Synopsis:

Organic Chemistry and the Potentials of the Bulk-Reduction of CO_2**

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Defining the reduction of CO_2 as the loss or replacement of C–O bonds, all chemical transformations of carbon dioxide with the exception of its hydration

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (1)$$

$$CO_2 + H_2O \rightleftharpoons H^{\oplus} + HCO_3^{\ominus} \qquad (2)$$

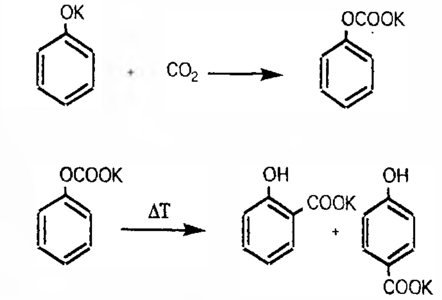
illustrate that CO_2 represents the highest oxidation state of carbon.

Compared with CO, the use of CO_2 in organic chemistry is surprisingly limited, both for the variety of reactions and its annual global consumption.

Among the reactions of industrial interest, we may mention *the carboxylation of active hydrogen compounds*[1], e.g. the Kolbe-Schmitt reaction (Scheme 1) and *the synthesis of urea and urea derivatives*, the first being of great industrial importance. Reaction (3) requires rather rigorous conditions as far as pressure and temperature are concerned.

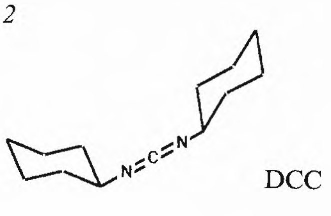
$$CO_2 + 2\,NH_3 \rightarrow H_2NCONH_2 + H_2O \qquad (3)$$

Scheme 1



Urea derivates from primary and secondary amines may, however, be obtained under milder experimental conditions using tertiary amines as a catalyst and dicyclohexylcarbodiimide (DCC), for example, as a condensing agent[1] (Scheme 2).

Scheme 2



$$RNH_2 + CO_2 + Et_3N \rightarrow RNHCOO^{\ominus} + Et_3NH^{\oplus}$$

$$RNHCOO^{\ominus} \xrightarrow{DCC} RN{=}C{=}O + HO^{\ominus}$$

$$RN{=}C{=}O + RNH_2 \rightarrow RHNCONHR$$

Among *polymerization reactions*, we should mention polyureas[1,2], polycarbonates[1,3], and copolymers with aziridines[1,4], epoxides[1,5] and episulfides[1,6].

In the present discussion concerning the use of CO_2 for the conversion and storage of solar energy, there seems little interest to go into further details of these and other types of reactions with CO_2 and to discuss their efficiencies and specificities, since it is not our interest to add another review to the great number of those already published in the last fifteen years[1]. Conventional stoichiometric processes consume CO_2 too slowly and are, with the exception of urea, only used to produce specific monomeric or polymeric products (fine chemicals). Since large quantities of CO_2 must be reduced, it seems in fact much more appropriate to focus this evalution on catalyzed reactions.

The relative little use of CO_2 as a building block in organic synthesis, compared to the already large and growing importance of CO (e.g. Fischer-Tropsch synthesis), seems surprising and may lead to a discussion about new techniques (e.g. reaction (4)[7]) for reducing the former to the latter[8,9].

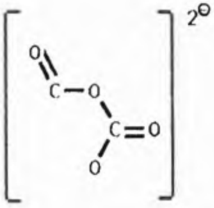
$$\begin{aligned}&[FeL_4(CO_2)] + CO_2 \rightarrow [FeL_4(CO_2)_2]\\&[FeL_4(CO_2)_2] \rightarrow [FeL_3(CO)(CO_3)] + LO\end{aligned} \qquad (4)$$

However, there would be little to gain in trying to «reverse» one of the largest industrial chemical processes, i.e. the production of hydrogen by oxidation of methane and homologous low molecular weight hydrocarbons.

$$CH_4 \xrightarrow{H_2O/O_2} CO + 3\,H_2 \xrightarrow{H_2O} CO_2 + 4\,H_2 \qquad (5)$$

Electrochemical and photoelectrochemical reductions of CO_2[10,11] in aprotic solvents lead to the intermediate $CO_2^{\cdot\ominus}$ which further reacts, to form either oxalate by dimerization (6) or CO and $CO_3^{2\ominus}$ by dismutation (7); both reactions are thought to proceed via a C–O bonded intermediate[12].

$$2\,CO_2 + 2\,e^{\ominus} \rightarrow \begin{cases} (COO)_2^{2\ominus} & (6)\\ CO_3^{2\ominus} + CO & (7)\end{cases}$$



Unless $CO_2^{\cdot\ominus}$ can be used as a building block in organic synthesis, reactions (6) and (7) are only economically feasible for potential bulk applications[13]. A potential breakthrough was accomplished by *Hori* et al. who found a rather significant yield of ethylene in the electrochemical reduction of aqueous hydrogencarbonate solutions using a copper electrode[14,15]. Since no light-induced reduction with $\Phi_{red} \gg 1$ for CO_2 is presently known, this kind of process is therefore of limited use due to the number of photons which can possibly be absorbed in a unit of time. It will be interesting to see if light-induced reactions at high temperatures lead to new discoveries in this field.

The application of electrochemical reduction to reaction (6) or (7) is also limited to bulk products for the same economic restrictions. Modern electrochemical engineering can apply rather large currents for electrochemical organic synthesis[16], however, a potential industrial procedure would depend on the effective increase of the CO_2 concentration within the reaction medium.

Looking at the results published in the last several years, metal- and especially transition metal-catalyzed reduction of CO_2 will remain a principal area for new discoveries and techniques in this field.

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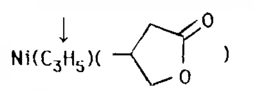
Carboxylations might, in fact, become practical, if *CO_2 can be efficiently inserted into a metal-substrate bond,* i.e. metal-carbon bond (e.g. reaction (8)[17]).

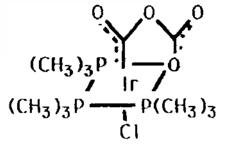
$$CO_2 + Ni(C_3H_5)_2 \rightarrow Ni(C_3H_5)(OCOCH_2CHCH_2)$$



(8)

This type of reaction constitutes one of the key interests of research in this domain. At present, however, these reactions are only successful in homogeneous media, and even these are hindered by low efficiency, due to CO-poisoning and potential hydrolysis of complexed intermediates[18]. Nevertheless, industrialists plainly favour this technique, with regard to heterogeneously catalyzed procedures, and are highly optimistic that further discoveries and developments will be made[19].

Instead of inserting CO_2 into a metal–carbon bond within a substrate, *CO_2 might alternatively be activated by metal coordination.* Preparative procedures using CO_2 as a building block would then require a *C*-bonded metal-CO_2 intermediate, since *O*-bonded species lead to either oxalates or formates[20]. The dismutation of the above mentioned C–O bonded dimer of $CO_2^{\ominus}$ is in fact accelerated by metal catalysis (9)[21]. In addition to electrochemical reduction of CO_2 in aqueous solution and metal-OCO activation, formate production is also observed either with metal hydrides



(9)

$$[CoH(N_2)(PPh_3)_3] + CO_2 \rightarrow [Co(OOCH)(PPh_3)_3] + N_2 \qquad (10)$$

or in the presence of hydrogen[22,23]. Coordinated formates react readily with alkyl halides to yield alkyl formates.

A π-bonded metal-CO_2 intermediate has been postulated for the Ni-catalyzed CO production from CO_2[24].

Activation of CO_2 might also be advantageous for insertion-type reactions as mentioned above. However, the simultaneous coordination of a substrate and CO_2 by one or two different metal centers introduces a far too complex reaction scheme for a bulk-reduction of CO_2 with acceptable specificity.

In conclusion, the use of carbon dioxide as a building block in organic chemistry is at present virtually limited to a small number of classes of reactions, mostly based on the reactivity of CO_2 with organic (Lewis) bases. Further development of these processes might be initiated by decisions to prepare new target molecules along the same reaction principles and would therefore be outside the scope of new developments linked to solar energy conversion and storage.

The photoelectrochemical or electrochemical reduction of CO_2 as a means of conversion and storage of solar energy is at present known to lead to products which, for economical reasons, would have to be prepared in bulk quantities in order to remain within realistic limits of costs. The discovery of ethylene production may, however, open new horizons for developments in this field. No results have been found so far in the literature in which $CO_2^{\ominus}$ has been linked to other organic substrates.

The potentials for bulk-reduction of CO_2 seem then mainly linked to the further development in fundamental and applied research of (photo)catalyzed reduction and insertion reactions.

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