CO_2 ACTIVATION

Fixed into acetamides

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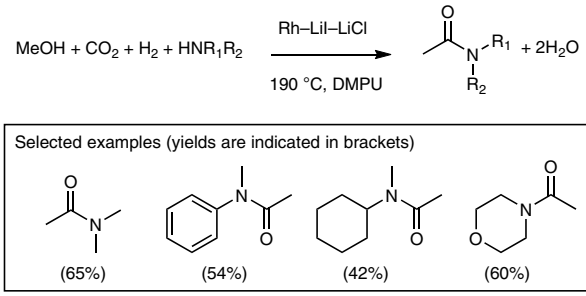

Carbon dioxide offers attractive possibilities as a C1 synthon for the preparation of a wide variety of chemicals besides fuel molecules. Acetamides, for example, feature excellent solvent properties and are often encountered as functional groups within active pharmaceutical ingredients and pesticides. Although the synthesis of formamides from CO_2 has been extensively reported, the incorporation of this crucial greenhouse gas into valuable acetamides has remained elusive. Now, Qingli Qian, Buxing Han and colleagues reported a method for the preparation of different acetamides by combining CO_2 with methanol, hydrogen and an amine in the presence of a rhodium catalyst (pictured).

Using dimethylammonium dimethylcarbamate — a masked dimethylamine — as the precursor, the authors performed a screening of catalysts and reaction conditions for the synthesis of dimethyl acetamide. $Rh(acac)(CO)_2$ in combination with LiI or LiCl as the promoter and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) as the solvent proved an effective catalytic system affording the desired acetamide in 65% yield. In general, the process yield showed a positive correlation with the pressure and, in fact, the best results were obtained when CO_2 and H_2 were introduced to the reactor at five and three MPa respectively. Moving to more complex amine substrates, the authors showed that the method works well with aromatic, aliphatic and heterocyclic amines, the only exception being heteroaromatic compounds. During the investigation, acetic acid occurred as a by-product, hinting at a Rh-catalysed methanol hydrocarboxylation as the possible intermediate step. Thus, the formed acetic acid further participates to the acetylation of the amine, according to the proposed reaction mechanism. Control reactions with isotopically labelled methanol supported this hypothesis. Moreover, replacing CO_2 with CO as the carbon synthon led to no product formation, confirming the direct participation of carbon dioxide to the process.

The reported method can inspire the development of further catalytic schemes that target the preparation of a variety of specialty chemicals using carbon dioxide as building block. However, carbon footprint considerations will be of crucial importance if such protocols are to be deployed within carbon-neutral production schemes in industry.

Davide Esposito

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