

FUEL OXYGENATES: ORGANIC CARBONATE SYNTHESIS

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INTRODUCTION

Owing to the 1990 amendments to the Clean Air Act, two major programs, namely the oxygenated fuels program and the reformulated gasoline program have been mandated. Currently, ethers (MTBE, ETBE, and TAME) and alcohols (mainly ethanol) are employed as fuel oxygenates. However, several dialkyl carbonates exhibit attractive fuel properties and might emerge as future fuel oxygenates. This paper consists of an overview of related literature and highlight of some of our work on the synthesis of organic carbonates from C₁ feedstocks.

Dialkyl carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) exhibit excellent gasoline blending properties such as high blending octane numbers and low blending Reid vapor pressures (RVP). Owing to their significantly higher oxygen content compared with alcohol (e.g., ethanol) and ether (e.g., MTBE, ETBE, and TAME) oxygenates, lower volume percent of the carbonate blending components will be needed to satisfy the 2.7 and 2.0 wt% oxygen requirements of the oxygenated and reformulated gasoline programs, respectively (1).

Dimethyl carbonate, for example, may be used as a fuel oxygenate, as a nontoxic and nonpolluting solvent, or as an environmentally harmless chemical in place of toxic and corrosive phosgene in the preparation of isocyanates, polycarbonates, synthetic lubricants, and various agricultural and pharmaceutical intermediates.

Dimethyl, diethyl, and dipropyl carbonates are manufactured, for use as specialty chemical or solvent, by the reaction of the corresponding alcohols with phosgene. Major producers of dialkyl carbonates by the conventional phosgene route are Van de Mark (USA), SNPE (France), BASF and Bayer (Germany). However, tremendous amount of research and development work has been going on worldwide for over thirty years to develop environmentally compatible and economically viable nonphosgene routes for the large scale production of these dialkyl carbonates.

BACKGROUND

Among the nonphosgene routes for the preparation of dialkyl carbonates, direct oxidative carbonylation of alcohols in the presence of various metal complex catalysts has been most widely investigated. A concise description of significant patents and publications in this area during 1963 to 1983 is given below.

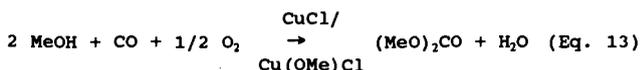
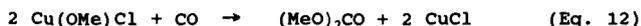
Mador et al(2) disclosed the preparation of aliphatic carbonates from alcohols and CO in the presence of costly platinum or palladium salts and usually large excess of an oxidizing metal salt such as copper (II) chloride. The need to use oxygen or air as an additional oxidizing agent was not mentioned. Alkyl halides, ethers, and CO₂ were obtained as undesired side products. The use of toxic mercuric salts in an organic solvent was described by D. M. Fenton (3).

The carbonylation of copper salts such as copper (II) dimethoxide or copper (II) methoxychloride was reported by Saegusa et al (4). In the presence of pyridine, the reaction proceeded even at room temperature. The reaction of copper (II) methoxychloride with CO was studied in great detail by Romano et al (5-7). Perotti et al (8,9) claimed the employment of copper complexes of pyridine and other amines, nitriles, and alkyl or aryl phosphines. However, Rivetti et al (10) showed that the reaction of methanol with CO to give dimethyl oxalate (DMO) and dimethyl carbonate (DMC) in the presence of palladium (II) acetate was inhibited almost completely by a trialkyl or an arylalkyl phosphine. Triaryl phosphines led to the formation of mostly DMO, whereas the yield of DMC was poor (1-6%). Gaenzler et al (11) patented the use of a catalyst system containing a copper salt and a phosphine oxide, phosphite, phosphate or a phosphonate.

routes. EniChem (Italy) has been successfully operating a stirred-tank DMC process involving the direct oxidative carbonylation method since 1983. At present, EniChem's DMC capacity at its plant in Ravenna is about 12,000 metric tons per year. EniChem has also licensed its DMC technology to GE and its joint venture partners Mitsui Sekka and Nagase & Co. for a 25,000 metric ton per year of polycarbonate plant in Japan. In 1993, Ube Industries (Japan) began operation of a semicommercial 3,000 metric ton per year DMC plant based on its proprietary vapor phase process via methyl nitrite which employs multimetallic (Pd-Cu-Mo-K) halides supported on activated carbon as a fixed bed catalyst (32). Furthermore, Ube is contemplating a 40,000 metric ton unit.

OXIDATIVE CARBONYLATION OF METHANOL

Preparation of dimethyl carbonate (DMC) by the reaction of methanol with carbon monoxide and oxygen in the presence of copper(I) chloride/copper(II) methoxychloride may be carried out in a stirred tank reactor by either a two-step batch process (Eq. 11 and 12) or a one-step catalytic process (Eq. 13), as follows.



Production of DMC by the oxidative carbonylation of methanol is exothermic and occurs with the coproduction of an equimolar amount of water. The produced water should be continuously removed from the reactor for several reasons. The catalyst activity as well as selectivity to DMC may be reduced at higher water concentration. Direct oxidation of carbon monoxide to carbon dioxide is likely to increase due to formation of water soluble catalytic species. At high water concentration, the possibility of DMC decomposition due to hydrolysis is also higher.

However, continuous removal of water from the reactor, separation of the catalyst system from reactants and products, and separation of DMC from methanol and water are challenging problems. To develop an improved and continuous DMC process, one should satisfy the following conditions:

- (i) the rate of DMC formation should be augmented,
- (ii) the heat of reaction should be dissipated, and
- (iii) the desired activity/stability of the catalyst system should be maintained while removing DMC and water from the reaction mixture.

It is noteworthy that DMC/water cannot be removed by an evaporative procedure without increasing the water concentration in the reaction mixture containing a methanolic slurry of Cu(I)Cl/Cu(II) (OMe)Cl as catalyst.

We have found that on the average, the rate of DMC formation may be enhanced by about eight times in the presence of N-methyl-2-pyrrolidone (NMP) as a high boiling point cosolvent which also helps in dissipating the heat of reaction (23). NMP can also serve as a catalyst carrier during the removal of DMC/H₂O by any flash procedure. Thus, a hot reaction mixture may be flashed to remove volatiles including DMC and water while the catalyst system, dissolved/suspended in NMP, may be recycled back to the reactor.

Low rates of DMC formation with copper(I) chloride/ copper(II) methoxychloride are partly due to low solubilities of these salts in methanol. Higher reaction rates can be attained with a solubilizing metal halide promoter such as calcium chloride (24), a phase-transfer agent such as benzyltriethylammonium chloride (25) or a polar cosolvent such as HMPA (26) or 2-pyrrolidone (23). The ability of copper to bind and activate carbon monoxide can be augmented with a nitrogenous ligand such as pyridine (27), imidazole (28), or a suitable cosolvent such as NMP or urea (29). For example, high rates of DMC formation can be achieved with copper(II) methoxychloride or imidazole-copper(II) methoxychloride in methanol-NMP.

CONCLUSIONS

A new and improved copper based homogeneous or slurry phase DMC process involving direct oxidative carbonylation of methanol can be successfully carried out in the presence of various ligands, promoters and organic cosolvents. A suitable high boiling point cosolvent (i.e., NMP) enhances the reaction-rate, helps in maintaining uniform temperature by dissipating the heat of reaction and serves as a catalyst carrier during the separation of methanol, DMC and water from the reaction mixture by a flash technique.

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