Chapter 16

CARBON DIOXIDE AS A BUILDING BLOCK FOR ORGANIC INTERMEDIATES: AN INDUSTRIAL PERSPECTIVE

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1. INTRODUCTION

In this Chapter, current industrial processes will be described, in which carbon dioxide is used as a C1 building block for the syntheses of organic intermediates. So, other interesting processes which also use carbon dioxide, but not as a synthetic building block (e.g., as a cheap neutralising agent in the textile industry, or as a solvent, or as a blowing agent for plastic foams, or in the production of inorganic carbonates), will not be further mentioned.

Exploiting carbon dioxide as a raw material offers a well known paradox. On one side, there are several reasons for producing chemicals from it: i) carbon dioxide is widely recognised as a very cheap, hardly toxic C1 building block which could, in principle, replace toxic reagents like phosgene; ii) carbon dioxide is a renewable feedstock, unlike oil or coal; iii) producing chemicals from carbon dioxide would help in controlling its atmospheric concentration. On the other hand, only very few processes use it as a raw material. The explanation of this paradox is the great thermal stability of carbon dioxide itself, witnessed by its very negative $\Delta G^\circ (-394.6 \text{ kJ/mole})$ [1]. Because of this stability, relatively few processes are known which are thermodynamically allowed, i.e. with $\Delta G < 0$.

Nevertheless, a large proportion of all the recovered carbon dioxide is used in the synthesis of methanol and urea, quite often in the same place where its production occurs. Much smaller amounts of other chemicals
(salicylic acid, other aromatic hydroxycarboxylic acids, cyclic organic carbonates) are also produced using carbon dioxide as a raw material.

2. METHANOL

Most of the methanol produced world-wide is derived from synthesis gas which, in turn, is obtained by the steam reforming of natural gas (methane). So:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3\text{H}_2 \\
\text{CO} + 2\text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH}
\end{align*}
\]

The steam reforming allows to produce a synthesis gas with a \(\text{H}_2/\text{CO}\) ratio close to 3, whereas a \(\text{H}_2/\text{CO}\) ratio of 2 is optimal for the methanol synthesis. For this reason, in order to reach the best stoichiometry for methanol synthesis, carbon dioxide is added, when available, to the synthesis gas at the exit of the steam reformer, to exploit the reaction:

\[
\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

which is still an exothermic reaction (although to a lesser extent compared with carbon monoxide hydrogenation: \(\Delta H_{300K}^\circ = -49,16\) and -90,77 kJ/mol, respectively [2]), due to the formation of a very stable water molecule. So, ideally, the overall stoichiometry of methanol synthesis is:

\[
3\text{CO} + \text{CO}_2 + 9\text{H}_2 \rightleftharpoons 4\text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

Worldwide annual production of methanol is around \(20 \times 10^6\) t [2, 3]. However, it has been estimated that only 25% of the maximum possible amount of carbon dioxide is actually employed [3]. So, a consumption of ca. \(2 \times 10^6\) t/year of carbon dioxide would result for the methanol synthesis.

3. UREA

Urea is the most important fertiliser in the world. Almost two-fifths of the world’s population rely, particularly in less developed countries, on urea for food supply. World urea demand has been estimated to be, in 1997, ca. \(89 \times 10^6\) t/y [4]. Urea prices are very different, e.g., in U.S.A. and Europe: assuming, however, an average price of 130 €/t [5]; exchange rate: 1 € = 1