed to the polynuclear rhodium complex of CO_2, which has a characteristic absorption band in the region of 1630 cm^{-1}; on interaction with methyl iodide, it gives rise to methyl acetate[4].

X-Ray diffraction analysis of the complex $Ni(CO_2)(PPh_3)_2$ confirmed the planar structure corresponding to the type (3) bond with the bent configuration of the CO_2 coordinated to the nickel atom[10]:



These data concerning the formation and properties of transition metal complexes containing CO_2 lead to ways of seeking new synthetic and catalytic reactions. The presence of CO_2 in the complexes as a ligand can be inferred from the evolution of CO_2 on heating the complexes or on treating them with acids and also from the displacement of CO_2 by carbon monoxide. The complex $Pt(CO_2)(PPh_3)_2$ has been obtained[4] from $Pt(PPh_3)_3$ and CO_2. In the presence of oxygen this reaction proceeds with formation of a platinum carbonate complex[19]:

$$Pt(PPh_3)_3 + O_2 + CO_2 \rightarrow Pt(CO_3)(PPh_3)_2 + PhPO \ .$$

Subsequently the platinum carbonate complex was obtained[19] by the reaction of $PtO_2(PPh_3)_2$, synthesised beforehand, with CO_2; in this case the CO_2 molecule is inserted in the metal–oxygen bond. The fixation of CO_2 in the complex $Mo(C_2H_4) \cdot (dpe)_2$ (where dpe = $Ph_2PCH_2CH_2PPh_2$) was achieved at room temperature[20] under the influence of u.v. radiation with formation of the molybdenum complex *cis*-$Mo(CO_2)(dpe)_2$ in boiling toluene. The authors explained the formation of the molybdenum carbonyl complex by the rupture of one C–O bond with the simultaneous oxidation of diphenylethane. The complex $Mo(CO_2)_2(PMe_2Ph)_2$ is unstable and, when an attempt is made to recrystallise it from tetrahydrofuran (THF), it is readily converted into the dinuclear complex $(PMe_2Ph)_3(CO) \cdot Mo(CO_3)_2Mo(CO)(PMe_2Ph)_3$. It has been suggested[15] that CO_2 is then reduced to CO_3^{2-} via the mechanism

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

The analogous reactions involving the formation of carbonyl complexes from CO_2 and transition metal complexes have been described[20–23]. The following four most characteristic types of reaction can be distinguished among them:

$$(C_5H_5)(PPh_3)NiBr + Mg \rightarrow (C_5H_5)(PPh_3)NiMgBr \xrightarrow[MgBr_2]{CO_2} [(C_5H_5)(PPh_3)NiCOOMgBr] \rightarrow$$
$$\rightarrow [(C_5H_5)(PPh_3)NiCOOMgBr] \rightarrow [(C_5H_5)(PPh_3)NiCO^+] \rightarrow (PPh_3)_2Ni(CO)_2 \ ;$$

$$(C_5H_5)_2MoH_2 + AlMe_3 \rightarrow [Mo_2{-}Al_3 \text{ polynuclear complex }] \xrightarrow{CO_2+H_2O} [(C_5H_5)_2Mo(CO)Br]^+ \ ;$$

$$RhCl(PPh_3)_3 + CO_2 \xrightarrow{HSi(OEt)_3} [RhH\{Si(OEt)_3\}Cl(PPh_3)_2] \rightarrow RhCl(CO)(PPh_3)_2 \ ;$$

$$RuCl_2(PPh_3)_3 + CO_2 \xrightarrow{HSi(OEt)_3} RuCl_2(CO_2)(PPh_3)_2 \ .$$

The opposite case, involving the interaction of CO_2 with the triphenylphosphine complex of copper and formation of the copper carbonate complex, has also been described in the literature[16]:

$$iso\text{-}BuCu(PPh_3)_2 + 2CO_2 \xrightarrow[0.5\ h;\ -40\ ^\circ C]{THF}$$
$$iso\text{-}BuCCu(CO_2)(PPh_3)_2 \xrightarrow[6\ h;\ 0\ ^\circ C]{CO_2} Cu_2(CO_3)(PPh_3)_4 \ .$$
$$\|O$$

The reaction proceeds via a stage in which an acyl complex is formed and, when carbon dioxide is passed into its solution for a long time, is converted into a crystalline copper carbonate complex. When this complex interacts with hydrochloric or sulphuric acid solutions, CO_2 is evolved in molar proportions of 1 : 2 in relation to copper.

2. CO_2 Insertion Reactions

In order to synthesise various organic compounds, it is necessary that the carbon dioxide activated by coordination to transition metal complexes should form a new substrate via insertion in the M–H, M–C, M–O, or M–N bonds. Such insertion can be regarded as nucleophilic attack on the carbon atom in the CO_2 molecule which proceeds via two possible pathways:

(1) normal insertion with formation of the M–O bond and the formate:

$$M^{\delta+}-L^{\delta-} + O^{\delta-}\equiv C^{\delta+}=O \rightarrow M-O-\overset{O}{\overset{\|}{C}}-L \ ;$$

(2) anomalous insertion with formation of compounds with a metal–carbon bond—metal-carboxylates:

$$M^{\delta-}-L^{\delta+} + O^{\delta-}\equiv C^{\delta+}=O \rightarrow M-\overset{O}{\overset{\|}{C}}-O-L;$$
$$L=H,\ C,\ O,\ N \quad etc.$$

The anomalous insertion of CO_2 in the M–L bond is encountered extremely rarely.

Reactions involving insertion in the M–H and M–C bonds have been examined in detail in another review[17] and we shall therefore deal with them extremely briefly.

(a) *The insertion of CO_2 in the M–H bond.* The reaction of CO_2 with a nitrogen-containing cobalt hydride complex and subsequent methylation of the reaction products by methyl iodide lead to both methyl formate—the product of the normal insertion of CO_2 in the M–H bond[24,25]—and to acetic acid and methyl acetate—the products of the anomalous insertion of CO_2:[18]

$$(PPh_3P)_3Co(N_2)H + CO_2 \longrightarrow \left[\text{Co}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}\text{H}\right] \xrightarrow{MeI} HCOOMe;$$
$$(PPh_3P)_3Co(N_2)H + CO_2 \longrightarrow \left[\text{Co}-\text{COOH}\right] \xrightarrow{MeI} MeCOOH.$$

The reaction proceeds via a stage in which a cobalt formate complex is formed, which also happens when CO_2 interacts with $CoH_3(PPh_3)_3$.

On interaction with CO_2 at room temperature, ruthenium and rhodium hydride complexes[26–28] give rise to a formate complex with a single hydride atom, in contrast to the formate complex, formed on pyrolysis or on interaction with PPh_3, N_2, H_2, CO, CS_2, HHal, and RHal, which readily splits off CO_2.

Iron hydride complexes in the crystalline state or in solution readily interact with CO_2 under the influence of light to form an iron diformate complex[29]:

$$\left.\begin{array}{l} FeH_4(PEtPh_2)_3 + 2CO_2 \xrightarrow{-H_2} \\ FeH_2(N_2)(PEtPh_2)_3 + 2CO_2 \xrightarrow{-N_2} \end{array}\right\} \longrightarrow Fe(OOCH)_2(PEtPh_2)_2 + PEPh_2.$$

In contrast to the insertion of CO_2 in the Ru–H bond, this reaction is irreversible; when the resulting complex interacts with methyl iodide, ethyl formate is formed.

(b) *The insertion of CO_2 in the M–C bond.* Various organic compounds with functional groups can be obtained by the insertion of CO_2 in the M–C bond. Organometallic complexes having the general formula $M(CH_2Ph)_4$ (where M = Ti or Zn) effectively absorb CO_2 in solution in the molar proportions 1 : 2 and subsequent hydrolysis of the resulting substrate leads to the formation of phenylacetic acid and triphenylmethanol[30], which indicates a normal mechanism of the insertion of CO_2 in the M–C bond with formation of a cyclic complex:

$$(PhCH_2)_3M\begin{array}{l}\diagup O \\ \diagdown O\end{array}C-CH_2Ph.$$

Similarly, the interaction of dimethyltitanocene with CO_2 results in the formation of a stable titanocenium acetate, the reaction of which with methanol yields methyl acetate[31]. The formation of the above cyclic metal-containing structure has been confirmed spectroscopically[32].

The reaction of CO_2 with an organometallic cobalt compound containing the ethyl group proceeds via both pathways with formation of cobalt propionate (normal insertion) and a metal-carboxylate ester (anomalous insertion) as insertion products[18,33]. A carboxylate complex of cobalt is formed when propionic acid acts on the complex $LCO(CO_3)COOEt$. When the carbonate complex is treated with methyl iodide, methyl propionate and a small amount of methyl formate are formed[18].

The intermediate complex containing the COOEt group [ν(CO) = 1713 cm^{-1}] is formed from the iridium[34], cobalt[35], ruthenium, and osmium complexes in the presence of alcohol and carbon monoxide[36]. The insertion of CO_2 in the Rh–C bond in a phenylrhodium complex proceeds via the normal pathway[37]:

$$RhPh(PPh_3)_3 + CO_2 \xrightarrow[C_6H_6]{20\ atm,\ 20^\circ C} Rh(O_2CPh)(PPh_3)(C_6H_6)_{0.5}.$$

A triphenylphosphinealkylcopper complex readily interacts with CO_2 at room temperature via the anomalous insertion pathway (involving the Cu–C bond) to form unstable metal carboxylate complexes and copper carbonates[13,14,38]:

$$RCu(PR_3)_2 + CO_2 \rightarrow RCO_2Cu(PR_3)_2 + RC(O)OCu(CO)_2(PR_3)_2.$$

The initial alkyl complex of copper is used as the catalyst in the synthesis of nitroalkanecarboxylic acid from CO_2 and a nitroalkane[38]. The reaction with the cyanomethyl complex of copper proceeds via the normal pathway involving the insertion of CO_2 in the Cu–C bond with formation of a copper cyanoacetate complex[39], which can be used to synthesise carboxylic acids from acetylenic hydrocarbons at atmospheric pressure[40]. There are data concerning the insertion of carbon dioxide in benzyl–titanium or benzyl–zirconium[41], methyl–titanium[7,42], and Pd–C [43] bonds.

(2) *The insertion of CO_2 in the M–O bond.* Transition metal alkoxides and hydroxides interact with CO_2 via insertion in the M–O bond (normal insertion). Copper alkoxides interact at room temperature with CO_2 to form copper acetate, which is followed by the formation of a dialkyl carbonate under the influence of an alkyl iodide[44]:

$$Cu(OMe)_2 + 2CO_2 \underset{\text{pyridine/DMF, } 80^\circ C}{\overset{\text{pyridine, } 20^\circ C}{\rightleftharpoons}} Cu(OC(O)OMe)_2 \xrightarrow{RI} ROC(O)OMe;$$
R = Me or Et.

The presence of absorption bands in the region of 1665 and 1305 cm^{-1} in the infrared spectrum of the copper acetate complex and the formation of an asymmetric dialkyl carbonate on interaction with RI confirm the normal insertion of CO_2 in the Cu–O bond[44]. In benzene solution the analogous copper compound reacts with CO_2 to form an alkyl carbonate complex[45]:

$$t\text{-BuOCu(t-BuCN)}_3 + CO_2 \underset{C_6H_6,\ N_2}{\overset{C_6H_6,\ 20^\circ C}{\rightleftharpoons}} t\text{-BuOC(O)OCu(t-BuCN)}_3.$$

The normal insertion of CO_2 in the M–C bonds is observed also for $Ti(OBu)_4$, $Zr(OBu)_4$, $Fe(OEt)_3$, $Nb(OEt)_3$, and $Zr(OEt)_4$.[46] All these reactions proceed via the mechanism

$$M(OR)_n + CO_2 \xrightarrow{C_6H_6,\ 30^\circ C} [M(OR)_{n-1}(OC(O)OR)] \xrightarrow{EtI} EtOC(O)OR;$$
M=Ti, Zr, Fe, or Nb.

The reactions with zinc[47], mercury[48], and tin[49,50] compounds proceed via an analogous mechanism involving the insertion of CO_2 in the M–O bond. The hydroxo-complexes of cobalt and other transition metals also react with insertion of CO_2 in the M–O bond and the formation of carbonate complexes[51,52]:

$$[Co(OH)(NH_3)_5]^{2+} + CO_2 \underset{}{\overset{H_2O}{\rightleftharpoons}} [Co(CO_3H)(NH_3)_5]^{2+};$$
$$M(OH)(CO)(PPh_3)_2 + CO_2 \xrightarrow{EtOH} M(OCO_2H)(CO)(PPh_3)_2:$$
M = Ir or Rh.

The reaction with the hydroxocobalt complex proceeds in an aqueous medium and the reactions with the hydroxo-complexes of iridium and rhodium take place in alcohol. In the presence of alcohol *in vacuo* alkoxomanganese reacts with CO_2 in the vapour phase to form a complex with an Mn–O bond[53]:

$$EtO-Mn + CO_2 \rightarrow \begin{array}{l}\text{Et}\\ \text{O}\\ \text{O}\cdots\text{C=O}\\ \vdots\quad\vdots\\ \text{Mn}\quad\text{O}\end{array} \rightarrow \begin{array}{l}\text{Et}\\ \text{O}\\ \diagdown\\ \text{C=O}\\ \diagup\\ \text{Mn-O}\end{array} \rightarrow Et-O-\begin{array}{l}\text{C}\\ \diagup\ \diagdown\\ \text{O}\quad\text{O}\\ \diagdown\ \diagup\\ \text{Mn}\end{array}.$$

(d) *The insertion of CO_2 in the M–N bond.* Reactions involving the insertion of CO_2 in the M–N bond also proceed via the normal pathway in accordance with the mechanism[54–60]

$$M(NMe_2)_n + n\,CO_2 \rightarrow M(O_2CNMe_2)_n;$$
$$M = Ti, Zr, V, \text{or } Mo\ (n=4);\ Nb \text{ or } Ta\ (n=5);\ Mo \text{ or } W\ (n=3).$$

The group $\rangle C{=}O$, of a metal carbamate complex, readily exchanges for $^{13}CO_2$, forming a labelled compound detectable by NMR:[58]

$$ML_n^* + x^{12}CO_2 \rightleftarrows ML_mL^*_{n-m} + m^{12}CO_2 + (x-m)^{13}CO_2;$$
$$L = O_2^{12}CNMe;\ L^* = O_2^{13}CNMe.$$

The activation energy for the exchange reaction of the zirconium complex is 44 ± 8 kJ mol^{-1} and that for the tungsten complex is about 96 kJ mol^{-1}. When the *N,N'*-ethylenebis-(salicylideneiminato)cobalt(II) complex is reduced with sodium, the product is a mixed $NaCo^I$ complex, which readily reacts with CO_2 to form Co–C(O)–ONa.[61] The use of the latter as the catalyst can lead to new possibilities for the synthesis of different functional compounds. Aluminium[62], boron[63], silicon[64], germanium[6], tin[65,68], phosphorus[65], arsenic[67], and zinc[69] amide compounds also react with CO_2, forming carbamide complexes (via the normal insertion pathway).

III. THE REACTIONS OF CO_2 WITH ORGANIC COMPOUNDS

1. The Addition of CO_2 to Carbanions

It is known that, when organomagnesium compounds are acted upon by CO_2, carboxylic acids are formed[70]:

$$RMgX + CO_2 \rightarrow RCOOMgX \xrightarrow{H_2O} RCOOH.$$

However, the reaction of CO_2 with dimethoxymagnesium proceeds with formation of methanol[73]:

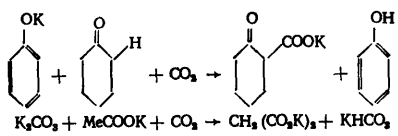
$$Mg(OMe)_2 + NO_2Me + CO_2 \rightarrow NO_2CHCOOMg + 2MeOH$$

or

$$Mg(OMe)_2 + CO_2 \rightleftarrows MeOMgOCOOMe;$$
$$MeOMgOCOOMe + NO_2Me \rightleftarrows NO_2CHMg + 2MeOH.$$

Ethylene and propene react with CO_2 in the presence of EtMgBr [71] and $Sn(OCH_2CH_2NMe_2)_2$ to form ethylene and propylene carbonates respectively in quantitative yields at 100 °C and a CO_2 pressure of 5–9 atm.

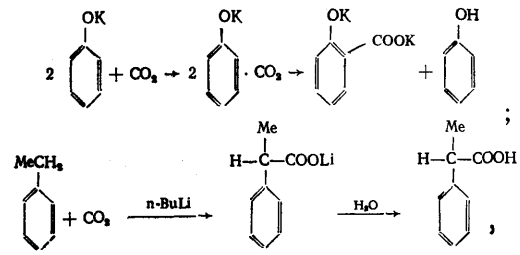
The carboxylation of cyclohexanone[74] and an acetate salt[75] proceeds differently—via the substitution of mobile hydrogen atoms in the molecule:



$$K_2CO_3 + MeCOOK + CO_2 \rightarrow CH_2(CO_2K)_2 + KHCO_3.$$

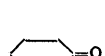
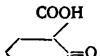
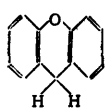
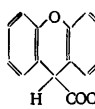
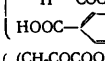
Table 2 presents data for the carboxylation of various organic compounds with a mobile hydrogen atom in the α-position in the presence of potassium carbonate and THF.[76] The data presented show that the yields of the reaction products per unit time depend on the basicity of the initial reactant.

The Kolbe–Schmidt reaction, occurring as a consequence of π-electron transfer from the aromatic ring to CO_2,[77] which has found industrial applications, and the carboxylation of ethylbenzene[78],



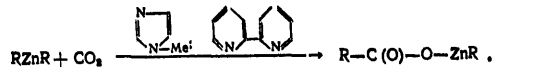
constitute prototypes of the reactions presented above. They can be regarded as nucleophilic interaction of a carbanion, with a characteristic relation between the reactivity and electronegativity of the initial reactants.

Table 2. Carboxylation of organic compounds in the presence of K_2CO_3.[76]

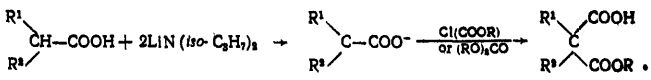
Initial reactant	pK_a	t, °C	p_{CO_2}, atm	τ, h	Reaction products	Yield, %
	<15	room	1	2		40
$MeNO_2$	11	room	1	2	NO_2CH_2COOH	25
$EtNO_2$	9	room	1	2	$NO_2C(COOH)HMe$	15
$PrNO_2$	—	room	1	2	$NO_2C(COOH)HEt$	10
$MeC(NO_2)HMe$	9	room	1	2	$MeC(COOH)(NO_2)Me$	0
MeCN	25	70	2	45	$CNCH_2COOH$	1
	—	70	2	—	 	0.3 0.3
MeCOMe	20	room	1	11	$MeCOCH_2COOH$ $HOOCCH_2COCH_2COOH$	7 7
MeCOOMe	24	70	2	72	$HOOCCH_2COOMe$  	10 1 1
	29	95	1	4	 	10 20
MeCOCOOMe	0	—	1	1	$(CH_2COCOOMe)_2$ $C(COOH)H_2COCOOMe$	33 15

According to Pauling's data[1], alkyl derivatives of metals (R_xM) with an electronegativity less than 1.5 interact with carbon dioxide, but when the electronegativity is greater than 1.5, they do not react. Thus trialkylaluminium (the electronegativity of aluminium is 1.5) readily interacts with CO_2, while dialkylzinc (the electronegativity of zinc is 1.6)

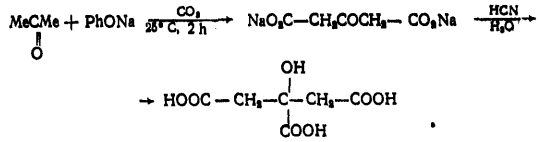
does not react with CO_2 at room temperature at atmospheric temperature[79,80]. Only the introduction of tertiary amines of the type of methylimidazole or pyridine into the reaction medium increases the reactivity of the initial reactant[81]:



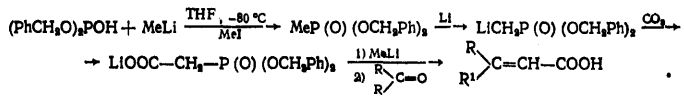
The synthesis of acids with the iso-structure, which are derivatives of malonic acid (yield 46–80%), proceeds via a carbanionic mechanism[82]:



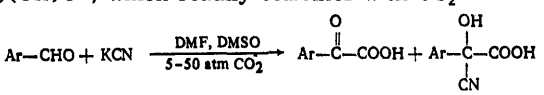
Citric acid has been obtained from acetone and CO_2 in solution in diglyme[83]:



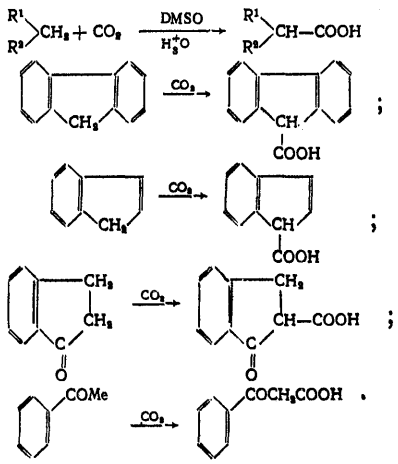
Butadiene reacts with CO_2 in a solution of sodium phenoxide in dimethylformamide (DMF) at 50 °C with formation of muconic acid (yield 81%).[84] By analogy with the Wittig–Horner vinylcarboxylation reaction, α,β-unsaturated carboxylic acids have been obtained from dibenzyl phosphate and CO_2 in the presence of Me_3Li and MeI at −80 °C:[85]



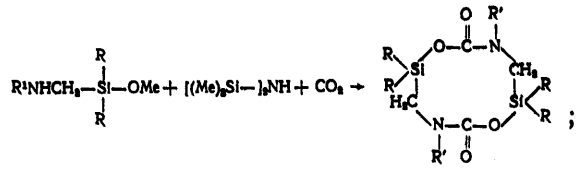
When an aldehyde reacts with potassium cyanide in DMF or dimethyl sulphoxide (DMSO), the product is the carbanion $R(CN)(OH)C^-$, which readily combines with CO_2:[86]



The possibility of synthesising carboxylic acids and their derivatives in yields of 30–80% by the carboxylation of a ketone and hydrocarbons with a mobile hydrogen atom had been demonstrated[86,87]:

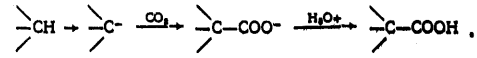


The carboxylation of organosilicon compounds proceeds via a carbanionic mechanism[88]:



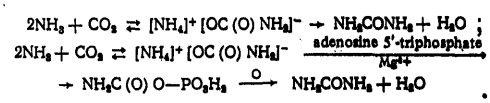
R=Me; MeO; R'=H, CH_2=$CHCH_2^-$, Me_2CH–CH_2^-, or n-Bu.

Organic compounds with a weak acidity and tending to be metallated with subsequent formation of a carbanion enter into the above reactions; the nucleophilic attack by this carbanion on CO_2 leads to the formation of carboxylic acids or their derivatives via the mechanism



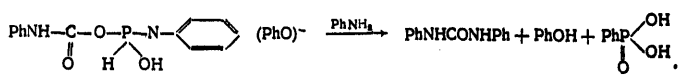
2. Reactions of CO_2 with Nitrogen-Containing Compounds

Urea, which is of practical importance, is obtained by the reaction of carbon dioxide with ammonia at 200–300 °C under pressure[89–91]:



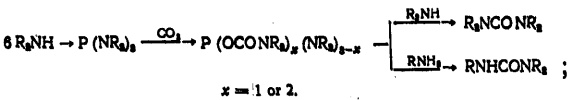
We may note that in the living organism urea is continuously biosynthesised, leading to the fixation of ammonia, which is harmful to the organism.

The synthesis of urea derivatives from an amine and CO_2 at atmospheric pressure in a quantitative yield was achieved for the first time by Yamazaki[92]. When CO_2 was passed into a solution of $(PhO)_2POH$ and $PhNH_2$ in pyridine for 4 h (at 40 °C), *N,N'*-diphenylurea was formed in 85% yield, while in THF the yield was 93%:



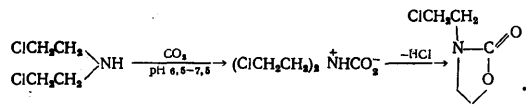
When carbon dioxide is replaced in this reaction by carbon disulphide, the product is PhNHCSNHPh (yiled 100%). These reactions can be used to synthesise polyureas or polythioureas[93].

Primary or secondary amines react with CO_2 in the presence of PCl_3 and pyridine at 60 °C with formation of symmetrical disubstituted ureas[94]:



Under analogous conditions, aromatic amines react with CO_2 in the presence of $PhOPCl_2$ in pyridine to form polyureas[95].

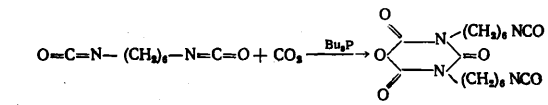
3-(2-Chloroethyl)-2-oxazolidinone has been obtained from CO_2 and di(2-chloroethyl)amine in the presence of 0.6 mole of sodium bicarbonate at 31 °C:[96,97]



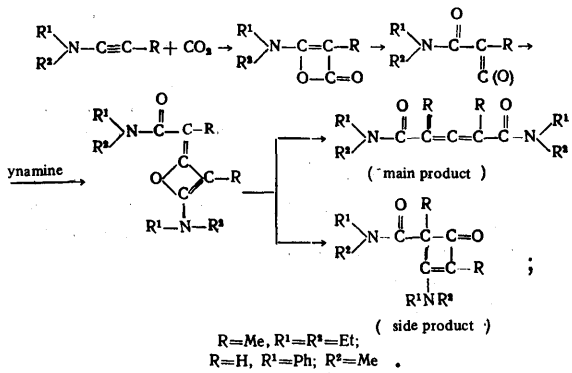
Dialkyl-substituted formaldehydes have been obtained from primary and secondary amines, CO_2, and H_2 at pressures up to 30 atm in the presence of phosphine complexes of ruthenium of the type $(PPh_3)_4RuH_2$, $(PPh_3)_4RuCl_2$, $Ph_2PCH_2CH_2PPh_2$–$RuCl_3$–EtAl, or $(PhO)_3P$–$RuCl_3$–EtAl at 130 °C (yield 60%).[98] The reaction can proceed catalytically in the presence of cobalt, rhodium, iridium, palladium, platinum, and copper complexes under analogous conditions[98]:

$$R_2NH + CO_2 + H_2 \rightarrow HC(O)NR_2 + H_2O .$$

In the presence of Bu_3P diisocyanates react with CO_2 to form oxadiazinone compounds[99]:



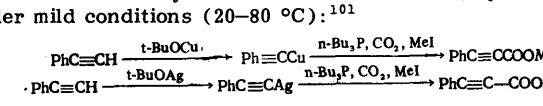
Unsaturated compounds with a high electron density of the type of ynamine readily react with CO_2 at 20 °C to form allenedicarboxamide derivatives in 100% yield[100]:



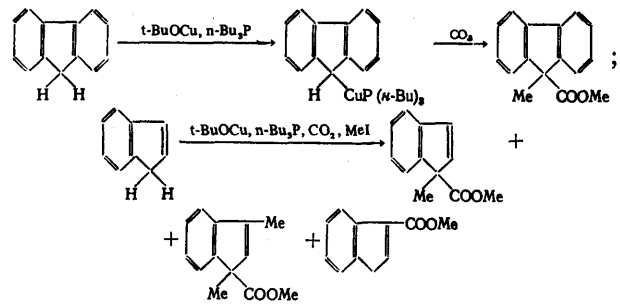
R=Me, R^1=R^2=Et;
R=H, R^1=Ph; R^2=Me .

3. Reactions of CO_2 with Unsaturated Hydrocarbons and Their Derivatives

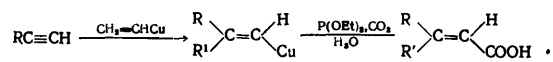
As already mentioned above, the insertion of CO_2 in the M–C bond can serve as the basis of the synthesis of various compounds with functional groups from unsaturated hydrocarbons and their derivatives. Thus the insertion of CO_2 in the Cu–C and Ag–C bonds, depending on the σ-donor ligand (whose presence is essential), constitutes the basis of the synthesis of carboxylic acids from unsaturated hydrocarbons under mild conditions (20–80 °C):[101]



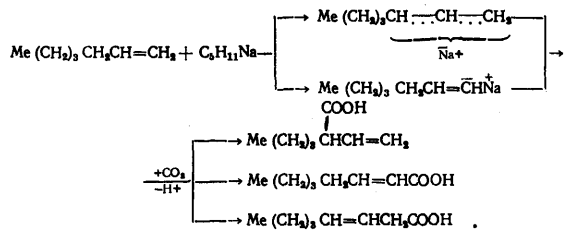
The yield of phenylacetylenecarboxylic acids from phenylacetylene and CO_2 in the presence of ligands of the type of n-Bu_3P and t-BuNC or t-BuOCu and t-BuOAg was 70%. Fluorene[101] and indene[45] are carboxylated under analogous conditions in the presence of methyl iodide with formation of methyl esters of methylfluorenecarboxylic and methyl- and dimethyl-indenecarboxylic acids respectively:



Methyl- and butyl-acetylenes react with CO_2 in the presence of vinylcopper and triethoxyphosphine $P(OEt)_3$ in hexamethylphosphoramide at −30 °C with formation of stereospecific β,β′-unsaturated carboxylic acids (yield 96%):[102]



When α-olefins are metallated by pentylsodium or alkyllithium in aprotic solvents at room temperature a hydrogen atom attached to a carbon atom in the allyl or vinyl position is substituted with formation of organometallic compounds. Carboxylation of the latter yields unsaturated acids[103,104]:



The reactivity of α-olefins in the metallation reaction is usually attributed to the ability of the hydrogen atom to be converted into a proton under the influence of bases of appropriate strength[103]. The use of complex-forming solvents in metallation reactions involving alkyl-lithium[105–109] as well as alkylmagnesium[110,111] leads to the coordination of the electron-donating groups of the solvent to the metal cation, which tends to increase the polarity of the metal–carbon bond. The most effective solvent in the metallation reaction proved to be triethylamine, in the presence of which the overall yield of carboxylic acids reached 97.7%.[112].

Indene, fluorene, acetophenone, and benzyl thioacetate are carboxylated at the active CH_2 group in triethylamine or triethylenediamine in the presence of $MgCl_2$ at p_{CO_2} = 5 atm at room temperature with a yield of the required product up to 80%.[113] Indene-3-carboxylic acid, fluorene-9-carboxylic acid, phenylacetic acid, and benzylthiocarboxylic acid were obtained from indene, fluorene, acetophenone, and benzyl thioacetate respectively. The reaction conditions were as follows: an equimolar amount of $MgCl_2$ in relation to the carboxylated reagent and duration of experiment from 17 to 72 h.

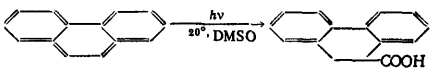
Diene hydrocarbons with conjugated double bonds (butadiene, isoprene, 2,3-dimethylbutadiene, and penta-1,3-diene) are readily carboxylated with formation of dicarboxylic acids under mild conditions with participation of an alkali metal phenoxide[114]. Thus at atmospheric pressure in THF and in the presence of an equimolar amount of sodium phenoxide, butadiene is carboxylated at 50 °C to muconic acid in 81% yield:

$$CH_2{=}CH-CH{=}CH_2 + 2CO_2 \xrightarrow[50^\circ C]{PhONa,\ THF} HOOC-CH{=}CH-CH{=}CH-COOH.$$

The reactions considered are characteristic of unsaturated hydrocarbons and their derivatives capable of forming an M–C bond in which CO_2 can be inserted via the anomalous pathway with formation of compounds of the metal-carboxylate type.

4. Reactions Involving the Addition of CO_2 to a Radical-Anion

It has been shown that CO_2 can readily add to a radical-anion with formation of a charge-transfer complex between a donor base and an acceptor. Thus, the carboxylation of phenanthrene in a solution of $PhN(CH_3)_2$ in DMSO at p_{CO_2} = 4 atm and room temperature under the influence of u.v. for 17 h yielded 9,10-dihydrophenanthrenecarboxylic acid (yield 41%):[115]



The reaction proceeds analogous with anthracene, naphthalene, pyrene, and biphenyl in a tertiary amine and dimethylaniline[1]. The mechanism of these reactions has been treated in terms of the intermediate formation of a charge-transfer complex under the influence of ultraviolet light between a strong electron donor (an amine) and aromatic hydrocarbons of the type $ArH{\cdot}R_3\overset{+}{N}$. CO_2 then attacks the complex with formation of the radical-anion $(ArH)^{\cdot}-COO^-$, which readily combines with a hydride hydrogen atom from the solvent:

$$(ArH)\begin{matrix}H\\ \diagup\\ \diagdown\\ COO^-\end{matrix} \rightarrow (ArH)\begin{matrix}H\\ \diagup\\ \diagdown\\ COOH\end{matrix}.$$

In the presence of acetonitrile and p-NCC_4H_4NC, p-methoxystyrene gives rise, under the influence of ultraviolet light to a radical-cation, which interacts with CO_2.[116]

The free radicals formed in the homolytic dissociation of the C–C bond under the conditions of the cracking of alkanes proved to be extremely reactive in relation to CO_2. Thus the vapour-phase cracking of the higher C_{17}–C_{19} paraffins and C_{20}–C_{40} paraffin wax in CO_2 at 500–700 °C yielded a mixture of saturated carboxylic acids (contact time 0.1–10 s):[117]

$$R-CH_2-Me \rightarrow R^{\cdot} + \dot{C}H_2Me;$$
$$R^{\cdot} + CO_2 + RCH_2Me \rightarrow RCOOH + R\dot{C}HMe;$$
$$\dot{C}H_2Me + CO_2 + RCH_2Me \rightarrow MeCH_2COOH + R\dot{C}HMe.$$

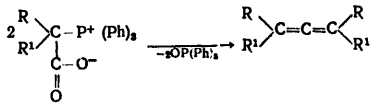
5. Reactions Involving the Addition of CO_2 to Ylid Compounds of Phosphorus

Ylid compounds of phosphorus readily interact with CO_2 at room temperature and atmospheric pressure with formation of betaine compounds (A), capable of being converted into carboxylic acid on hydrolysis in an alkaline medium[118]:

$$\begin{matrix}R\\ R^1\end{matrix}\!\!>C{=}P(Ph)_3 + CO_2 \rightarrow \begin{matrix}R\\ R^1\end{matrix}\!\!>C(COO^-)-P^+(Ph)_3 \xrightarrow{OH^-/H_2O}$$
(A)
$$\rightarrow \begin{matrix}R\\ R^1\end{matrix}\!\!>CH-COO^- + OP(Ph)_3 \xrightarrow{H^+} \begin{matrix}R\\ R^1\end{matrix}\!\!>CH-COOH.$$

Table 3 presents data for the synthesis of carboxylic acids from various P-ylids and CO_2.

Allene has been obtained in yields up to 36% by the pyrolysis of such a betaine at 200 °C:[118]



It has been suggested[118] that the reaction proceeds via a stage in which a keten is formed. On subsequent decarboxylation, the allene is formed from two molecules. This hypothesis is confirmed by the mechanism of the synthesis of an isocyanate by the reaction of CO_2 with the dialkyl N-alkylphosphoramidate anion via a stage involving the formation of carbamate at room temperature[119]:

$$(EtO)_2P(O)-NHR \xrightarrow{OH^-} (EtO)_2P(O)-\overline{N}R \xrightarrow[25^\circ C]{CO_2} (EtO)_2P(O)-NR-\overset{O^-}{\underset{\|}{C}}=O \xrightarrow{80^\circ C} (EtO)_2P(O)-O^- + R-N{=}C{=}O.$$

The yield of isocyanates is 73% for R = iso-C_4H_9, 80% for R = C_6H_{11}, and 88% for R = t-C_4H_9. We may note that the dialkyl N-alkylphosphoramidate anion reacts with carbon disulphide to form an isothiocyanate under analogous conditions[119].

Table 3. Carboxylation of P-ylids[118].

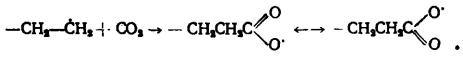
R	R¹	Yield of betaine (A), %	Yield of carboxylic acids, %
$-(CH_2)_2-$		94	90
$-(CH_2)_3-$		91	89
$-(CH_2)_5-$		98	86
$-(CH_2)_6-$		82	85
Me	Me	99	85
Ph	H	68	80

6. Organic Syntheses Based on CO_2 Under the Influence of Radiation

Alcohols, amines, carboxylic acids, and saturated and unsaturated hydrocarbons can be carboxylated with the aid of ionising radiation under the influence of free radicals, radical-ions, free atoms, and biradicals[120]. The chemical processes induced by the ionising radiation are analogous to photochemical reactions. However, whereas photochemical reactions proceed selectively, under the influence of ionising radiation the molecules are supplied with such a large amount of energy that they are involved in a wide variety of chemical processes, occurring simultaneously, which leads to a decrease of selectivity.

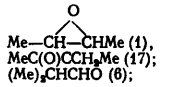
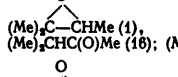
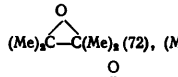
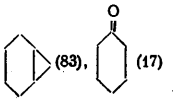
The yield of products (G) of the reaction occurring under the influence of radiation is usually calculated from the number of molecules formed following the absorption of 100 eV of energy. The reaction is performed in an aqueous solution of HCOOH or HCOONa. Thus, irradiation of a mixture of solid carbon dioxide and ethanol with γ-rays having an energy of 2 MeV yielded lactic acid ($G = 0.06$), while the use of cyclohexane, cyclohexene, and ethylamine instead of ethanol resulted in the formation of cyclohexanecarboxylic acid ($G = 0.07$),[120] a mixture of cyclohexenecarboxylic acids ($G = 0.11$), and α-alanine ($G = 0.17$).[121] Furthermore, acetic acid had been obtained from CH_4 and CO_2 by a gas-phase reaction. The replacement of CO_2 by formic acid does not affect the composition of the reaction products. Hummel and Barzynski[122] obtained carboxylic acids with a number of carbon atoms greater by unity than in the initial compound in yields of 0.15, 2.12, 2.16, 2.24, 0.33, and 0.37 by the reaction of CO_2 with cyclohexane, n-hexane, n-heptane, cyclo-octane, benzene, and toluene respectively under the influence of γ-radiation.

Ethylene reacts with CO_2 at 100 °C under the influence of γ-radiation with formation of a mixture of linear carboxylic acids having a molecular weight of 670.[123] It has been suggested that these acids are formed as a result of the addition of CO_2 to a polyethylene radical via a stabilised resonance radical, which is energetically unsuitable for further chain growth:



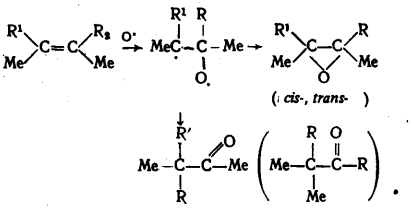
When an aqueous solution of CO_2 from which oxygen has been removed is γ-irradiated, formaldehyde and acetaldehyde are formed; the yields depend on the pH of the medium[124–126]. The addition of an insignificant amount of $FeSO_4$ (10^{-3} M) in an alkaline medium leads to a sharp increase of the yield of aldehydes. When the reaction is carried out in an acid medium, carboxylic acids are formed preferentially: HCOOH, $(COOH)_2$, CHOCOOH, and glyoxal[127].

Table 4. Radiolysis of olefins and CO_2 at room temperature.

Olefin	Relative velocity k_1/k_2	Reaction products (yield, %)
cis- Me—CH=CH—Me	1.0	 Me—CH—CHMe (1), MeC(O)CH$_2$Me (17); (Me)$_2$CHCHO (6);
(Me)$_2$C=CHMe	1.3	 (Me)$_2$C—CHMe (1), (Me)$_2$CHC(O)Me (16); (Me)$_3$CCHO (7);
(Me)$_2$C=C(Me)$_2$	1.7	 (Me)$_2$C—C(Me)$_2$ (72), (Me)$_2$C—COMe (28)
	1.3	 (83), (17)

Alicyclic and cyclic olefins mixed with H_2CO_3 in a steel autoclave (molar ratio olefin : CO_2 = 1 : 100) are converted into epoxy- and carbonyl compounds at room temperature or at 0 °C under the influence of γ-radiation (see Tables 4 and 5).

The formation of *cis*- and *trans*-2,3-epoxybutanes is treated as a result of stereoisomeric transformations of the adduct resulting from the radical addition of an oxygen atom to *cis*-but-2-ene:



The data in Table 5 show that the reactions of aromatic olefins proceed with formation of a mixture of epoxy- and carbonyl compounds with the exception of 1,1-diphenylethylene, which does not form epoxy-compounds but is converted into carbonyl compounds and oligomers (degree of conversion 97%).

Table 5. Radiolysis of aromatic olefins and CO_2 at 0 °C.

Olefin	Conversion, %	Reaction products (yield, %)
Ph—CH=CH$_2$	—	 PhCHO (4), PhCH—CH$_2$ (74) PhCH$_2$CHO (22)
PhC(Me)=CH$_2$	—	 PhC(O)Me (35), PhC(Me)—CH$_2$ (31), PhC(Me)HCHO (34)
cis- PhCH=CHPh	75	 PhCHO (21), PhCH—CHPh (*cis*-21, *trans*-53), (Ph)$_2$CHCHO (3), PhCH=CHPh (*trans*-2)
trans- PhCH=CHPh	52	 PhCHO (37), PhCH—CHPh (*cis*-1, *trans*-56) (Ph)$_2$CHCHO (2), PhCH=CHPh (*cis*-4)
(Ph)$_2$C=CH$_2$	97	PhC(O)Ph (13), (Ph$_2$)CHCHO (13), oligomer (74)

Under a CO_2 pressure up to 1 atm or in the presence of an equimolar amount of Na_2CO_3, ethanol gives rise to lactic acid under the influence of γ-radiation,[129,130] whose yields depend on the pH of the medium. $G = 1$ in an acid medium and reaches 2 in an alkaline medium. At pH 4–6 methanol reacts with CO_2 to form glycolic acid with $G = 1$–2.3.[130,131] The reaction proceeds via the mechanism

$$H_2O \rightarrow e^-_{aq},\ H_3O^+,\ H^+,\ OH^-,\ H_2,\ H_2O_2$$
$$MeOH + H^+ \text{ (or; } OH^-) \rightarrow \dot{C}H_2OH + H_2 \text{ (or } H_2O)$$
$$CO_2 + H^+ \rightarrow COOH \quad (k \leqslant 8 \cdot 10^6 \text{ mol}^{-1}\text{ s}^{-1}),$$
$$CO_2 + e^-_{aq} \rightarrow CO_2^- + n\,H_2O \quad (k = 7.67 \cdot 10^9 \text{ mol}^{-1}\text{ s}^{-1});$$
$$\dot{C}H_2OH + COOH \rightarrow CH_2(OH)COOH;$$
$$\dot{C}H_2OH + CO_2 \rightarrow CH_2(OH)COO^-;$$
$$CH_2(OH)COO^- + H_3O^+ \rightarrow CH_2(OH)COOH + H_2O.$$

In order to suppress the formation of CO_2^-, the reaction is carried out with methanol freed from oxygen.

The radiation-induced carboxylation of aliphatic amines under conditions analogous to those in the carboxylation of

alcohols, gives rise to aminoacids[132,133]. Thus, when a solution of methylamine saturated with CO_2 is irradiated with γ-rays, glycine is formed with a yield $G = 0.8$ at pH 9:

$$MeNH_2 + H^{\cdot} \rightarrow \dot{C}H_2NH_2 + H_2;$$
$$MeNH_2 + OH^{\cdot} \rightarrow \dot{C}H_2NH_2 + H_2O;$$
$$\dot{C}H_2NH_2 + CO_2 \rightarrow CH_2NH_2COO^{\cdot};$$
$$\dot{C}H_2NH_2 + \dot{C}OOH \rightarrow CH_2NH_2COOH;$$
$$CH_2NH_2COO^- + H_3O^+ \rightarrow CH_2NH_2COOH + H_2O.$$

At pH > 9 the yield of glycine falls sharply, owing to the decrease of the amount of CO_2 and the occurrence of side reactions. An analogous behaviour has been observed also in the carboxylation of ethylamine[133].

The radiation-induced carboxylation of formic acid with the aid of $^{14}CO_2$ at pH 3.5 leads to the formation of labelled oxalic acid ($^{14}COOH.COOH$) with $G = 1.2$.[129,130] An increase of the pH of the medium from 5 to 6 leads to an increase of the yield of oxalic acid to $G = 7.2$ and $G = 7.6$ respectively[134,135]:

$$CO_2^{\cdot-} + HCOO^- \rightarrow (CO_2^{\cdot-} \cdot HCOO^-);$$
$$(CO_2^{\cdot-} \cdot HCOO^-) + CO_2 \rightarrow CO_2^{\cdot-} + (COO \cdot COOH^-).$$

In neutral and alkaline media the reaction proceeds with the preferential formation of oxalic acid, which is suppressed in an acid medium as a consequence of the reaction $COOH \rightarrow HCOO$.[136]

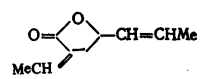
The effect of γ-radiation on aromatic hydrocarbons of the type of benzene, toluene, and xylene in a mixture with CO_2 at 0 °C leads to the formation of substituted phenols[137]. Since the addition of SF_6, which is a powerful electron acceptor, in the reaction between CO_2 and toluene did not result in the formation of cresol and only lines corresponding to O^- and CO_3^- were noted in the mass-spectrum of CO_2, the following reaction mechanisms were proposed:

$$MePh \rightarrow MePh^+ + e;$$
$$CO_2 \rightarrow CO_2^+ + e \text{ (were } CO + O);$$
$$O + e \rightarrow O^-;$$
$$MePh + O^- \rightarrow MePhO^-;$$
$$O^- + CO_2 \rightarrow CO_3^-;$$
$$MePh + CO_2^- \rightarrow MePhO^- + CO_2;$$
$$MePhO^- + M^+ \rightarrow MePhOH + M.$$

7. Catalytic Syntheses Based on CO_2

Catalytic reactions based on CO_2 constitute a relatively little investigated field of organic chemistry. It was noted above that the insertion of CO_2 in molecules of complex compounds can serve as a basis of catalytic processes designed to obtain different functional compounds. Thus the reaction of a cobalt carboxylate complex containing an ethyl group with MeI or H^+ yields respectively ethyl acetate or ethyl formate[18,33]. The anomalous pathway in the insertion of CO_2 in the M–L bond with formation of compounds containing a metal–carbon bond (metal-carboxylic acids) suggests the possibility of the synthesis of unsaturated carboxylic acids.

The triphenylphosphine complex of palladium in an active catalyst of the carboxylation of ethylene with formation of propionic acid. In the presence of $(PPh_3)_2PhCl_2$ and H_2O at an overall C_2H_4 and CO_2 pressure of 350 atm ethylene is carboxylated at 165 °C with formation of propionic acid, the yield being up to 400 moles per mole of the catalyst introduced[138]. Propene reacts with CO_2 and H_2 only under more severe conditions (300 °C, $p_{CO_2} = 1000$ atm) in the presence of cobalt carbonyl modified with trialkylphosphine and a condensed system incorporating a carboxylic acid and a nitrogen-containing Lewis base; the reaction leads to the formation of 2-ethylhexanal or 2-ethylhexanol[139]. The reaction of CO_2 and H_2 with butadiene in the presence of $Pd[Ph_2P(CH_2)_2PPh_2]_2$ in DMF at 84–120 °C results in the formation of 12.3% of 2-ethylidenehept-5-ene-4-olide:



The reaction is accompanied by the formation of up to 53.3% of polyene-hydrocarbons[140].

Carbon dioxide can also be inserted in the Co–H bond with formation of a formate fragment, which is converted by an alkyl halide into a formate ester. This reaction is also catalysed by the complexes $L_3OS(CO)HCl$, L_3IrHCl, and L_2PtHCl (where L = PPh_3).[31] Using as an alkylating agent a solution of BF_3 in CH_3OH, Hashimoto and Inoue[141] synthesised a formate ester via the mechanism

$$L_nMX + H_2 + L_nMH \xrightarrow{CO_2} L_nMOC(O)H + HCOOMe \xrightarrow{MeOH} L_nM(OH) \xrightarrow[-H_2O]{H_2} L_nMH.$$

The reaction proceeds at atmospheric pressure at a temperature of 20–100 °C. The results obtained are presented in Table 6. Group VIII metal (iron, cobalt, nickel, and platinum) hydride complexes catalyse this reaction, which takes place in tertiary amines with a yield of methyl formate up to 23.4 moles per mole of complex[142]. Sodium formate has been obtained in 73.1% yield by the reaction of sodium carbonate or CO_2 with H_2 at a pressure of 108 atm and a temperature of 280 °C. $PtCl_2.H_2O$ was used as the catalyst[143].

Table 6. The synthesis of methyl formate from CO_2 and H_2.[144]

Complex	t, °C	Yield of HCOOCH*	Complex	t, °C	Yield of HCOOCH*
$(PPh_3)_4RuCl_2$	100	9.0	$(PPh_3)_3IrH_3$	100	38.2
$(PPh_3)_4RuCl_2$	20	1.0	$(PPh_3)_3IrH_3$	20	0.9
$(PPh_3)_4RuH_4$	100	4.2	$(PPh_3)_3IrHCl_2$	100	0.2
$(PPh_3)_4RuH_2$	20	0.6	$(PPh_3)_2Ir(CO)Cl$	100	0.2
$(PPh_3)_3RuHCl$	100	17.0	$(PPh_3)_3Os(CO)HCl$	100	0.6
$(PPh_3)_3RuCl_2$	100	9.0	$(Et_3P)_2PtCl_2$	100	0.1

*The yield is given in moles of HCOOMe per mole of the catalytic complex.

In the presence of Group VIII metal complexes secondary amines react with CO_2 and H_2 at 50–60 atm and 100–125 °C with formation of dialkylformamides and equimolar amounts of water[98,144]:

$$CO_2 + H_2 + R_2NH \xrightarrow{\text{catalyst}} HCONR_2 + H_2O$$

The catalysts $CoH(dpe)_2$, $CuCl(PPh_3)_3$, and $IrCl(CO)(PPh_3)_2$, in the presence of which the yield of DMF from dimethylamine reached 1200 moles per mole of catalyst in benzene, showed the highest activity. When n-hexane is used as the solvent, the phosphine complex of ruthenium catalyses this reaction under the same conditions (the yield of DMF is 57.4% [144]—Table 7).

Table 7. The synthesis of dimethyl formamide from CO_2 and an amine[144].

Catalyst	Amount of catalyst, mmoles	Me_2NH, mmoles	t, °C	Yield of DMF*
$(PPh_2CH_2CH_2PPh_2)_2CoH$	1.08	138	100	5
$(PPh_2CH_2CH_2PPh_2)_2CoH$	0.05	131	125	1000
$(PPh_3)_3RhCl$	0.3	122	100	43
$(PPh_3)_3RhCl$	0.02	138	125	170
$(PPh_3)_2(CO)RhCl$	0.38	144	100	1
$(PPh_3)_2(CO)IrCl$	0.35	133	100	28
$(PPh_3)_2(CO)IrCl$	0.2	138	125	1200
$(PPh_3)_2(CO_3)Pd$	0.79	159	100	120
$(PPh_3)_2(CO_3)Pd$	0.7	155	125	104
$(PPh_3)_2Pt$	0.56	155	125	19
$(PPh_3)_3RuCl_2$	0.39	132	125	8
$(PPh_3)_3CuCl$	0.63	133	100	8
$(PPh_3)_3CuCl$	0.03	142	125	900
$H_2PtCl_4 \cdot 6H_2O$	0.56	124	125	11

*The yield is given in moles of DMF per mole of catalyst.

Catalysts based on ruthenium, rhodium, palladium, and platinum are active in the synthesis of urea from NH_3 and CO_2 at temperatures betwen 0° and 300 °C, the presence of small amounts of H_2 and O_2 in the initial CO_2 not influencing the yields of the required product[145].

In solution in a mixture of acetonitrile and ether saturated with CO_2, diethylaminopropyne is converted in 1 h at -60 °C (or at room temperature under CO_2 pressure) into the *N*-methyl-*N*-phenyldiamide of allene-1,3-dicarboxylic acid, the hydrogenation of which on a platinum catalyst gave rise to the *N*-methyl-*N*-phenyldiamide of glutaric acid in up to 85% yield[146]. The continuous synthesis of aminoacids from CO_2 and amines at atmospheric pressure and in the presence of ion-exchange resins is extremely interesting and promising from the practical point of view[146]. Primary and secondary C_1–C_{16} amines, C_1–C_{15} di- and tri-amines, aminoalcohols, and alkyl aminocarbonates readily react with CO_2 at 20–80 °C in the presence of ion-exchange resins of the type Amberlite-45, A-400, 410, IR-45, and Dowex-3 as well as $CuCl_2$ or $Cu(OAc)_2$, forming the corresponding α-aminoacids in up to 85% yield.

Since nitro-groups are powerful electron acceptors, nitroalkanes exhibit in many reactions the properties of a weak acid and are capable of splitting off a proton with formation of a carbanion, which undergoes nucleophilic addition to CO_2 in the presence of alkylcopper complexes[101]:

$$MeNO_2 + RCu(PPh_3)_3 \xrightarrow{-RH} O_2N{-}CH_2{-}Cu(PPh_3)_3 \xrightarrow{CO_2} \rightarrow O_2NCH_2COOCu(PPh_3)_3 \xrightarrow{H_2O} O_2NCH_2COOH .$$

The reaction proceeds via a stage involving the formation of a nitroalkylcopper complex with insertion of CO_2 in the M–C bond and the formation of a carboxylic nitroacid on subsequent hydrolysis with water. This reaction is used nowadays as a model for the investigation of the chemical properties of biotin (vitamin H).[76]

Extremely interesting results have been obtained using sodium phenoxide as a catalyst in the carboxylation of methyl esters of alkanecarboxylic acids with carbon dioxide. The reaction proceeds via a carbanion formation stage. In the presence of sodium phenoxide in DMF at atmospheric pressure and a temperature of 50–70 °C methyl acetate is readily carboxylated with formation of malonate esters (yield 70 to 90%):[147–151]

$$MeCOOMe + CO_2 \xrightarrow[DMF]{PhONa,CH_3N_3} MeCOOCH_2COOMe .$$

Instead of PhONa, it is possible to use the sodium derivatives of *p*-cresol, 3,5-xylenol, and resorcinol[150].

Below 25 °C, sodium phenoxide catalyses the carboxylation of dialkyl ketone to oxoglutaric acid and its derivatives (yield 47–75%):[152–154]

$$MeCMe \underset{O}{\parallel} + 2CO_2 \xrightarrow[DMF]{PhONa} HOOCCH_2C(O)CH_2COOH .$$

The yield of oxoglutaric acid increases to 85% at $p_{CO_2} = 10$ atm.[153]

In the presence of sodium phenoxide[155] and potassium 2,6-di-t-butyl-*p*-cresoxide[156] aliphatic and aromatic nitriles readily react with CO_2, forming carboxylic cyanoacids:

$$MeCN + CO_2 \rightarrow NCCH_2COOH \quad \text{(yield 88\%)};$$

$$C_6H_5CH_2CN + CO_2 \rightarrow C_6H_5CH(CN)COOH \quad \text{(yield 30\%)}.$$

Sodium amalgam (Na–Hg) catalyses the carboxylation of allyl chloride to acrylic acid in an aprotic polar solvent[157]. In the presence of NaCl, KCl, and CoI_2 at 450 °C and p_{CO_2} = 25–50 atm sodium phenoxide itself is carboxylated to trimesic acid (benzene-1,3,5-tricarboxylic acid) in 70% yield[158,159].

The metal hydrides $LiAlH_4$, NaH, LiH, $NaBH_4$, and $LiAl(OCMe)_3$ proved to be active catalysts of the carboxylation of pyridine, which takes place in THF at atmospheric pressure with formation of nicotinic acid[160], the yield of which reaches up to 90% at $p_{CO_2} = 10$ atm in dioxan.

According to the generally accepted view[161–165], the catalytic synthesis of MeOH from CO_2 and H_2 proceeds via the intermediate formation of carbon monoxide:

$$CO_2 + H_2 \rightarrow CO + H_2O ;$$
$$CO + 2H_2 \rightarrow MeOH .$$

However, the experimental data obtained using labelled $^{14}CO_2$, which served as a basis for a new mechanism suggested that the synthesis of methanol proceeds with direct participation of CO_2:[166]

$$CO_2 \begin{cases} \xrightarrow{+3H_2} MeOH + H_2O \\ \xrightarrow{+H_2} CO + H_2O \end{cases} .$$

The conversion of CO into CO_2 has been demonstrated by the transfer of the label from carbon monoxide to carbon dioxide. The transfer of the label via MeOH is ruled out.

The syntheses of hydrocarbons and dimethyl ether from CO_2 and H_2 in the presence of the graphite–$PdCl_2$–N catalytic system, which take place under mild conditions, have been described[167]. The addition of HCHO or MeOH to the reaction zone increases the rate of formation of dimethyl ether. The use of $RhCl_3$, $IrCl_3$, $CoCl_2$, $OsCl_3$, and $FeCl_3$ instead of $PdCl_2$ causes a sharp decrease of the yields of the reaction products. It has been suggested[167] that the reaction proceeds via a stage involving the formation of intermediate MeO or HCO radicals, produced as a result of the reduction of CO_2 by hydrogen, Pd^{2+} passing at the same time to the lowest oxidation state (Pd^+ or Pd^0).

IV. INDUSTRIAL PROCESSES WITH PARTICIPATION OF CO_2

In the form of liquid carbonic acid and dry ice, carbon dioxide is used as a cooling agent and a solvent, in the casting industry, and in the synthesis of urea, sodium carbonate, and ammonium carbonate.

Large-scale industrial syntheses based on CO_2 have not so far been achieved with the exception of the industrial method for the synthesis of salicylic and hydroxybenzoic acids by the Kolbe–Schmidt reaction[168]. The *p*-hydroxybenzoid acid and its derivatives obtained by this procedure are widely used in the food, light, and polymer industries.

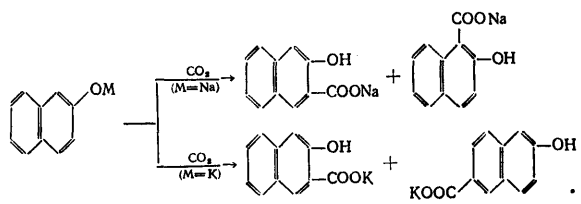
Table 8 presents the results of the carboxylation of sodium phenoxide in a homogeneous system in an aprotic solvent. The reaction proceeds with preferential carboxylation in the *para*-position, while carboxylation in a heterogeneous system takes place with the preferential formation of salicylic acid, i.e. with carboxylation in the *meta*-position. The introduction of potassium into the reaction zone and an increase of temperature to 220 °C tend to increase the yield of the required product above 80%.[169–171]

Table 8. Carboxylation of alkali metal phenoxides (PhOM) in aprotic solvents. ($\tau = 30$ min).[171]

M	Solvent	P_{CO_2}, atm	t, °C	Yield*, %	Compn. of reaction product, %		
					p-hydroxybenzoic acid	salicylic acid	4-hydroxyisopthahlic acid
K	DMF	bubbling	100	24.2	88	12	0
K	DMF	bubbling	150	30.8	83	16	1
K	DMSO	bubbling	100	22.0	94	2	4
K	DMF	5	140	33.5	88	9	3
K	DMF	5	180	41.5	83	13	4
K	DMSO	5	100	23.9	94	2	4
Na	DMF	bubbling	100	10.0	66	32	2
Na	DMF	bubbling	140	22.0	63	36	1
Na	DMSO	bubbling	100	16.5	83	11	6
Na	DMF	5	140	36.1	70	27	3
Na	DMF	5	180	45.4	53	35	12
Na	DMSO	5	140	41.1	81	13	6

*The overall yield of hydroxybenzoic acid and its derivatives is given.

The nature of the alkali metal cation influences markedly the composition of the reaction product. Thus, whereas sodium phenoxide gives rise to salicylic acid, carboxylation of potassium phenoxide under the same conditions leads to a mixture of salicylic and *p*-hydroxybenzoic acids. The influence of the cation on the mode of the reaction involving a series of naphthalene and quinoline derivatives is striking[168]:



The reaction is carried out either by treating the corresponding dry alkali metal phenoxides with CO_2 at 120–130 °C or by heating a mixture of the phenol with an excess of K_2CO_3.

The Kolbe–Schmidt reaction constitutes the main industrial method for the synthesis of salicylic acid from phenol, of aminosalicylic acid from *m*-aminophenol, and of β-hydroxynaphthoic acid from β-naphthol.

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Thus syntheses based on CO_2 make it possible to obtain a wide range of organic compounds of practical importance. At the same time, very few reactions based on CO_2 have been utilised in industry, which is due primarily to the lack of effective carboxylation catalysts[171]. Advances in the field of metal complex catalysis in recent years as well as in the field of the activation of small molecules suggest that active and selective catalytic systems will be developed, on the basis of which the problem of the wide-scale employment of CO_2 will be resolved.

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