

Carbon Dioxide as a Source of Carbon in Chemical Synthesis

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Abstract

Modern achievements in the chemistry of carbon dioxide have been considered. When utilizing carbon dioxide in chemical synthesis, two groups of reactions: reactions of carboxylation (carboxyamidation) of organic compounds with carbon dioxide and reactions of carbon dioxide reduction – are supposed to be the most prospective.

Introduction

Uncontrolled exhausts including carbon dioxide increase their greenhouse effect. Now, accumulation of anthropogenic greenhouse gases has resulted in the increase of average global temperature of the Earth's surface by more than 0.5°C. The further rise in this temperature can lead to irreversible catastrophic consequences: to the change of the climate due to the global warming, thawing of the high-mountainous and polar glaciers, flooding of a significant part of the land, etc. Therefore, mankind faces a complex urgent problem of decreasing emission of greenhouse gases, first of all, that of carbon dioxide. Different ways of decreasing the emission of carbon dioxide are proposed, which may be divided into three main groups:

1. Minimization of carbon dioxide emission. This way is already being realized by introducing new ecologically friendly industrial technologies. In future, this way may become the most real one. Highly effective methods of obtaining electric power, conservation of energy and recycling of products are supposed to be used. Combined production of electric and thermal energy may contribute to the capacity of power plants.

2. Exclusion of carbon dioxide emission. This way supposes a wider use of the energy of nuclear fission, the sun, the wind, geothermal water and

water power as well as combustion of the biomass being restored and reduction of felling area.

3. Control over carbon dioxide emission. This way supposes the removal of carbon dioxide from production waste gases and its utilization in different branches of industry including chemical industry as a source of carbon for chemical synthesis.

The third group of the ways of decreasing accumulation of carbon dioxide in the atmosphere is quite real and is of great interest. The removal of CO₂ from production waste gases is not difficult from the technological point of view. There already exist large power plants which trap carbon dioxide from waste gases in full volume. For example, in Shady Point (Oklahoma, the USA) there is an electric power station with the capacity of 300 MW which traps 200 tons of carbon dioxide from waste gases of hydrocarbon fuel combustion a day [1]. The removed carbon dioxide is liquefied and purified to be used in liquid and solid states in food industry. To trap carbon dioxide, monoethanolamine is used which sorbs CO₂ at low temperature ($\approx 20^{\circ}\text{C}$) and desorbs it when heated (150°C). This method is very effective and allows obtaining CO₂ of high degree of purity.

There are different ways of utilization of carbon dioxide in commercial scales. One should note its wide use in oil fields of the USA and Canada to enhance oil recovery. There are also other different ways of utilization of CO₂ as a refrigerating medium (in the form of "dry ice"), a solvent, for

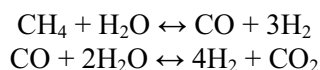
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carbonation of drinks, for acceleration of growth of plants under glass. etc. Of special interest is its use as a carbon raw material in industrial chemical synthesis.

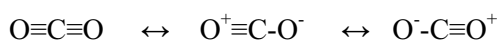
Carbon dioxide as a chemical raw material

Carbon dioxide may be considered to be the most important and cheap source of carbon raw material in future. Oil and coal reserves are being quickly exhausted. At present, they are estimated to be $(5\div 10) \cdot 10^{12}$ t in terms of carbon. The reserves of natural gas will be depleted soon after exhaustion of oil and coal. The total amount of CO_2 in the atmosphere and ocean makes up $\sim 1.5 \cdot 10^{14}$ t (in terms of carbon), i.e. by an order and a half greater and in the lithosphere it is greater by two orders of magnitude.

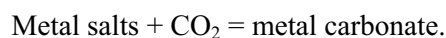
Despite enormous reserves of CO_2 , it can't be used as a chemical raw material in large scales due to its low concentration in the atmosphere (only 0.03%). In the lithosphere, carbon dioxide occurs in a concentrated state in the form of natural carbonates, however, decomposition of carbonates requires great consumption of energy. The most prospective sources of CO_2 as a raw material may be waste gases of power plants (electric power stations), of many other industrial enterprises as well as natural gases. The content of carbon dioxide in some natural gases reaches 30-90%. A great amount of CO_2 is obtained by oxidizing conversion of methane with production of hydrogen (conversion of water gas):



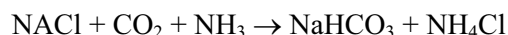
Analysis of the available data shows that CO_2 , regardless of the wide-spread notions, can enter various reactions with other molecules. Reactivity of carbon dioxide is much higher than that of nitrogen. The molecule of CO_2 has a linear structure with the value of ionization potential of 13.7 eV and affinity to electron of 3.8 eV. The greater part of electron charge density is concentrated on atoms of oxygen. Formation of bonds in CO_2 may be described with the help of three resonance structures:



Synthesis of metal carbonates may serve as an example of a large-scale use of CO_2 in inorganic synthesis:



This method (Solvey method) is used to produce sodium bicarbonate from CO_2 , NaCl and NH_3 . The world annual production of sodium bicarbonate makes up about 30 mln tons.



Sodium carbonate is produced by calcination of NaHCO_3 :



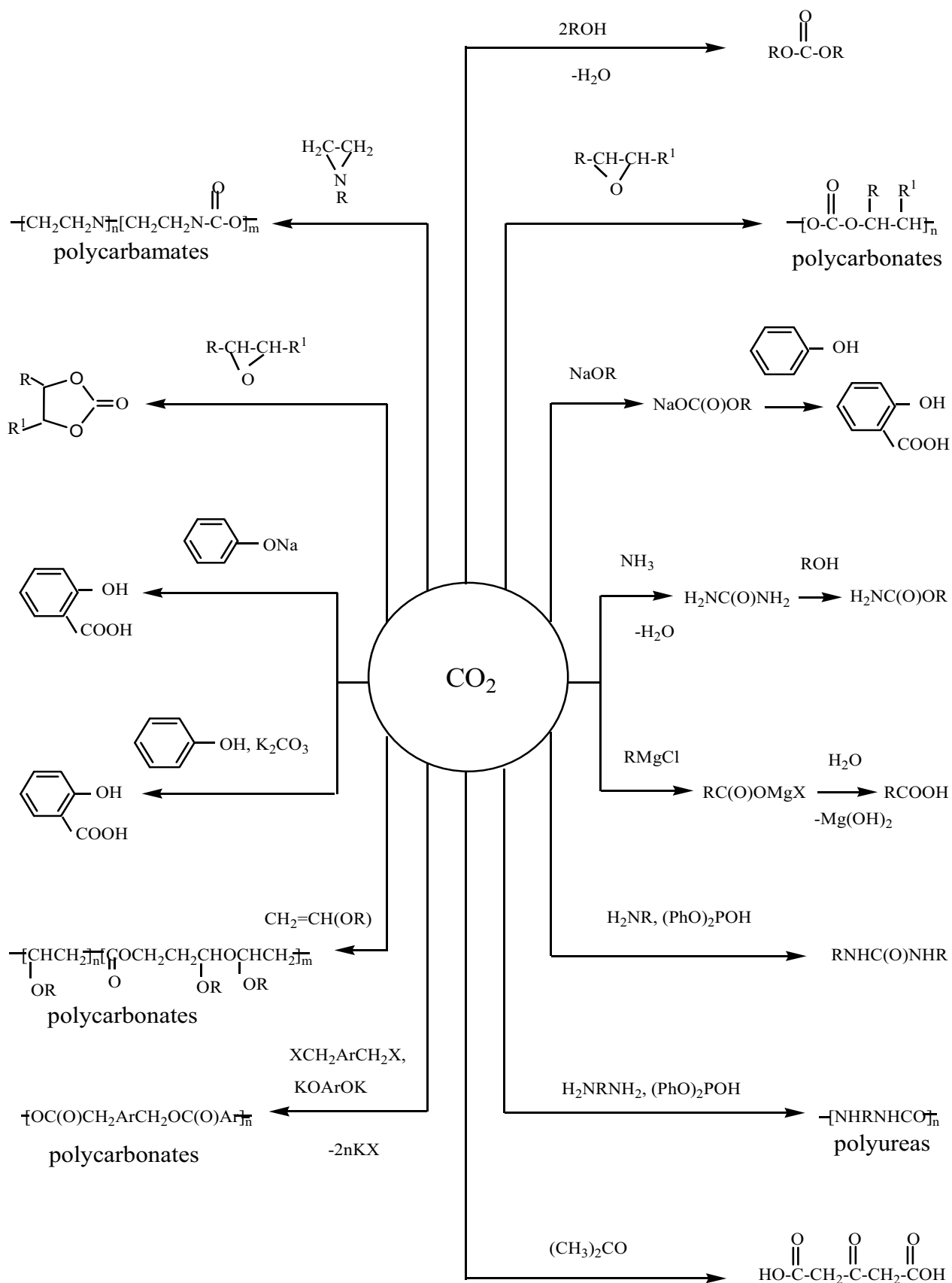
The use of carbon dioxide in organic synthesis is prospective. The modern development of carbon dioxide chemistry allows supposing the development in this direction of two main groups of reactions:

1. Reactions of carboxylation and carboxyamidation of organic compounds with carbon dioxide;
2. Reactions of carbon dioxide reduction;
3. The first group reactions may be both non-catalytic and catalytic, mainly homogeneous-catalytic at low temperatures. At present, the second group reactions are realized, as a rule, at high temperatures in the presence of heterogeneous catalysts (metal, metal oxides).

Reactions of carboxylation (carboxyamidation) of organic compounds with carbon dioxide

This direction in utilization of carbon dioxide in organic synthesis is that it is used for synthesis of organic compounds containing a carboxyl group – $\text{C}(\text{O})\text{O}$ - (carbonic acids, esters, lactones and others) or a carboxamide group – $\text{C}(\text{O})\text{-NR}$ - (carbamide, amides and others) (Scheme 1).

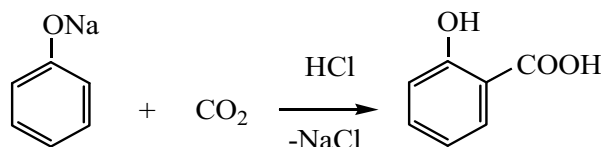
An example of a large-scale use of carbon dioxide in this direction is synthesis of carbamide (urea) by interaction of CO_2 with NH_3 at 120-300 atm at 160-210°C. The reaction proceeds via intermediate formation of ammonium carbamide:



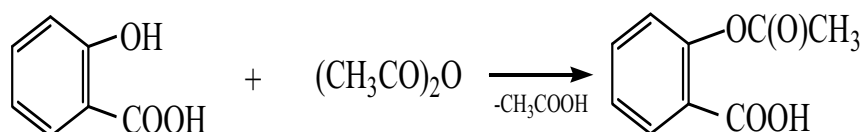
Scheme 1

The world volume of carbamide production makes up more than 110 mln tons a year. Carbamide is widely used as a fertilizer, fodder additive and in production of plastics.

Another example of the use of carbon dioxide in organic synthesis is production of salicylic acid by carboxylation of sodium phenolate with carbon dioxide under pressure (Kolbe-Schmidt reaction):



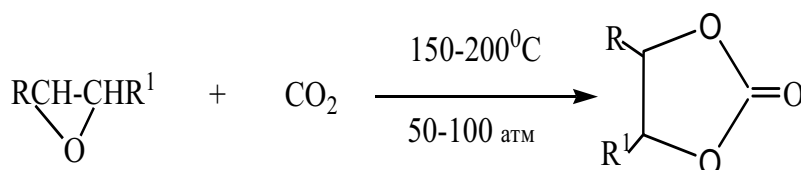
A medicinal preparation – aspirin (acetylsalicylic acid) is produced from salicylic acid.



The USA alone produces 25 thousand tons of aspirin a year.

Synthesis of organic carbonates on the basis of

carbon dioxide has been developed lately. Organic carbonates may be produced by interaction of oxyranes with carbon dioxide.



A wide spectrum of useful products may be produced on the basis of organic carbonates (Scheme 2)

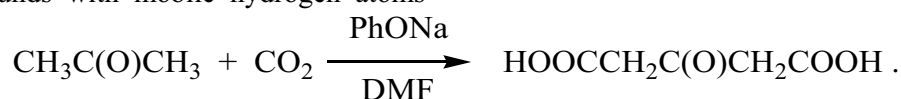
Syntheses of carbonic acids and their derivatives on the basis of carbon dioxide using metal-organic

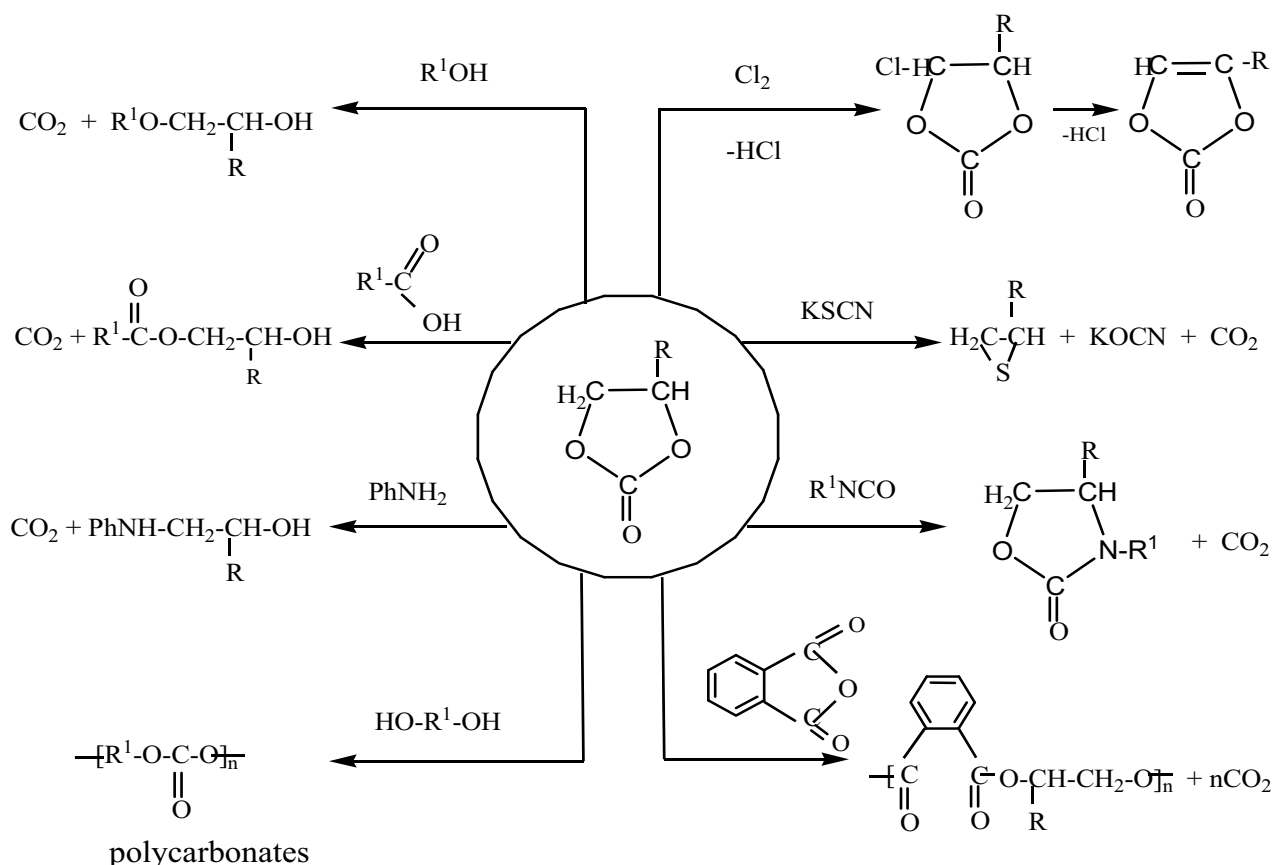
compounds are widely known. For example, a well-known laboratory method of synthesis of carbonic acids by interaction of carbon dioxide with metal-organic compounds:



This reaction may be considered as a nucleophilic interaction of carbon dioxide with carbanion R^- being formed from alkyl magnesium halogen. The above mentioned Kolbe-Schmidt reaction proceeding due to the transfer of π -electron from the aromatic nucleus to carbon dioxide refers to the same type of reaction. Carboxylation of organic compounds with mobile hydrogen atoms

(C-H acid compounds) by carbon dioxide proceeds by the same carbanionic mechanism. These reactions catalyze strong bases. For example, at the temperature lower than 25°C sodium phenolate catalyzes the reaction of carboxylation of acetone with formation of ketoglutaric acid (with the yield of 47-75%) [3]:

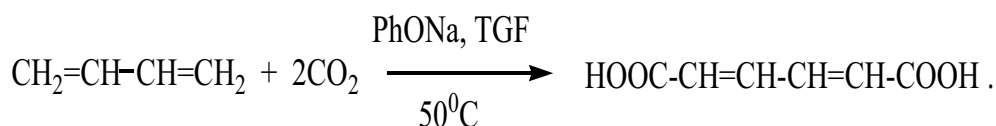




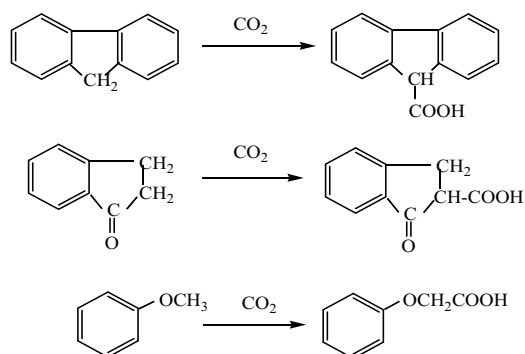
Scheme 2

Diene hydrocarbons with conjugated double bonds (butadiene, isoprene, pentadien-1.3) are easily carboxylated with formation of dicarboxylic acids in the presence of alkaline metal phenolates.

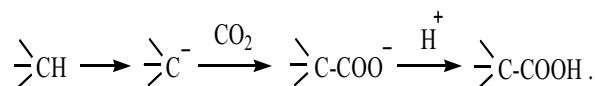
So, butadiene is carboxylated at 50°C into muconic acid with the yield of 87% at atmospheric pressure in an equimolar amount of sodium phenolates [4]:



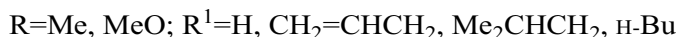
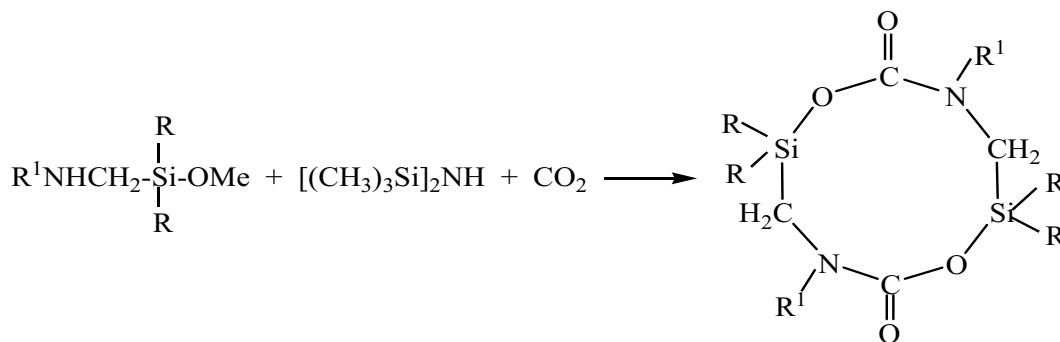
The possibility of synthesis of the corresponding carbonic acids with the yield of 30-80% by carboxylation of the mentioned below compounds with mobile atoms of hydrogen is shown [5,6]:



Such are the reactions of organic compounds characterized by weak acidity and a tendency to metallization followed by formation of carbanion. The nucleophilic attack of carbon dioxide by this carbanion results in formation of carbonic acids or their derivatives according to the scheme [7]:

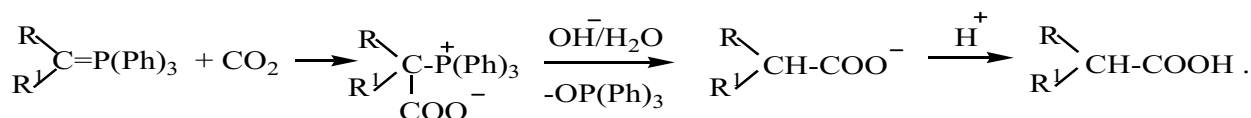


The reaction of carboxylation of silicon organic compounds proceeds by the carbanionic mechanism [8]:



Phosphorus ylides readily interact with CO_2 at room temperature and atmospheric pressure with

formation of betaines which, being hydrolyzed in an alkaline medium, transform into carbonic acids [9]:



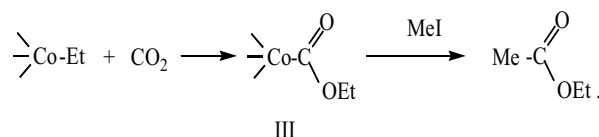
Activation of CO_2 by metal complexes holds out strong hopes. The molecule of CO_2 has a filled electron shell and, therefore, possesses a low reactivity. The main difficulty is that the binding energy of carbon dioxide with the transition metal atom (20-60 kJ/mole) in the complex is low and there is no time for CO_2 molecule to react with another molecule in the coordination sphere of metal: its life-time is short.

Therefore, it is necessary to enhance the reactivity of carbon dioxide in the intermediate active complex by choosing appropriate ligands, metal-complex formers, etc.

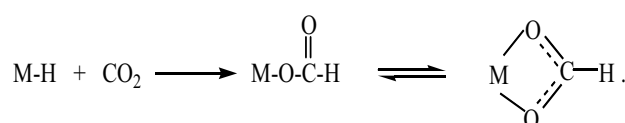
Unlike the case with carbon monoxide, there are few works dealing with the description of CO_2 complexes with transition metals. Formation of complexes on account of interaction of CO_2 with a metal as an electron acceptor (I) or as a nucleophile (II) is most probable. In the first case, coordination bond is formed via carbon atom with transition of metal electrons on it and formation of metal organic compounds (the derivatives of metal-carbonic acids), and in the second case – via formation of a π -complex with participation of a double bond $\text{C}=\text{O}$. One can judge about the presence of carbon dioxide as a ligand in the complexes by evolution of CO_2 when heating complexes or treating them with acids as well as by removing carbon dioxide with carbon monoxide.



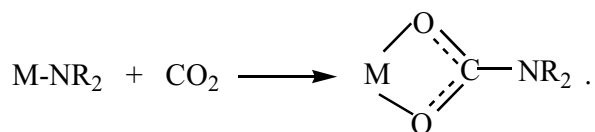
It is stated that carbon dioxide activated in the coordination sphere of a metal-complex former may enter interstitial reactions by bonds M-H, M-C, M-O or M-M (where M is a transition metal) [10-12]. With introduction of CO_2 by M-C bond, carboxylate complexes are formed. For example, the reaction of carbon dioxide with ethyl derivative of cobalt yields a carboxylate complex (III) the treatment of which with iodous methyl results in formation of ethyl acetate [13, 14]:



Introduction of CO_2 by M-H bond results in formation of formiate complexes:



Introduction of CO₂ by M-N bond results in formation of carbamate complexes:

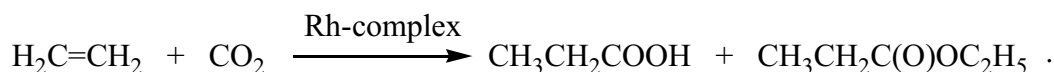


The results of CO₂ introduction by M-O bond is formation of complexes with monoethers of carbonic acid. Copper alcoholate reacts with carbon dioxide at room temperature with formation of copper acetate which forms dialkylcarbonate under the action of alkyl iodide:



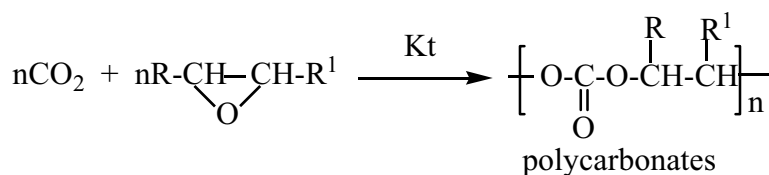
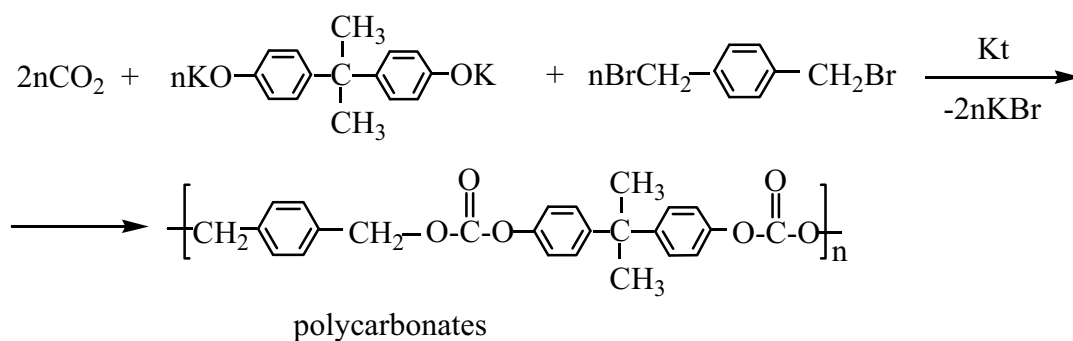
Interaction of carbon dioxide with organic compounds by C-H bond in the presence of metal complex catalysts is the basis of synthesis of carbonic acids and their derivatives. So, propionic

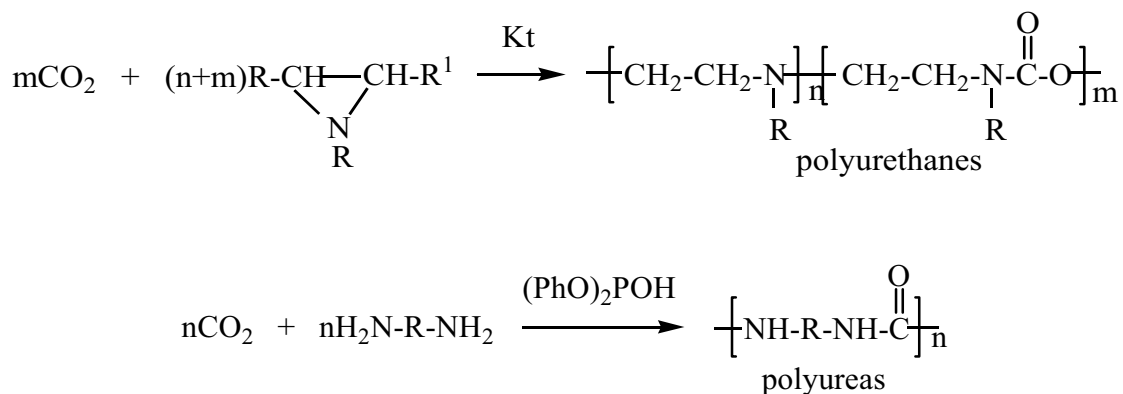
acid and its ethyl ether were obtained by carboxylation of ethylene at high pressure and temperature 165°C on a rhodium complex promoted by halogen acids [15]:



Finally, one should note great successes in the field of using carbon dioxide for producing polymer materials [16]. Systematic information on synthesis, structure and properties of copolymers on the basis of carbon dioxide has become available since the middle of 1980-ies. At present, some polymer materials on the basis of CO₂ (polypropylene-carbonate and others) are produced on pilot plants

[17]. Polymers with participation of carbon dioxide are formed by the methods of polycondensation of the latter with reactive monomers of bifunctional nature, such as dihalogenides of aliphatic and aromatic hydrocarbons, diols, diamines, as well as by polycombination reactions of epoxides, cyclic ethers, episulphides, aziridines, vinyl ethers, dienes and other monomers with carbon dioxide [16]:

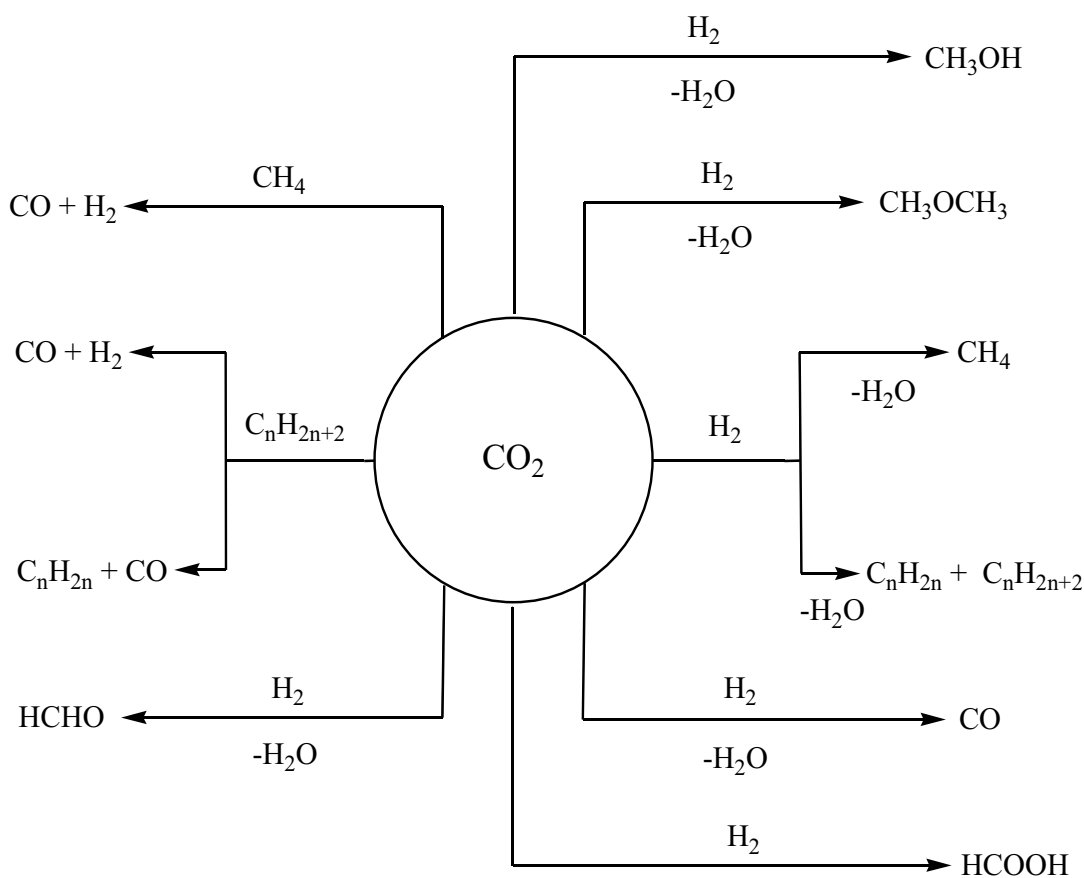




Reactions of carbon dioxide reduction

From the point of view of a large scale utilization of carbon dioxide it is commonly recognized that this group of reactions on the basis of carbon dioxide is the most promising [1,2]. Hydrogen and such cheap reagents as hydrocarbons of natural sources of raw materials (oil, gas) may be used as reducing agents in the reactions of carbon

dioxide reduction. This group of reactions on the basis of carbon dioxide may provide large scaled syntheses of such valuable products as methane (and other higher alkanes and alkenes), carbon monoxide, formaldehyde, formic acid, methanol as well as synthesis-gas – a quite valuable raw material for many large-scaled industrial processes (Scheme 3).

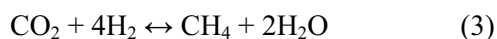
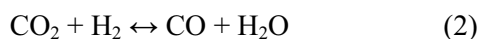


As is known, in nature, in plants and some microorganisms with the help of chlorophyll, which transforms the absorbed energy of sunlight into a chemical energy, under mild conditions there proceeds the reaction of reduction of carbon dioxide by water and in an enormous scale synthesis of organic compounds is being realized. Though numerous attempts have been made to simulate this natural photochemical process, at present chemists are still far from solution of this problem. It is obvious that solution of this problem might be of great importance for utilization of carbon dioxide. Apparently, in future there will appear two approaches to solution of this extremely important and interesting problem:

1. Development of effective photo transforming systems on the basis of transition metal complexes for transformation of the energy of visible light into a chemical energy, i.e. simulation of photosynthesis.
2. The use of enzymes extracted from bacteria.

It should be noted that the carried out investigations on the reactions of carbon dioxide reduction were based, mainly, on the use of heterogeneous catalysts (metals, metal oxides). One of the most studied reactions is the reaction of reduction of carbon dioxide by hydrogen. Undoubtedly, in case a cheap source of hydrogen is found it is this reaction that may become the basis of the most large-scaled use of carbon dioxide.

From the point of view of a large-scaled utilization, the most important reactions of carbon dioxide with hydrogen are: the reaction of synthesis of methanol (reaction 1), a reversible conversion of water gas (reaction 2) and synthesis of methane (and other higher alkanes) according to Sabatier reaction (reaction 3):

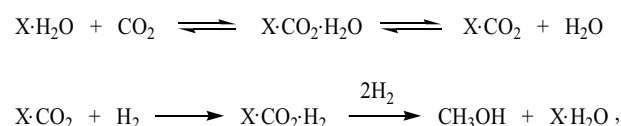


Production of methanol from carbon dioxide according to reaction (1) is most prospective. At present, synthesis-gas ($\text{CO} + \text{H}_2$) in the presence of copper-zinc-oxide catalysts is known to be used for synthesis of methanol.

According to the latest data [18], not CO, as it was thought earlier, but CO_2 which is formed from CO reacts with hydrogen. This holds an attractive possibility to synthesize methanol directly from

carbon dioxide according to reaction (1), though from the thermodynamical point of view according to this reaction it is profitable to produce not methanol but dimethyl ether.

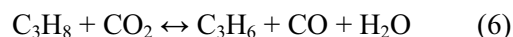
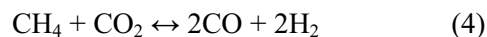
To synthesize methanol by reduction of carbon dioxide by hydrogen, a lot of catalysts are used, and there are different points of view on the mechanism of the process. So, on copper-zinc-oxide catalysts the process is supposed to proceed via the stages of adsorption substitution [19, 20]:



where X is a copper containing centre of the surface which does not belong to the phase of copper, for example, a doublet of copper ions in the lattice of zinc oxide [19].

Another prospective direction of carbon dioxide utilization is synthesis of methane and other higher alkanes according to reaction (3). In future, commercial realization of this process will allow to produce hydrocarbon fuels from carbon dioxide. Sabatier reaction proceeds at temperatures higher than 200°C in the presence of different catalysts, the best of which are ruthenium or nickel on carriers [2].

At the temperature higher than 590°C the equilibrium of reaction (3) shifts to the left side: vapor conversion of methane takes place. Among other reducers, of great interest is the use of hydrocarbons due to their cheapness (they are produced from natural sources of oil and gas). As a result of these reactions (reactions 4-7), a valuable chemical raw material – synthesis-gas and olefins are obtained:



Different methods are used for commercial production of synthesis-gas from the mixture of CH_4 and CO_2 (reaction 4). The so-called “Kalkor-process”-conversion of the mixture of natural gas (or oil gas) with carbon dioxide is known [21]. The firm “Topse” uses mixture $\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O}$ to reduce nickel catalyst poisoning and blocking up the tubes with coal [22, 23].

Conclusions

At present, carbon dioxide in all its physical states (gas, liquid, solid) has various practical applications. In the USA the commercial use of carbon dioxide which, to some extent, reflects the world use of carbon dioxide in industry is as follows [24]:

A cooling agent	40%
Carbonation of drinks	20%
Enhancement of oil recovery	5-10%
Casting industry	10%
Chemical industry	10%
Other uses	10%

Carbon dioxide is most widely used in food industry as a cooling agent (in the form of dry ice) for storing and transportation of food products and for carbonation of drinks. Carbon dioxide is injected into oil pools to enhance oil recovery. Carbon dioxide is used as a solvent and extracting agent, for growing flowers and other plants under glass, in casting industry and in other branches of national economy.

As it was mentioned above, the examples of the most large-scale use of carbon dioxide in chemical industry are syntheses of carbamide (≈ 110 mln tons a year), soda ash (≈ 30 mln tons a year), salicylic acid as well as oxidizing conversion of methane for production of hydrogen. The share of carbon dioxide utilization in chemical production is only 10%. In future, with the development of carbon dioxide chemistry this share is sure to increase many times.

As is seen from the analysis given above, syntheses on the basis of carbon dioxide allow to produce a wide range of useful chemical products. The small number of commercially realized reactions on the basis of carbon dioxide is due to, first of all, the absence of effective catalysts. Successes in the field of catalytic organic synthesis, particularly in the field of homogeneous metal complex catalysis, and achievements in the field of activation of one carbon molecules (including those of carbon dioxide) allow to suppose with confidence that in the nearest future active and selective catalysts will be developed, on the basis of which it will be possible to solve the ecologically important problem of creating large-scale industrial processes of utilization of carbon dioxide.

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