Developments in the production and application of dimethylcarbonate

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Abstract

Manufacturing methods of dimethylcarbonate (DMC) are examined, in particular those which have been industrially exploited. Apart from the old phosgenation process, two processes based on the oxy-carbonylation of methanol went on stream: the copper chloride catalysed, one step liquid-phase process, by EniChem, and the palladium catalysed, two steps gas-phase process, via methylnitrite, by UBE. Two further technologies are attractive for full-scale development in the next future: the gas-phase direct methanol oxy-carbonylation and the alkylenecarbonate transesterification process. In the last few years, the use of DMC in the chemical industry has considerably grown, due to its chemical properties and its non-toxicity, an outstanding example being represented by the non-phosgene production of aromatic polycarbonates. Other very promising fields of large scale DMC application are as solvent and as oxygenate in reformulated fuels. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Dimethylcarbonate (DMC) is achieving increasing importance in the chemical industry mainly for two aspects: first, its versatility as reagent and solvent; second, its non-toxicity for human health and environment, as indicated by its toxicological and eco-toxicological properties [1, 2].

The current interest toward the development of DMC manufacturing processes and applications is witnessed by the growth of literature and patents references, accounting now to about 2500 C.A. citations, mainly in the most recent years.

The traditional synthesis of DMC used to require toxic, hazardous phosgene as reagent. These observations prompted researchers to investigate new routes, as depicted in Fig. 1, in order to match the principles of “Green Chemistry” toward the lowest impact on human health and environment. Among these alternative routes, two processes based on the oxy-carbonylation of methanol have been already successfully developed up to the industrial scale: first, the copper chloride catalysed, one step liquid-phase process was introduced by EniChem, followed by the palladium catalysed, two steps gas-phase process, via methylnitrite (MN), by UBE.

In this short review, we present some recent developments in the production and application of DMC.

2. Dimethylcarbonate production technologies

2.1. By phosgenation

The phosgenation of methanol was the most important method to produce DMC till the 1980s [3]. The reaction is carried out contacting phosgene with...
methanol, through the formation of methylchloroformate as intermediate, according to (1a and 1b)

$$\text{COCl}_2 + \text{CH}_3\text{OH} \rightarrow \text{ClCOOCH}_3 + \text{HCl} \quad (1a)$$

$$\text{ClCOOCH}_3 + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{O})_2\text{CO} + \text{HCl} \quad (1b)$$

Reaction (1a) occurs quite easily, whereas reaction (1b) is slower and can be accelerated using an acid scavenger such as a tertiary amine or an inorganic base, e.g. NaOH [4].

2.2. By methanol oxy-carbonylation

2.2.1. Liquid-phase syntheses

The methods of DMC preparation which are based on the catalytic reaction of methanol with carbon monoxide and oxygen, according to reaction (2), have been the subject of intensive studies

$$2\text{CH}_3\text{OH} + \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O} \quad (2)$$

Since the 1970s, EniChem set up a project aimed at the development of a non-phosgene synthesis of DMC for large volume usage [5]; as a result, a new industrial process was established, based on a liquid-phase methanol oxidative carbonylation in the presence of copper chlorides as catalysts [6]. This catalytic system was highly effective in DMC production: the reaction was carried out by feeding at the same time methanol, carbon monoxide and oxygen to the suspension of the catalyst in a mixture of water, methanol and DMC [7] and recovering DMC by distillation after the catalyst separation. Besides, the process was not influenced by the carbon monoxide purity: diluents such as hydrogen did not interfere with the catalytic system [8]. The first industrial plant, based on the developed technology went on stream since 1983 [5,9]; up to now the world-wide total capacity installed is over 70 kt per year.

In the most recent development of the EniChem technology [10], at 2.4 MPa and 130°C a DMC productivity as high as 135 g/h was reported; values up
to 250 g/l h have been reached under optimised conditions. In this continuous process, the product recovery is carried out by vaporising out of the reactor, together with excess carbon monoxide, a stream of unreacted methanol, water and DMC. The catalyst life can be indefinitely prolonged feeding some hydrochloric acid to the reaction medium for in situ catalyst regeneration [11].

Modification of the copper chloride catalyst has been sought by different research groups in the effort to improve the catalyst performance, examples are: (i) the use of a CuCl/KCl eutectic mixture as catalyst combined with the pressure swing technique [12]; (ii) the introduction of high boiling co-solvents/ligands in the reaction mixture [13].

Methanol oxy-carbonylation is a redox two steps reaction. According to a simplified scheme [6] the reaction proceeds through CuCl oxidation by oxygen to cupric methoxychloride (Eq. (3))

\[ 2 \text{CuCl} + 2 \text{CH}_3 \text{OH} + \text{O}_2 \rightarrow 2 \text{Cu(OCH}_3\text{)}\text{Cl} + \text{H}_2 \text{O} \quad (3) \]

The latter is reduced by carbon monoxide to DMC (Eq. (4)), restoring CuCl and allowing the set-up of the catalytic cycle

\[ 2 \text{Cu(OCH}_3\text{)}\text{Cl} + \text{CO} \rightarrow (\text{CH}_3\text{O})_2\text{CO} + 2 \text{CuCl} \quad (4) \]

This scheme does not appear fully adequate [1], since it was observed that the reduction of cupric methoxychloride under carbon monoxide hardly proceeds under strictly anhydrous conditions, but it is promoted by addition of even small amounts of soluble cupric species, such as CuCl₂. The same effect is obtained by addition of some water, bringing Cu(II) in solution, by hydrolysis. Moreover, diethylcarbonate is produced when Cu(OCH₃)Cl is reacted in ethanol under CO. Therefore, polymeric, insoluble cupric methoxychloride cannot be considered the true reaction intermediate. As a matter of fact, a methanol dispersion of Cu(OCH₃)Cl synthesised by CuCl oxidation with oxygen in methanol presents a ESR spectrum with a resolved signal typical of a cupric ion in solution over the enlarged signal peculiar to the insoluble, polymeric species.

Although the reaction pathway is not known in detail, a scheme complying with the above observations is shown in Fig. 2. Attack of methanol on carbon monoxide co-ordinated to a solvated copper(II) chloride species would generate the carbomethoxy moiety. Nucleophilic attack of a second molecule of methanol would then bring to the formation of DMC and regeneration of CuCl. Cu(OCH₃)Cl would act on one side as a Cu(II) source, while on the other its methoxy ligands buffer the system acidity. In the presence of HCl generated in the reaction system, DMC formation is adversely affected and selectivity is lower, due to formation of methyl chloride and dimethyl ether [6].

In systems containing high water concentrations, as generated by direct oxygen re-oxidation under technical conditions, exhaustive hydrolysis of copper methoxychloride leads to a number of soluble and insoluble cupric species containing chloride and hydroxide anions such as CuCl₂ and CuCl₂(OH)₃ (atacamite). This reaction system brings, by reduction under CO, to DMC and cuprous chloride formation, provided that copper and chloride are balanced. Halide anions appear to be very important to establish the catalytic cycle.

In the presence of amine ligands, such as pyridine, dipyrindyl and tetramethylethylene diamine (TMEDA), the catalytic effectiveness increases [1,14], but the practical use of this system is hampered because it fails to produce DMC under technical conditions, mainly due to water sensitivity [5]. In the amine–copper system, catalyst of DMC formation by Cu(I), through the carbonyl complex CuCl(CO), was observed [15], this feature being reminiscent of the mechanism of CO to CO₂ oxidation by Cu(II) in aqueous solutions [16].

Other redox metallic systems are able to perform the alcohol oxy-carbonylation to carbonates. Palladium(II) chloride complexes stoichiometrically give carbonates in the presence of a base such as Na₂CO₃ [17] or NEt₃ [18] under very mild conditions. In the methanol oxy-carbonylation with palladium(II) acetate complexes, dimethyl oxalate (DMO) is produced along with DMC [19]. The selectivity toward DMC could be driven by the choice of the phosphine ligand, the carbon monoxide pressure and by addition of base. A lot of effort has been carried out with the aim to make the oxy-carbonylation catalytic with respect to palladium, by addition of some co-catalyst for palladium(0) re-oxidation. When using air or oxygen as oxidants, water is co-produced. It is known that the system Pd(II)–CO in the presence of water easily brings about carbon dioxide formation. It was
reported that the addition of phosphonium salts or nitriles as co-solvents/ligands to the reaction mixture improves carbon monoxide selectivity to DMC, ranging from 50 to 80%, according to the reaction conditions [20]. Besides, by addition of alkali earth metal salts and 2-hydroxypropyline to the palladium-copper salts system, the CO selectivity toward DMC could be increased up to 90% [21]. To prevent the formation of water in the reaction medium, use of dialkyl peroxides as oxidants, in the presence of a copper–pyridine complex as co-catalyst [22], or an electrochemical oxidation have been proposed [23,24].

Cobalt(II) complexes bearing ligands with nitrogen and oxygen donors such as Schiff bases, acetylacetonate, or picolinate [25], produce DMC with high selectivity in methanol under carbon monoxide and oxygen, especially in the presence of weakly co-ordinating solvents such as nitriles, amides or amines. These cobalt-based systems appear very attractive because they are halogen-free and non-corrosive compared to systems containing chloride, especially copper chlorides [26]. In contrast to palladium and copper, simple cobalt salts, such as chlorides, are inactive as catalysts.

A possible mechanism for the cobalt–Schiff base catalysed oxy-carbonylation of methanol to DMC is shown in Fig. 3.

**Fig. 2.** Catalytic redox cycle in copper catalysed DMC synthesis by methanol oxy-carbonylation.

**Fig. 3.** Proposed mechanism of cobalt–Schiff base catalysed methanol oxidative carbonylation to DMC. Salen: 1,6-bis(2-oxo-phenyl)1,2,5-diaza-1,5-hexadiene.
Redox couples, such as Se/Se$^{2-}$ [27] (in the presence of sodium alkoxide) and Br$_2$/Br$^{-}$ [28], without any added base, are also able to produce DMC starting from methanol and CO under mild conditions.

2.2.2. Gas-phase syntheses

A lot of effort has been done to develop a gas-phase oxy-carbonylation process. First, EniChem described gas-phase DMC production using CuCl dispersed on alumina [29]. Dow Chemical studied CuCl$_2$, alone or in combination with alkali and alkali earth halides, and the pyridine complex of Cu(OCH$_3$)$_2$Cl, both supported on active carbon, as catalysts [30]. The catalysts activity was not high and decreased during the tests in a relatively short time (20–40 h), depending on the catalyst loading; it was restored by in situ regeneration of the catalyst by addition of HCl. It was reported that both high selectivity and DMC productivity are obtained when using a CuCl$_2$ catalyst supported on active carbon and modified by treatment with alkaline hydroxides [31], a stable catalytic activity was claimed after 100 h. Recently, a study of the structural change in a CuCl$_2$ active carbon supported catalyst used in the DMC synthesis was reported [32]. Cuprous chloride supported on a Y-type zeolite by high temperature anhydrous reaction (HAR) gave a DMC productivity as good as the active carbon supported catalyst [33]. Addition of tetraalkyl ammonium chlorides to copper chlorides on zeolites or alumina increased the DMC productivity and the catalyst life [34]. In any case, active carbons are the most preferred supports for this reaction, compared to zeolites or alumina, because of higher DMC productivity when working with copper(II) chlorides.

Cobalt(II)–Schiff base and picolinate complexes, when supported by impregnation on active carbon, also produce DMC by methanol oxy-carbonylation [35].

The DMC productivity increases by addition of palladium salts to copper salts supported on active carbon [36]. It is worth pointing out that, although copper salts without halides are practically inactive in the reaction, the use of halogen-free palladium/copper salts supported on active carbon reportedly gives high DMC productivity and CO selectivity [37].

When palladium salts are used for methanol oxy-carbonylation to DMC, reaction conditions are milder than using copper only; however, methanol and CO selectivities are lower due to the formation of dimethyl oxalate as by-product and to the higher ratio between CO$_2$ and DMC production rates. Despite the large amount of work on the catalytic systems, no process based on gas-phase direct methanol oxy-carbonylation to DMC has been established.

2.3. By carbonylation of methylnitrite

Recently two reviews about the synthesis of DMC via methylnitrite (MN) appeared [38,39]. Starting from methanol, carbon monoxide and oxygen as raw materials, the process takes place in two steps in gas-phase: in the first, methanol reacts at about 50$^\circ$C with nitrogen oxides and oxygen to give MN and water, without any catalyst, according to reactions (5 and 6), which involve N$_2$O$_3$ as intermediate species.

$$2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{N}_2\text{O}_3 \quad (5)$$

$$2\text{CH}_3\text{OH} + \text{N}_2\text{O}_3 \rightarrow 2\text{CH}_3\text{ONO} + \text{H}_2\text{O} \quad (6)$$

In the second, MN reacts with carbon monoxide to produce DMC at 100–120$^\circ$C and 0.5–1 MPa, in the presence of a palladium supported catalyst, in a fixed bed reactor according to (7).

$$2\text{CH}_3\text{ONO} + \text{CO} \rightarrow (\text{CH}_3\text{O})_2\text{CO} + 2\text{NO} \quad (7)$$

In the catalytic process, the NO produced in the latter reaction is converted again to MN according to reactions (5 and 6).

The above DMC synthesis using MN was discovered at UBE [40], and a plant based on this technology has recently gone on stream with a capacity of about 6 kt per year. Reaction (7) is catalysed by supported palladium(II) halide complexes, which allow high (90–95%) CO selectivity. The addition of a co-catalyst such as copper chloride is required to avoid the reduction of palladium(II) to palladium(0), since the last one catalyses DMO formation.

Many different catalytic systems based on palladium with various co-catalysts and supports were studied [41–43]. The nature of the support influences the catalyst performance; it is important to avoid the presence of both acid sites, to avoid MN decomposition to methylformate and methylal, and basic sites which increase the dimethyl oxalate production. The catalyst must contain chloride anions to be effective and to
keep the oxidation state of palladium(II). Therefore, loss of chlorides in the outlet stream of the reactor as organic or inorganic compounds must be counteracted by addition of chlorinated organic compounds or HCl in the feed, to maintain the catalyst performances [44]. Surprisingly, palladium(II) salts supported on NaY zeolite produce DMC, even without halogens [45,46]. The preferred support seems to be active carbon compared to zeolites because of higher DMC selectivities based on both MN and carbon monoxide, >95% in the case of active carbon and 80–90% in the case of zeolites. Palladium chloride/copper chloride on active carbon is likely used as catalytic system in the industrial process. Since the carbonylation of MN to DMC occurs without water co-production, the use of palladium salts as catalysts does not adversely affect selectivity. In the carbonylation reactor outlet some amount of methylchloroformate is present [47], as expected since it is known that palladium(II) chloride supported on alumina or silica catalyses the reaction between MN, CO and HCl to give methylchloroformate [48]. The presence of halides ions in the catalytic system and the methylchloroformate generation likely raise some corrosiveness issues.

A possible mechanism of the MN palladium catalysed carbonylation to DMC is shown in Fig. 4.

The methyl nitrite process, studied both at UBE and Bayer [49], is a new and valuable process for the DMC synthesis; nevertheless, there are some concerns about the toxicity and handling of MN [39].

2.4. By ethylenecarbonate or urea transesterification

An alternative to the oxy-carbonylation processes is the transesterification of ethylenecarbonate (EC) with methanol. In this process, DMC is co-generated with ethylene glycol (EG), according to (8)

\[ CH_2(O)CO + 2CH_3OH \rightleftharpoons HO-CH_2-CH_2-OH + (CH_3O)_2CO \] (8)

Ethylenecarbonate can be prepared by a well known process from ethylene oxide and carbon dioxide with a catalyst such as a quaternary ammonium halide at 150–175 °C [50]. Addition of a co-catalyst such as zinc chloride to a quaternary ammonium iodide allows milder reaction conditions (50–100 °C) [51]. Reaction (8) takes place in the presence of a catalyst at about 100–150 °C at moderate pressure, for example by working in an homogeneous phase in the presence of tin, zirconium or titanium complexes [52]. Both homogeneous and heterogeneous basic or acid

Fig. 4. Catalytic cycle for palladium catalysed DMC formation from methyl nitrite and CO.
catalysts can also be used for the reaction, however the base catalysed reaction appears to be the most effective for the synthesis of DMC [53]. Recently a new heterogeneous catalyst based on potassium carbonate treated titanium silicate (TS-1) molecular sieve was reported [54]. Unfortunately, the transesterification reaction of EC with methanol is an equilibrium reaction and the formation of DMC is thermodynamically not favoured. Several methods have been suggested to improve the low yield of DMC, for example by removal of the reaction product as DMC/CH$_3$OH azeotrope from the reaction mixture by distillation [55] or by selective solvent extraction of the DMC produced [56]. In this reaction EC and methanol conversion are typically in the range 50–60% and 15–20%, respectively, whereas the DMC selectivity, based on both converted EC and methanol, is about 98%.

This process also suffers from the complications associated with the co-generation of two compounds. This problem could be overcome recycling ethylene glycol to produce EC, for example via urea transesterification according to reaction (9)

\[
\text{HO–CH}_2\text{–CH}_2\text{–OH} + \text{NH}_2\text{CONH}_2 \rightarrow \text{2NH}_3 (9)
\]

The driving force for reaction (9) is ammonia removal. By using an adequate catalyst such as zinc oxide, 95–98% EC selectivities based on ethylene glycol and urea have been reported, at total urea conversion, when using a small excess of ethylene glycol [57]. Although the direct synthesis of DMC starting from urea and methanol would be very attractive, its thermodynamics is not favourable, the calculated $\Delta G^\circ$ for the direct transesterification reaction being about $\approx 3$ kcal at 100 $^\circ$C [58]. The reaction involves two steps: first, urea is converted to methylcarbamate by reaction with methanol at relatively low temperatures (ca 100 $^\circ$C in the presence of a catalyst or ca 150 $^\circ$C without catalyst); then, the carbamate is further reacted with methanol at 180–190 $^\circ$C in the presence of a catalyst to produce DMC, according to (10a and 10b)

\[
\text{NH}_2\text{CONH}_2 + \text{CH}_3\text{OH} \rightarrow \text{(CH}_3\text{O})_2\text{CO} + \text{NH}_3
\]

As above the driving force for both reactions is ammonia removal. Both reactions (10a and 10b) are catalysed by a combination of a weak Lewis acid and Lewis base, such as equimolar amounts of Al(But)$_3$ and PPh$_3$. These bifunctional catalysts reduce the formation of by-products coming from carbamate decomposition [59]. The above reactions could be carried out in two separate steps or in one pot when in the presence of tin(IV) compounds as catalysts for the second reaction, as reported in [60].

In a recent development of this route [61], the reactions take place at the same time in a reactor with a distillation column at about 180 $^\circ$C and 0.5 MPa, in the presence of a tin(IV) alkoxide in a high boiling solvent such as triglyme, feeding methanol and urea in the reactor containing the catalyst and the solvent and removing DMC and methanol overhead. DMC selectivity, based on methanol is excellent (97–98%), and DMC yield is higher than previously reported. However, urea selectivity and conversion are more difficult to estimate. Some products of urea alkylation are produced in 1–3% yields whereas the formation of urea decomposition products (such as biuret NH$_2$CONHCONH$_2$ and other high molecular weight by-products) cannot be ruled out since their presence was not checked.

Synthesis of DMC from urea is attractive. In fact, by this process the synthesis of a carbonate starting from an alcohol and carbon dioxide would be achieved, since in principle the evolved ammonia can be recycled to the synthesis of urea.

### 2.5. Direct synthesis of DMC starting from CO$_2$

Conversion of carbon dioxide to useful industrial compounds has recently raised much interest in view of the so-called “Sustainable Society” and “Green Chemistry”. The direct synthesis of carbonates starting from alcohols and carbon dioxide, studied since the 1980s [62], fulfils this approach. In particular, the catalytic DMC synthesis starting from carbon dioxide and methanol is currently studied intensively. The reaction occurs at 140–190 $^\circ$C and 5 MPa in the presence of zirconia (ZrO$_2$) with a very high (ca 100%) methanol selectivity to DMC [63]. Unfortunately, the
methanol conversion is very low because the equilibrium of the reaction (11) is largely shifted to the left.

\[ \text{CO}_2 + 2\text{CH}_3\text{OH} \rightleftharpoons (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O} \]  

(11)

To avoid the formation of water as by-product, the reaction could be carried out using dehydrated derivatives of methanol, such as acetals (Eq. (12)). The carbonyl compound, formed along with DMC, can be recycled to prepare the corresponding acetal:

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

(12)

This reaction occurs at 190 °C under supercritical CO\(_2\) (30 MPa) via the carbomethoxy methoxy bridged dialkyl tin dimer intermediate depicted in Fig. 5 [64,65]. Yields, based on this tin intermediate are ca 60%.

DME appeared to be formed by an intramolecular pathway.

Further efforts in this very promising area are necessary to discover more efficient catalytic systems.

2.6. Other routes to DMC

A few other routes to DMC have been studied. Alkylation of metal carbonates with organic halides could be a method to prepare complex, functionalised carbonates under mild conditions, but it is unattractive for the synthesis of DMC from many points of view, both economic and ecological, even if some reports appeared [66,67].

DMC was prepared by decarbonylation of dimethyl oxalate in the presence of sodium methoxide or tetraphenyl phosphonium chloride as catalyst at 100 °C without solvent. Under these conditions, DMO is totally converted and the selectivity to DMC ranges between 85 and 95% [68,69].

The transesterification reaction between DMC and phenol is carried out in the liquid-phase in the presence of a variety of homogeneous catalysts [73]. According to the process developed by EniChem [5,74], DPC is obtained from DMC in two steps [Eqs. (13a) and (13b): in the first, DMC and phenol are reacted in the presence of a titanium alkoxide catalyst to give methylphenylcarbonate (PMC), in the second, PMC is disproportionated to DPC and DMC.

\[ \text{PhOH} + (\text{CH}_3\text{O})_2\text{CO} \xrightarrow{\text{Ti(OR)}_4} \text{PhO} \left(\text{CO}\right)\text{OCH}_3 + \text{CH}_3\text{OH} \]  

(13a)

\[ 2\text{PhO} \left(\text{CO}\right)\text{OCH}_3 \xrightarrow{\text{Ti(OR)}_4} (\text{PhO})_2\text{CO} + (\text{CH}_3\text{O})_2\text{CO} \]  

(13b)

3. Applications of DMC

DMC characteristics, coupled to its non-toxicity, are very attractive for the chemical industry. Only, the most relevant and meaningful applications will be shortly summarised. DMC applications will be sorted according to its use as a chemical intermediate (carbonylating or methylating reagent), solvent and fuel additive.

3.1. Polycarbonate production

By far the most prominent example of DMC industrial exploitation as a chemical intermediate is currently represented by the production of aromatic polycarbonates: a total world-wide capacity of about 170 kt per year aromatic polycarbonates via DMC has been installed by General Electric Plastics, while further 130 kt per year are scheduled for start-up in 2002 [70].

The DMC-based route to aromatic polycarbonates takes place via production of diphenylcarbonate (DPC) as intermediate and successive melt polymerisation between DPC and Bisphenol A, overcoming the previous technology, based on interfacial polymerisation with phosgene [2,71,72].
Aliphatic, –OH terminated polycarbonates, which can be prepared from short aliphatic diols and DMC by transesterification, are useful as “soft phase” in thermoplastic urethanes (TPU), thermoe lastomers, paints and adhesives [71,72]. DMC transesterification with allyl alcohol gives diallylcarbonate which is condensed with diethylene glycol to give monomers for the preparation of optical lenses [5,75].

3.2. Carbamate and isocyanate production

The reaction between DMC and primary or secondary amines brings to carbamates. Suitable catalysts are needed in order to achieve good reaction rates and high selectivities. When aliphatic amines are reacted, strong bases, such as alkali alkoxides, can be used to afford quantitative yields under mild conditions [76]. Interestingly, carbon dioxide has also been proved to be an effective catalyst in the reaction [77]. Lewis acids, such as AlCl₃ or AlI₃ and mercuric salts [78], zinc acetate [79,80], or lead oxides and salts [81] are required in the case of anilines. By these methods it is possible to obtain both mono- and dicarbamates.

The production of carbamates from DMC represents the first step of a non-phosgene route to isocyanates involving liquid or gas-phase thermolysis of the carbamate precursor, a process of potential outstanding industrial interest that is being pursued by several companies.

3.3. DMC as methylating reagent

DMC is a versatile reagent for methylation reactions at C, N, O and S centres, behaving as a good substitute for dimethylsulphate or methylhalides which are toxic and corrosive [5,82–84]. For the mono-methylation of activated methylene groups in substrates such as arylactonitriles, useful intermediates for anti-inflammatory drugs, DMC is better than other methylating agents for selectivity to mono-methylated derivatives [85–87]. Methylation of amines, amides, imide dyes, phenols and thioles [88–93] can be achieved by reaction with DMC in liquid-phase, in the presence of basic catalysts, (e.g. carbonates of cesium or potassium) and phase transfer agents, or in gas-phase, by gas-liquid-phase transfer catalysis (GL-PTC) in the presence of PEG 6000s or zeolites supported carbonates [94,95]. Finally, gas-phase methylation of substituted phenols on alumina supported alkali metal salts was recently reported [96–98].

Quaternary ammonium salts are obtained by exhaustive methylation of aliphatic tertiary amines [5]. An important application is the preparation, from trimethylamine and DMC, of electronic-grade tetramethylammonium hydroxide, free from chloride ion, by electrolysis of the hydrogen carbonate [99].

3.4. DMC as solvent

DMC represents a viable alternative to acetate esters and ketones in most applications, from paints to adhesives, taking advantage of its good solvency power [2]. It should also be reminded that DMC is the file leader of many derived carbonic esters, available by transesterification reactions, whose properties can be tailored according to the target applications, like in the field of lubricating oils [100]. DMC, as a non-aqueous electrolyte component, is finding increasing application in the field of lithium rechargeable batteries, as witnessed by the number of patents in the area (more than 200 in the last 3 years) [101].

A further example of DMC application is as blowing agent in polyurethane foam after CFC ban [102].

3.5. DMC and fuels

In recent years, DMC has been taken in consideration as oxygenate to reduce vehicle emissions associated to environmental and health risks. The reasons are the outstanding oxygen content in the DMC molecule (53.3 wt %) combined to its good blending properties [58]. The potential use of DMC in fuels prompted the study of its atmospheric chemistry. DMC was shown to have a photochemical ozone creation potential (POCP) negligible when compared to conventional fuels, and its use in fuels would be environmentally safe [103]. As a matter of fact, DMC has been reported to have the lowest POCP of all the oxygenated volatile organic compounds (VOCs) [104].

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