Carboxylation of Acetylene without Salt Waste: Using thermodynamic predictions to optimize the catalyst and the reaction solvent

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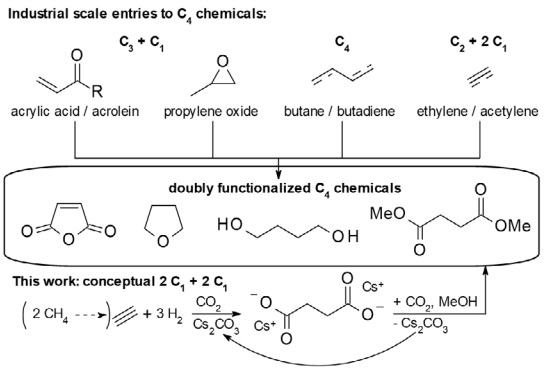
The utilization of CO_2 as C1 building block is a key towards a sustainable industrial synthesis of base chemicals. In this work, we developed a circular process for the production of the C4 chemical dimethyl succinate from CO_2 and acetylene, i.e. a C-H carboxylation reaction. The inherent formation of salt waste in such C-H carboxylations has so far been a major challenge. This was resolved in this work by esterification of the carboxylate product using methanol. The challenge of enabling a one-pot synthesis in such a reaction sequence is to find reaction conditions that are efficient for all reaction steps. Here, we applied ePC-SAFT to screen the reaction solvent and the base salt for the reaction to reach high solubility of both the salt base and the reactants.

Conventionally, C4 chemicals are synthesized from acrylic acid, propylene oxide, butane or ethylene, i.e. by coupling building blocks C3 + C1, C2 + C1 or directly using C4 units. In contrast, we were aiming at a route that uses CO_2 as a building block. However, it is known that it is very hard to activate CO_2 due to its thermodynamic low energetic level. Thus, a very common way to activate CO_2 is using molecular hydrogen to produce formic acid. In contrast, in this work we used CO_2 as a building block for a carboxylation reaction. A concept has been developed (c.f. Fig. 1) over the last years to carboxylate an alkyne, and we chose the example of acetylene carboxylation, yielding the C4- based chemical dimethyl succinate.

Figure 1: Synthetic entries to difunctionalized C4-commodities.



Our concept for sustainable C4 synthesis was as follows: At moderate CO_2 pressures, acetylene is doubly carboxylated, which requires basic conditions. The subsequent esterification of the succinate salt with methanol allowed regenerating the base salt. Realizing a one-pot synthesis of this concept requires a solvent that is efficient for all reaction steps. This solvent must provide high solubility of the salt base and the reactants acetylene and CO_2. Without fitting parameters, ePC-SAFT identified N-methyl-2-pyrrolidone (NMP) as most efficient solvent, c.f. Fig. 2. NMP provides high solubility for CO_2 and for acetylene, outperforming the other solvents (water, methanol, acetonitrile, THF). ePC-SAFT predicted that Cs_2CO_3 had the highest solubility in NMP among the considered carbonate bases.

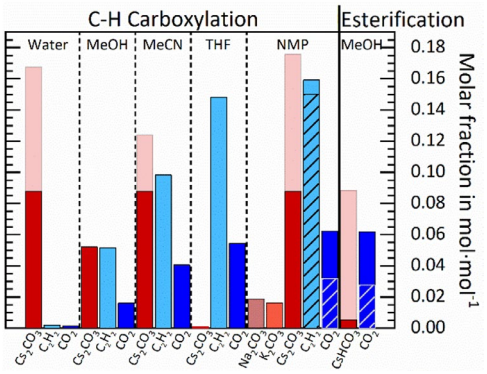


Figure 2: ePC-SAFT predicted solubility of gases at carboxylation conditions (T = 100 °C; p = 10 bar) and esterification conditions (T = 200 °C; p = 72 bar) and solubility of salts (T = 25°C). Solid bars represent solubilities in pure solvents. Striped bars is gas solubility in solvent + Cs_2C_{03}. Whenever the experimental amount of added salt (dark red bar) is lower than its solubility, the dark red bar is extended with a light red bar which represents the maximum solubility.

Summing up, our concept shown in Fig. 1 provides the proof of concept for a salt-free route to C4 chemicals based on CO_2 as C1 building block, and could potentially be used to valorize biogas (CH_4/CO_2).
ePC-SAFT proved to be efficient for optimizing the reaction medium of the one-pot synthesis of the C4 chemical from CO_2 by suggesting the optimal reaction solvent NMP and the optimal base Cs_2CO_3.

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