

Review

Rediscovering monoalkyl carbonates: a class of ubiquitous compounds

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Abstract: Monoalkyl carbonates (MACs) or, more broadly, hemiesters of carbonic acid (HECAs), constitute a class of compounds that are omnipresent in our lives, once formed by the reaction of carbon dioxide with alcohols. Despite their commonness, MACs are elusive in solution and went largely unnoticed by most researchers until the recent resurgence of interest in studying their properties, relevance (e.g., in CO₂ capture), and analysis (for example, in foods, drinks, and sugars), by using techniques like NMR, MS, and CE. This literature review, spanning almost two centuries, sheds light on the importance of the chemistry of MACs. Their subtle formation can be responsible for significant changes in the charge and electronic characteristics of compounds with an alcohol functional group, altering properties such as solubility, polarity, diffusion coefficient, and conductivity. Such changes in properties lead to the hypothesis that MAC formation may play an important role also in the biological environment, including membrane transport. Many questions remain open in the rich emerging research field of the chemistry of MACs, and better understanding is essential for advancing the knowledge of these ubiquitous compounds and their potential impact on various processes and products.

Keywords: Hemiesteres; Monoalkyl carbonates; adducts formation; alcohols; carbon dioxide

1. Introduction

Monoalkyl carbonates (MACs) are a class of compounds that are structurally like the bicarbonate anion (R-CO₃⁻). The term monoalkyl suggests that R is an alkyl chain, which initially covered the species prepared and studied. However, as species containing more complex structures and several functional groups began to be investigated, a more comprehensive nomenclature was introduced: hemiesters of carbonic acid, which emphasizes the class as containing possible esterification products of alcohols and carbonic acid. This nomenclature can be confusing, as the hemiester should be the protonated version of (R-CO₃⁻), which decomposes easily in water, like its analogue, H₂CO₃. Therefore, the use of the term monoalkyl carbonate (MAC) is well established in the literature, where hemiester of carbonic acid (HECA) is also used with the understanding that it is actually the anionic species (R-CO₃⁻). In **Fig. 1** some examples of hemiesters with a chain of 1 to 5 carbons are presented.

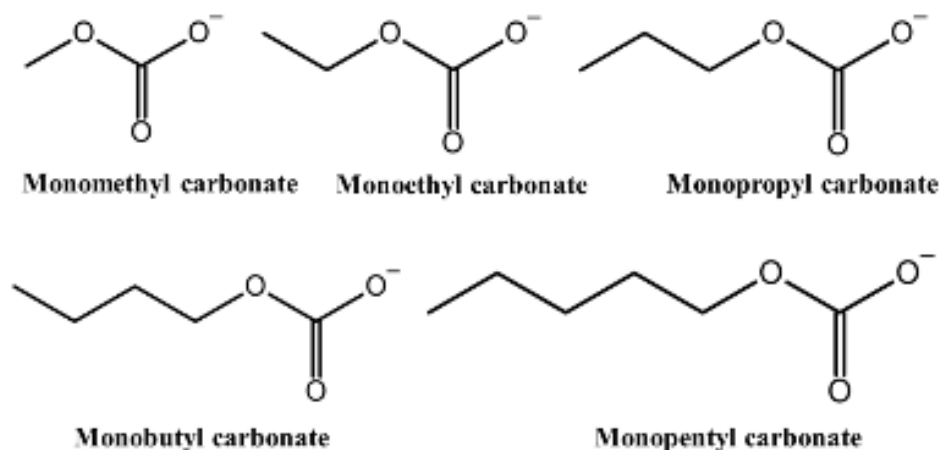
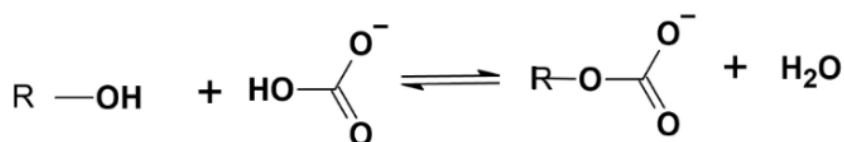


Figure 1. Example of some MACs

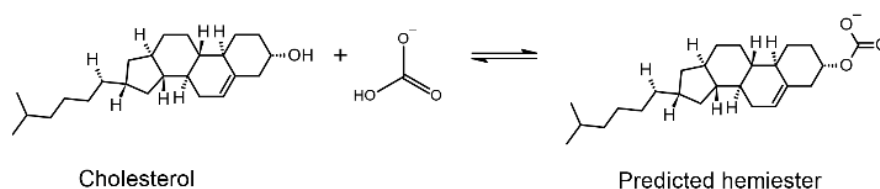
Although the existence of this class of compounds dates back to the 19th century, MACs are unnoticed by most researchers because of their elusive characteristics in solution and their chemical and spectral behavior, sometimes like bicarbonates, occasionally similar to the corresponding alcohol. In our lab, the interest in studying this class of compounds arose from the “rediscovery” of their existence when an unexpected additional peak systematically appeared in all electropherograms during an analysis of bicarbonate in ethanol fuel [1]. This unknown signal, after searching the literature and conducting a series of systematic studies, was attributed to the formation of one of the hemiesters. Due to the ease of decomposition of these compounds in aqueous media, they can generally remain unnoticed, which is probably the main reason for the lack of knowledge about these species. However, MACs are widespread in the most diverse environments, considering the infinity of hydroxylated compounds as well as the presence of $\text{HCO}_3^-/\text{CO}_2$, which are the necessary precursors for the formation of hemiesters. MACs have already been detected in alcoholic beverages [2] and in carbon capture processes [3], among other examples that will be presented, corroborating the hypothesis of ubiquity.

The main objectives of this review are to shed light on the formation and chemistry of MACs, analysis, potential applicability, as well as the effects of the formation of these compounds and their possible role in biological environments. The fact that the formation of MACs from a neutral R-OH generates a charged species leads to the hypothesis that these compounds may be relevant in the biological environment. **Scheme 1** shows the general reaction of forming a MAC.



Scheme 1. Formation of MAC from the hydroxy compound and bicarbonate

Converting an alcohol from a neutral to a charged species can completely change properties such as solubility, polarity, and conductivity. The alteration of the electrostatic properties allowed, e.g., its separation from neutral species in the studies by capillary electrophoresis [1-3]. An example of a phenomenon that could be explained due to hemiemester formation is that in the fertilization process, mammalian spermatozoa are activated before fertilization by high levels of bicarbonate, which facilitates cholesterol efflux mediated by lipoproteins [4-6]. In addition, there are indications that bicarbonate actuates on Ca^{2+} channel responses [5, 7]. These activation mechanisms are still not very well understood [7]; however, it is perfectly plausible that bicarbonate reacts with cholesterol, forming the cholesterol hemiemester as depicted in **Scheme 2**. Like Scheme 1, here also the charge of cholesterol changes, which should result in a variation in its solubility and polarizability. Such aspects may favor transport across membranes.



Scheme 2. Formation of MAC involving cholesterol and bicarbonate

For this review, a complete literature search was made in several databases. All the articles found that somehow mentioned the hemiesters were considered. A summary of these works was organized mostly in chronological order and highlighting the relevant information like synthesis and production, physical-chemical properties and analytical techniques that contributed to advances in the elucidation of issues related to MACs.

2. MACs in the 19th and 20th century

The first available records on monoalkyl carbonates date from the year 1837, when J-B. Dumas announced to the French Academy of Sciences, that his research team formerly prepared barium methyl carbonate and now also succeeded to synthesize potassium ethyl carbonate (“carbo-methylate de baryte” and “carbovinat de potasse” in the French chemical nomenclature of the time, recalling that “vin” refers to wine spirit or ethanol) [8]. Firstly, they reacted ethanol with potassium to form ethyl alkoxide, and then with dry gaseous CO_2 . The purification procedure of the salt was also described in the following studies, as well as its rapid decomposition in water to ethanol and bicarbonate [9–11].

In 1886, Haberman claimed to have obtained monomethyl carbonate as one of the products of the electrochemical oxidation of ethanol in water with potassium acetate as electrolyte [12]. In 1898, Hempel and Seidel described the synthesis of salts of monoalkyl carbonates of alcohols with one to five carbon atoms in a device developed for this purpose, and reported their low solidification and fusion temperatures [13]. Interestingly, they observed that the formation of MACs by the reaction of the alcohol with CO_2 occurs with strong volume contraction. In 1909, Siegfried and Howwjanz obtained calcium salts of MAC by passing CO_2 into aqueous solutions of different alcohols and sugars and excess of Ca(OH)_2 [14]. Motivated by the possibility of the natural occurrence of these MACs of sugars, Haworth and co-workers extended that previous study [15, 16]. However, they were not able to find any sugar carbonate in plants as they hypothesized. In 1917, A. Scrabal concluded that the second step of saponification of diethyl carbonate – the hydrolysis of monoethyl carbonate (MEC) – is immeasurably faster and assumed the global reaction to be a simple second-order process [17]. A decade later, this subject was revisited by Carl Faurholt, who published four articles in 1927 evaluating the kinetics of formation and decomposition of dimethyl and diethyl carbonates, the effect of pH, and the reaction in the absence of water [18-21]. In 1935, Miller and Case demonstrated that Scrabal's conclusions were erroneous due to the inappropriate choice of methyl orange as the pH indicator [22]. When the experiment done by Miller was repeated using phenolphthalein, results in agreement with the conclusions presented by Faurholt were obtained. In 1942, Heston, Dermer, and Woodside reported a clever experiment in which an excess of barium chloride was introduced in a solution prepared by the reaction of alkoxide (methanol or ethanol in an alkaline medium) with gaseous carbon dioxide to form alkyl carbonate [23]. Considering that the decomposition of alkyl carbonates takes some time at $0\text{ }^\circ\text{C}$, in less than 10 minutes they removed the BaCO_3 that precipitates immediately due to free carbonate remaining in solution and attributed the larger amount of precipitate formed afterwards to the decomposition of the alkyl carbonate. Conversion of up to 77 % of the added CO_2 into methyl carbonate was observed, while little precipitation occurred with phenol.

With the participation of other researchers, Faurholt continued to investigate the physicochemical properties of the monoalkyl carbonates until the mid-1950s including carbonates of propyl alcohol, benzyl alcohol, cyclohexanol, phenol, ethylene glycol, 2-chloroethanol, allyl alcohol, furfuryl, and tetrahydrofurfuryl alcohol [24-29] and carbonates of amino alcohols (mono-, di- and triethanolamine) [30, 31]. In subsequent years, J. Thamsen's group explored the formation of carbonates of sorbitol, mannitol, glucose, sucrose, and lactose [32, 33], and Toft and collaborators studied the formation of the monoalkyl carbonate of the glycolate ion [34]. In 1961, Eigen et al. suggested that HCO_3^- would be the direct product of a nucleophilic attack from H_2O to CO_2 – the slow step –, while H_2CO_3 would be the result of protonation of HCO_3^- therein formed [35]. In 1972, Hemmaplardh and King explored the solubility of methanol in compressed gases (N_2 , Ar, C_2H_6 , C_2H_4 , CH_4 , CO_2 and N_2O) in the range of 10 to 60 atm [36]. Deviations from ideality revealed the 1:1 association between carbon dioxide and methanol in

the gas phase, in agreement with earlier observations [13]. In the same year, Gattow and Behrendt described the synthesis of methyl hydrogen carbonate at low temperatures and its characterization, presenting infrared (IR) spectra with bands unequivocally assigned to the hemiemster [37]. In the following year, three papers published by the same group were dedicated to revisiting the preparation and properties of various hemiesters of carbonic acid by reaction of the alcoholates with CO₂ and characterization by IR, UV, and NMR, as well as thermal analysis and crystallography [38-40]. For the monomethyl carbonic acid, e.g., they determined a melting point of -36 °C and argued that the substance with the phase transition at -57 to -60 °C, formerly reported as methyl hydrogen carbonate, [13] probably consisted of a mixture of methanol and CO₂ under pressure.

In 1975, Sauers and collaborators performed kinetics and equilibrium studies for the reaction of fifteen alcohols with carbon dioxide in alkaline solutions [41]. They observed that the decarboxylation rate of the ionized form of the MACs is dependent on the alkyl group but not on the pH and determined that the logarithm of the rate of decomposition of the alkyl monocarbonate anions decays linearly with the increase of the pK_a of the alcohols. Based on these results, the authors made some previsions about the CO₂ fixed at the active site of carboxylating enzymes. In the following year, Ashworth and Singleton reported the preparation and characterization of a stable monoalkyl carbonate complex of ruthenium [42]. In 1978, Pocker et al. investigated the decarboxylation of sodium salts of mono-substituted derivatives of carbonic acid in water and deuterated water. Their results for the hydrolysis rate of a series of monoalkyl carbonates in neutral and slightly alkaline aqueous medium were reported and a few considerations were made regarding the formation of these species [43]. By comparing the reactions, the authors proposed a mechanistic analogy for the interaction of the enzyme carbonic anhydrase with alkyl carbonates.

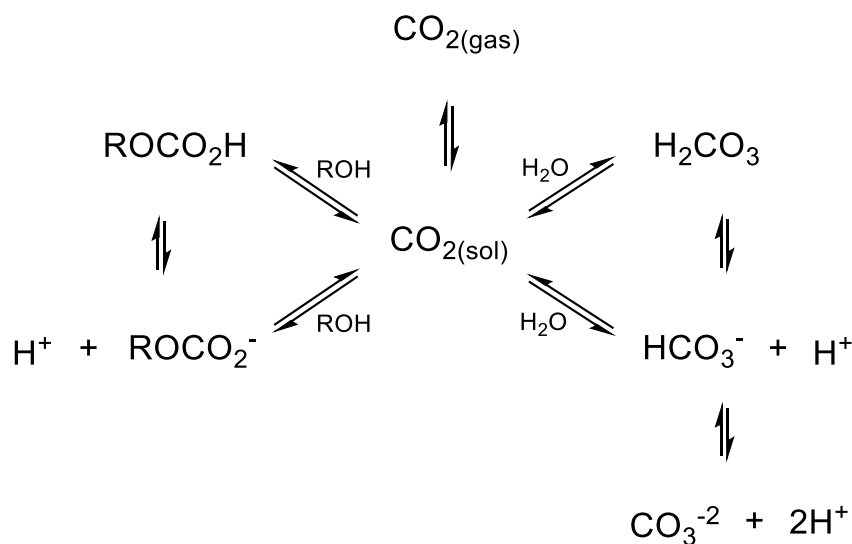
In the final two decades of the 20th Century, the lack of advances on MAC's research does not go unnoticed. In these 20 years, just one article in the field was published in 1988 on the kinetics of hemiesters formed by reactions of CO₂ with primary and secondary alkanolamines [44].

3. MACs in the 21st Century

At the beginning of the new century, renewed interest in MACs and greater availability of powerful instrumental analytical techniques led to the refinement of fundamental studies, especially in aqueous medium, verification of their ubiquity, postulation of their formation in biological systems, and investigations of the potential for different applications, including CO₂ fixation. For example, magnetic resonance was utilized to evaluate the structure of monoalkyl substituted derivatives and the formation of adducts between OH⁻ and HCO₃⁻ terminals [45, 46]. Flash photolysis was employed to release alcohols from photolabile alkanolamine, carbamates, or carbonates, showing that the rate of the reaction was limited by the decarboxylation of the analyzed compound [47]. The formation of the elusive and very labile monomethyl ester of carbonic acid, formerly characterized at low temperatures [37, 39], was confirmed in solution at room temperature by reaction of the methyl ester sodium salt and water or anhydrous HCl with help of ¹H and ¹³C NMR spectroscopy and DFT calculations, and its stability and reactivity were discussed [48].

Analogies between bicarbonate and alkyl carbonate anions are helpful for understanding their aqueous-phase equilibria. The reaction between CO₂ and water is a process known for centuries and is traditionally understood to involve a slow step generating H₂CO₃, which is followed by a rapid dissociation of the acid into HCO₃⁻. This statement disagrees with the earlier model proposed by Eigen [35]. Although recent studies suggest that the latest proposal is the most probable mechanism [2, 4, 49-51], a conciliatory scheme has been adopted, including both routes.

A set of similar reactions occurs when other hydroxyl compounds, such as alcohol, are present in the aqueous solution. In this case, the products are the alkyl carbonic acid and the monoalkyl carbonate, and **Scheme 3** shows the reaction involved in the formation of all these species derived from CO₂.



Scheme 3. CO₂ species equilibria in alcohol/water medium

Accurate dissociation constants of the alkyl carbonic acids in water are still unavailable, although values for some alcohols were published half a century ago [41]. In 2011, do Lago et al. showed, for the first time, that they are below 4.0 [1], but accurate pK_a values have not (yet) been obtained, because of their fast decomposition in acidic medium. The research group of do Lago took advantage of the technique of capillary electrophoresis (CE) to demonstrate the formation of MACs in several real matrices, like ethanol fuel [1]. A CE equipment operating with two capacitively coupled contactless conductivity detectors was used for the determination of various parameters of MACs formed by alcohols ranging from 1 to 5 carbons, like their mobility, diffusion coefficient and hydrodynamic radii [1]. A summary is presented in the following **Table 1**.

Table 1. Physical-chemical properties of some monoalkyl carbonates formed in aqueous medium at 25 °C, adapted and condensed from [1]

Hydroxyl compound ¹	Ionic mobility ² (10 ⁻⁵ cm ² V ⁻¹ s ⁻¹)	Diffusion coefficient ² (10 ⁻⁶ cm ² s ⁻¹)	K _{eq} ³
Methanol	44.20 ± 0.03	11.36 ± 0.02	4.2 ± 0.3
Ethanol	38.50 ± 0.04	9.89 ± 0.01	2.3 ± 0.1
n-propanol	34.90 ± 0.07	8.97 ± 0.01	1.56 ± 0.04
n-butanol	32.80 ± 0.01	8.42 ± 0.02	1.37 ± 0.05
n-pentanol	30.73 ± 0.02	7.90 ± 0.01	1.26 ± 0.05
n-hexanol	29.10 ± 0.06	7.48 ± 0.01	1.20 ± 0.08
3-methyl-1-butanol	30.62 ± 0.02	7.87 ± 0.01	1.42 ± 0.04
Allyl alcohol	37.92 ± 0.03	9.72 ± 0.08	1.16 ± 0.04
Cyclopentanol	31.40 ± 0.13	8.07 ± 0.03	1.1 ± 0.1
Cyclohexanol	29.63 ± 0.10	7.61 ± 0.02	1.1 ± 0.2
Glycerol	30.50 ± 0.02	7.84 ± 0.01	2.22 ± 0.07
Mannitol	23.97 ± 0.05	6.16 ± 0.01	1.9 ± 0.2
Glucose	24.30 ± 0.13	6.24 ± 0.03	0.35 ± 0.03
Fructose	24.82 ± 0.31	6.38 ± 0.10	n.a.
Sucrose	19.40 ± 0.11	4.98 ± 0.03	1.1 ± 0.2

¹ The corresponding monoalkyl carbonate is formed from the hydroxyl compound in aqueous solution containing HCO₃⁻ according to the equation ROH + HCO₃⁻ ⇌ ROCO₂⁻ + H₂O. For poly hydric compounds, different isomers can be formed. However, the technique used does not allow to distinguish the isomers formed. ² The values were obtained in aqueous NaHCO₃ 10 mmol/L (pH 8.3) and then extrapolated to infinite dilution. ³ The equilibrium constant is defined as K_{eq} = [ROCO₂⁻][H₂O]/[ROH][HCO₃⁻]; n.a. – not available

The formation of monoalkyl carbonates in carbonated alcoholic beverages was first demonstrated by do Lago et al. [2]. They estimate, e.g., that MACs concentrations are around 1.2 mmol L⁻¹ in lager beer and 4.1 mmol L⁻¹ in rum with cola drinks. To evaluate the extension of the formation of hemiesters of other organic hydroxyl compounds, fatty alcohols, and sugars were elected as representative classes due also to their biological importance [52]. The experiments demonstrated that even being formed in amounts as small as one molecule of MAC in 1000 to 10000 molecules of those sugars, they should also be present in living cells. The formation of

monoalkyl carbonates and pyrocarbonates in water was demonstrated using electrospray ionization mass spectrometry (ESI-MS) [53], while the physicochemical properties of peroxy-carboxylates (which are structural isomers of monoalkyl carbonates) were investigated by CE [54]. It was demonstrated that the peroxy-carboxylates present greater hydrodynamic radii in comparison with the corresponding monoalkyl carbonates. This difference was attributed to the different positions of the oxygen atoms causing a direct impact on the charge density and consequently affecting the hydration reaction. The association of CE and MS was used to determine monoalkyl carbonates [55], as represented in **Fig. 2**. In this study, it was demonstrated that temperature variations in the capillary connecting the CE (thermostated) to the MS introduce significant errors. To obtain reliable results, an ingenious 3D-printed cartridge was created to extend the thermostating of the interfacing capillary, allowing the quantification of concentrations in the order of $0.2 \mu\text{mol L}^{-1}$ [56].

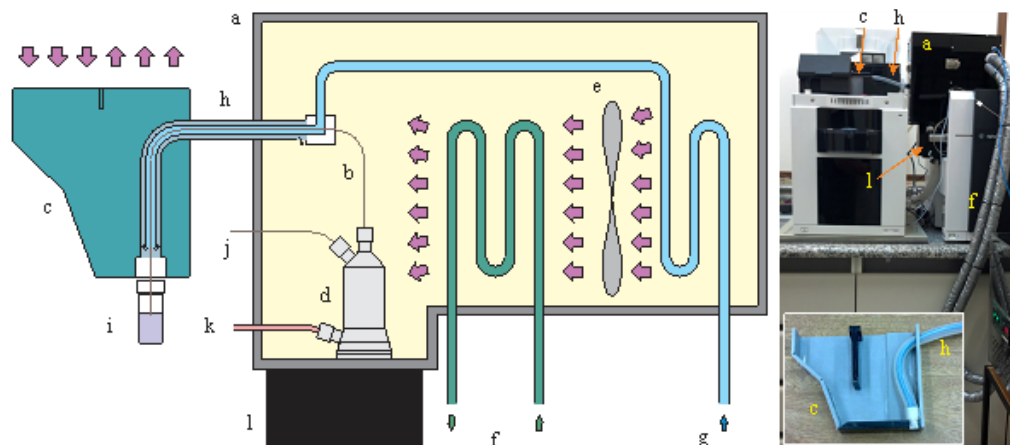


Figure 2. Scheme representing the CE-ESI coupling. A case for the thermal insulation (a) encompasses the outside part of the silica capillary (b) from the CE cartridge (c) to the ESI probe (d). Wind fan I forces air through a radiator that is fed with temperature-controlled water (f). A compressed air flow (g) passes through a copper tube inside the case and then to the inner PU tube (h) accompanying the capillary until the CE vial (i). The air flows back to the case through the external silicone tube (h). Part of the sheath liquid capillary (j) and nebulizer nitrogen flow (k) is also kept inside the thermostated case. The most important heat source is the ESI block (l), which is kept warm by the hot drying gas used to produce ions in the gas phase. Reproduced from [55] with permission from the Royal Society of Chemistry (RSC).

The formation of hemiesters of carbonic acid with poly-hydroxy compounds was investigated by the same group using ^{13}C NMR [57]. Glycerol and seven distinct carbohydrates were also investigated in the same study, and the percentages of isomers formed were quantified (results depicted in **Figure 3**). Based on the concentrations of glucose and bicarbonate in the human body and considering the equilibrium constant, the formation of these compounds in the blood was projected. The concentration of glucose 6-carbonate was estimated to be situated between 2 and $4 \mu\text{mol L}^{-1}$.

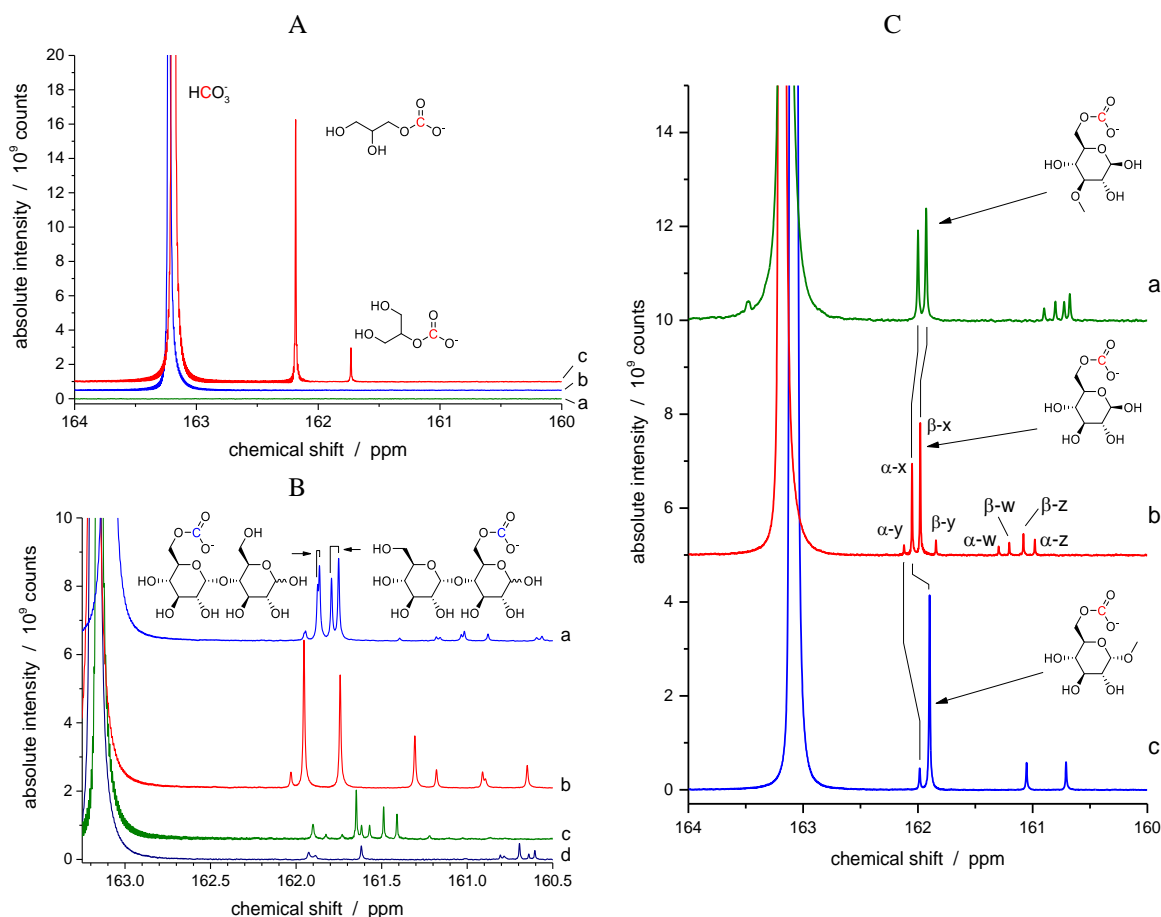


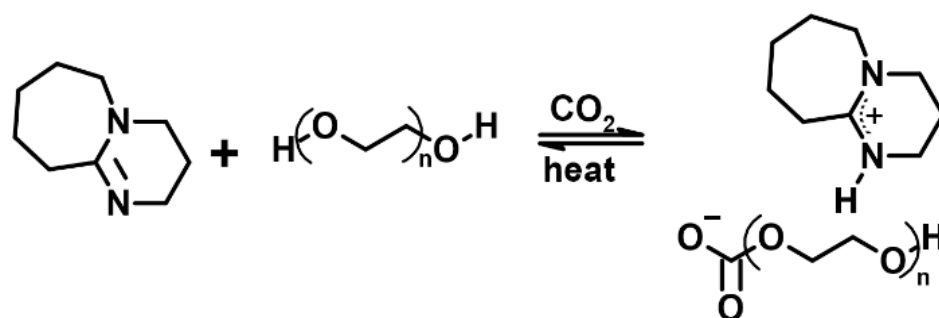
Figure 3. A. ¹³C NMR spectra of glycerol plus NaCl (a), NaH¹³CO₃ (b), and glycerol plus NaH¹³CO₃ (c). Fig. B. ¹³C NMR spectra of NaH¹³CO₃ and maltose (a), sucrose (b), fructose (c), and ribose (d). Maltose 6-carbonate and sucrose 6-carbonate were attributed to similarity with glucose 6-carbonate. Maltose 6'-carbonate is the only second option for a primary alcohol in the whole structure. The peak at 161.74 ppm could not be unequivocally attributed to either sucrose 1'-carbonate or sucrose 6'-carbonate. Fig. C. ¹³C NMR spectra of aqueous solutions containing NaH¹³CO₃ and G3M** (a), glucose (b), or G1M* (c). The α-β pairs for glucose carbonate were attributed, keeping simultaneously the peak area ratios as close as possible to 38/62. G1M renders only the α-isomers, which can be associated with the equivalent α-isomers of glucose carbonate. According to this attribution, glucose 1-carbonate is the non-detected isomer. The relative intensities of the peaks and the pKa values of the hydroxyl groups suggest that glucose 6-carbonate (β-d-glucopyranose 6-carbonate and α-d-glucopyranose 6-carbonate) is the most abundant isomer (x). The spectrum of G3M carbonate suggests that the isomer y is glucose 3-carbonate. The structures are the most abundant anomeric form of the most abundant positional isomer for each case. *(G1M) methyl α-d-glucopyranoside and **(G3M) 3-O-methyl-d-glucopyranose. Reproduced with permission from [57]. Copyright © 2016 Elsevier Ltd. All rights reserved.

An increased diversity of compounds and approaches has been explored in recent years. Examples include the search for solvent formulations for efficient absorption of CO₂ at low temperatures [58–61], the capture of CO₂ via reaction with cellulose in alkaline medium, even at low temperatures [62, 63], CO₂ reactions with ethanolamines [64–66], and the demonstration of the formation of anionic isomers of sugar hemiesters in an aqueous medium [56] or in a gaseous medium [65, 66]. Some aspects of these studies will be highlighted below.

The high solubility of NaOH in ethanol and the low solubility of sodium ethyl carbonate in this medium was used in the development of a CO₂ fixation process. When CO₂ enters in the solution, the synthesis leads to the separation of C₂H₅OCOONa by precipitation. For this process, cyclability and operational conditions were evaluated [58, 59]. A mixture of alkanolamines and other alcohols was used for the absorption and desorption of CO₂ in anhydrous medium [60] or in presence of 15% of water [61]. In the first study, the CO₂ was adsorbed at 20 °C and desorbed at temperatures between 65 °C and 80 °C, whereas in the second the temperature was situated between 30 and 45 °C for the absorption step and 80 to 90 °C for the desorption. Investigations using cellulose in alkaline medium to capture CO₂, revealed significant differences of absorption when CO₂ was introduced prior or after the dissolution of cellulose [62]. Analysis of ATR-IR of the cellulose regenerated from the solution (using ethanol) showed a new carbonate species, likely a cellulose carbonate. More recently, the same group performed accurate calculations, evaluating the changes in the chemical shifts detected by NMR, confirming the reaction of CO₂ with the OH group mostly on carbon 6 of the cellulose [63]. According to the authors, the values predicted using a simple computational method were in good agreement with the measured chemical shifts.

By NMR monitoring the equilibrium in CO₂ loaded (ethyl amino) ethanol aqueous solution it was shown quantitatively that the increase in CO₂ concentration, besides of the increase of carbonate species (HCO₃⁻/CO₃²⁻), elevates de formation of carbamate and, to a smaller extent, of alkyl carbonate and carbamate-carbonate. While the carbamate formation attained a maximum at a ratio 1:2 (mols) of carbonate to amine ratio, the formation of monoalkyl carbonate species became more significant at higher carbonate loadings [64]. In another study, it was demonstrated that both carbamates and monoalkyl carbonates play an important role in the capture of carbon dioxide by alkanolamines [65]. In the same study, ¹³C NMR was utilized to estimate the formation constants of MACs for choline as well as mono-, di- and triethanolamine. Similarly, NMR spectroscopy allowed in the same research to evaluate the formation of monoalkyl carbonate in the system methyldiethanolamine-H₂O-CO₂ [65]. In a subsequent study, the formation of monoalkyl carbonates in the monoethanolamine-H₂O-CO₂ system was explored over a wide range of concentrations of CO₂ and at different temperatures. The formation constants of monoalkyl carbonates were determined at each condition [66].

Currently carbon dioxide is a worldwide problem, since it is the main greenhouse effect gaseous compound that contributes to global warming. Annually billions of tons of CO₂ are emitted into the atmosphere, mainly from anthropogenic sources. CO₂ capture and storage (CCS) strategies have been investigated over the years, seeking environmentally friendly, economically viable and safe ways to remove CO₂ and subsequently transform it into a value-added product. Parallel to the request for efficient CO₂ collection processes, another challenge is the development of catalysts that operate with high efficiency at mild conditions, and which do not require high energy consumption. In the work proposed by Jessop and collaborators [67] an alternative approach to solve the energy penalty problem in the CCS process was proposed. The idea was to use a binary system composed of polyethylene glycol (PEG)/superbase (DBU (1,8-diazabicyclo-[5,4,0]-undec-7-ene)) for CO₂ capture. In this process, CO₂ binds to polyethylene glycol, forming the hemiester, which is the amidinium alkyl carbonate salt which is more reactive than free CO₂ and therefore can be more easily converted catalytically into value-added chemicals/fuels under extremely mild reaction conditions. (1 atm, 40 °C, metal-free process). The results of this work show a path for the development of green processes and innovation for practical low-energy and cost-effective CCS.



Scheme 4. CO₂ capture/activation by the DBU/PEG system

The reaction at Scheme 4 was previously described not for CCS but for creating a smart solvent that can be switched reversibly from one liquid with one set of characteristics to another with very different properties [68]. This was made possible by transforming a non-ionic liquid (an alcohol and an amine base) into an ionic liquid (a salt in liquid form) upon exposure to an atmosphere of carbon dioxide and then back to its non-ionic form when exposed to nitrogen or argon gas, as shown in **Fig. 4**. These tunable solvents should facilitate organic syntheses and separations, eliminating the need to remove and replace solvents after each reaction step.

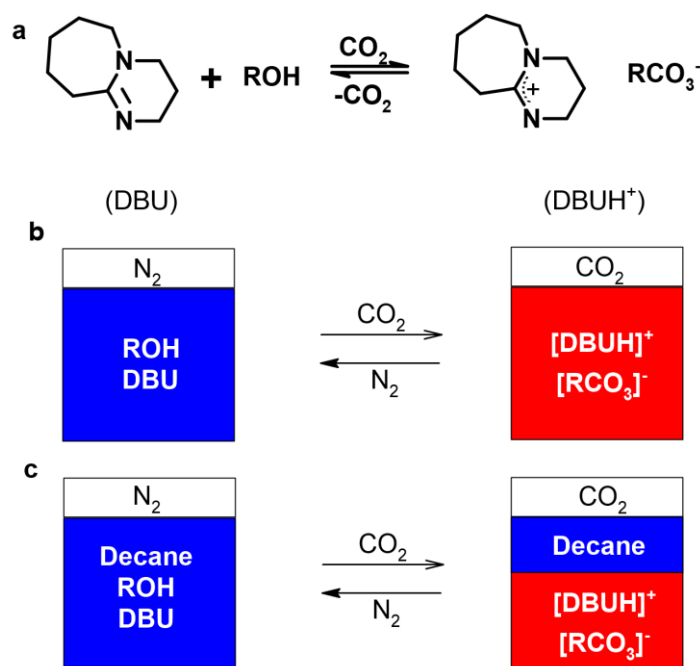


Figure 4. a) Protonation of DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene) in the presence of alcohol and carbon dioxide is reversed when CO₂ is removed. b) Polarity switching in the reaction shown in a, in which CO₂ causes a nonpolar liquid (shown in blue) mixture of hexanol and DBU to change over one hour into a polar, ionic liquid (shown in red); nitrogen gas reverses the process by stripping out CO₂ from the reaction. c) The different polarity of each liquid under the two conditions is illustrated by the miscibility of decane with the hexanol/DBU mixture under nitrogen, before exposure to CO₂; however, decane separates out once the mixture becomes polar in the presence of CO₂. Again, N₂ reverses the process. Adapted with permission from [67]. Copyright © 2005 Nature Publishing Group.

To evaluate the characteristics of the MAC, its solid form was isolated from ethanolic solutions of potassium bicarbonate. Surprisingly, the hemiacetal undergoes sublimation without decomposition and presents conformational isomerism in the gas phase at 210 K [69]. Recently, based on isotopic substitution experiments, including deuteration of OH and ¹³CH₃ in the molecule of HO-CO-OCH₃ and single molecule spectroscopy experiments, the occurrence of monomers and dimers of the ethyl carbonate was demonstrated [70]. In another study, the mechanism of formation of dialkyl carbonates directly from CO₂ and alcohols was detailed. The density function theory was applied to define the molecular mechanism [71]. The mechanism of the photochemical conversion of CO₂ to CO in the presence of the Re complex was investigated. The reaction pathways of the photocatalytic process were evaluated using density functional theory [72]. According to the authors, the reduction of CO₂ to CO occurs in two steps, with the second electron reduction occurring after the dissociation of the MAC followed by recombination with the rhenium center via carbon, generating Re-COOH species, which in sequence reacts with CO₂, generating tetracarbonyl complex and HCO₃⁻.

Out of the scope of this review, metal alkyl carbonates have also found use for the synthesis of catalysts and sol-gel materials to solubilize transition metal alkoxides by CO₂ insertion [73] and for the carboxylation of organic compounds [74]. In the big business of lithium-ion batteries, lithium mono- and dialkyl carbonates have been observed (among others species) as decomposition products at the electrolyte/electrode interface of lithium-ion batteries during repeated cycling of cells using, e.g., ethylene carbonate as main electrolyte solvent. To generate a more complete description of these compounds as a reference, lithium methyl and ethyl carbonates were synthesized by the (modified) Dumas – Peligot method and their structural and physicochemical characterizations were made by means of NMR, FTIR, XRD, XPS, and TGA techniques, and the decomposition by humidity was also evaluated [75].

Table 2 summarizes the main studies described in the literature about identification/characterization/quantification of monoalkyl carbonates. As can be seen, techniques such as NMR, capillary electrophoresis and mass spectrometry were fundamental for the study of these species. CE-MS should be highlighted, as the expressive increase in sensitivity and selectivity achieved with this coupling allowed the identification of many new species at extremely low concentrations. Considering that the number of compounds containing hydroxyl radicals in their structure is extremely large, whether in foods, drinks, or living organisms, and potentially carbonic acid hemiacetals can be formed anywhere a hydroxylated compound coexists with carbonate (or CO₂), it is evident

that Table 2 is still short to represent this myriad of compounds. Much more research is needed also because it is reasonable to suppose that MACs may perform important functions that are still unknown.

Table 2. Review on studies involving monoalkyl carbonates

OBJECTIVE OF STUDY	STUDIED PARAMETER	MONOALKYL CARBONATES	TECHNIQUE	Y E A R	REF.
Studies on the formation and hydrolysis of MACs	Kinetic constants	Monomethyl carbonate	_____	1 9 2 7	(18)
Studies on the formation and hydrolysis of MACs	Kinetic constants	Monomethyl carbonate	_____	1 9 2 7	(19)
Determination of kinetic constants	Velocity constants	Monomethyl carbonate	_____	1 9 3 5	(22)
To repeat Faurholt's measurements and extends them to greater concentrations of methanol	Rate of the reaction	Monomethyl carbonate	_____	1 9 4 3	(23)
Investigation of equilibrium conditions and the reaction mechanisms for the formation and decomposition	Velocity constant of the reaction, constant equilibrium, velocity of the decomposition	MACs of ethylene glycol and ethylene chlorohydrin, MACs of allyl alcohol	_____	1 9 5 2	(26)
		MACs of allyl alcohol	_____	1 9 5 2	(28)
		MACs of sorbitol, mannitol and glucose	_____	1 9 5 6	(32)
		MACs of sucrose and lactose	_____	1 9 5 6	(33)
		MACs of tetrahydrofurfuryl and furfuryl alcohol	_____	1 9 5 8	(29)
		Monoalkyl carbonate of glycolate ion	_____	1 9 6 0	(34)
Study of physicochemical properties of carbonic acid	_____	Sodium monomethyl carbonate	IR spectrum	1 9 7 2	(37)
1 - Study for a better understanding of enzyme-catalyzed carboxylation reaction 2 - Study of MAC formation and hydrolysis reactions	Hydrolysis rate of MACs in aqueous and alkaline media	Derivates from: CH ₂ OH; C ₂ H ₅ OH; CH ₃ OCH ₂ CH ₂ OH; CICH ₂ CH ₂ OH; CICH ₂ CH ₂ CH ₂ OH; HC=CCH ₂ OH; Cl ₂ CHCH ₂ OH; Cl ₃ CCH ₂ OH; i-C ₄ H ₉ OH; n-C ₃ H ₇ OH; I-C ₃ H ₇ OH; n-C ₄ H ₉ OH; n-C ₆ H ₁₃ OH; t-C ₄ H ₉ OH	NMR	1 9 7 5	(41)
Study stable cationic MACs Complexes of Ruthenium (II) from the Reactions of CO ₂ , with Alcohol Solutions of Ruthenium Hydrides	Stability by NMR spectrum	Bidentate monoalkyl carbonate	NMR/IR spectrum	1 9 7 6	(43)
Detailed decarboxylation parameters for methyl, ethyl, and sec-butyl carbonate monoanions in H ₂ O and D ₂ O, which are closely analogous to those of HCO ₃ ⁻	Acid catalysis and water catalysis	Monomethyl, monoethyl, and monosecbutyl carbonate	NMR	1 9 7 8	(44)
Determination of some physicochemical properties of different MACs	Formation and separation of MACs, Mobility, diffusion coefficient, and hydrodynamic radius, Acidity, Kinetic and equilibrium constants	Monomethyl carbonate, monoethyl, monopropyl, monoisopropyl, monobutyl, monoisobutyl, monosecbutyl, monopentyl, mono-3-pentyl, mono-2-methylbutyl, mono-2-hydroxycarbonate	CE-C ⁴ D	2 0 1 1	(1)
Proving the existence of MAC in some alcoholic beverages	Quantitation of MAC in beer, alcoholic drinks and sparkling wine	MEC	CE-C ⁴ D	2 0 1 2	(52)
Identify some possible classes of carbonated adducts of organic hydroxy compounds in biological conditions as well as to evaluate the pH effect on the kinetics of both formation and hydrolysis of these MACs	MAC quantitation and mobility calculation, pH effect	Monomethyl carbonate, monoethyl, monopropyl, monobutyl, monopentyl, monoexyl, monoisopentyl, mono-2-propenyl, monocyclopentyl, monocicloexyl carbonate,	CE-C ⁴ D	2 0 1 2	(53)

		mono-1-glycerol carbonate, mono-1-mannitol carbonate, glucose 6-carbonate, fructose 6-carbonate and sucrose 6-carbonate			
Introduce electrospray ionization mass spectrometry (ESI-MS) as a viable technique for detection of MACs in aqueous medium.	Formation of monoalkyl carbonates and pyrocarbonates in water	Monomethyl carbonate, monoethyl, monopropyl, monobutyl, monopentyl, isopropyl, mono-2-methylpropyl, monoisobutyl, monotertbutyl, mono-1-methylbutyl, 1-ethylpropyl, cyclohexyl, cyclopentyl, 2-enyl, 2-inyl carbonato	ESI-MS	2 0 1 3	(55)
Describe an efficient process for CO ₂ capture using some AMP-alkanolamine blends	Formation of MACs in carbon dioxide capture by alkanolamines	Monoalkyl carbonate, R-OCO ₂ ⁻ , (R = CH ₂ CH ₂ OH, CH ₃ , C ₂ H ₅ , n-C ₃ H ₇)	¹³ C CP-MAS NMR	2 0 1 3	(63)
A capillary electrophoresis/tandem-MS approach for the determination of monoalkyl carbonates	Separation and quantitation of MACs	Mono-3-pentyl, mono-1-butyl, mono-2-propyl, and monoethyl carbonates	CE-MS	2 0 1 4	(56)
Detection and identification of isomers of anionic sugar carbonates by using ¹³ C NMR achieved for the first time	Formation of isomers of anionic hemiesters of sugars and carbonic acid in aqueous medium	Glycerol 1-carbonate, d-glucopyranose 6-carbonate, Methyl α-d-glucopyranoside 6-carbonate, 3-O-methyl-d-glucopyranose 6-carbonate, d-fructopyranose Carbonate, d-ribose carbonate, Sucrose 6-carbonate + sucrose 6'-carbonate, Maltose 6'-carbonate, Maltose 6-carbonate	¹³ C NMR	2 0 1 6	(57)
Monoalkyl carbonate ((N-hydroxyethyl) (N-methyl) (2-aminoethyl) hydrogen carbonate) formation in the system methyldiethanolamine (MDEA)-water (H ₂ O) carbon dioxide (CO ₂) is investigated	Formation of ((N-hydroxyethyl) (N-methyl) (2-aminoethyl) hydrogen carbonate)	((N-hydroxyethyl) (N-methyl) (2-aminoethyl) hydrogen carbonate)	NMR	2 0 1 7	(65)
Demonstration that nitrogenated species containing an alcohol group also form MACs in conditions similar to those ones used for CCS	Both carbamates and monoalkyl carbonates are involved in carbon dioxide capture by alkanolamines	Choline carbonate, TEA-carbonate, MEA-carbonate, DEA-carbonate	¹³ C NMR	2 0 1 8	(3)
MAC formation in the system Monoethanolamine-water-carbon dioxide	Formation of MACs in carbon dioxide capture by alkanolamines	2-ammonioethyl carbonate (MEA2), and 2-(carboxylatoamino) ethyl carbonate (MEA3)	¹³ C NMR	2 0 1 9	(66)

4. Conclusion

This review addresses an important class of compounds that is still almost neglected. Even being a ubiquitous compound, as a rule, its presence is predominantly unknown or not considered by most scientists. The evolution of the instrumentation was determinant to proportionate many advances for the study of MACs. Techniques such as NMR, mass spectroscopy, and electrophoresis (with special modifications) were decisive to detect, quantify and determine kinetic and thermodynamic parameters of MACs. Recent studies reveal the presence of these compounds in foods, drinks, cellulose, and sugars. The systematic investigation of the enrolment of monoalkyl carbonates (besides carbamates) in the development of alkanolamine-based CO₂ capture processes – of great importance nowadays – also opens opportunities for practical applications. The charge alteration of the alcohol group after reaction with CO₂ forming a MAC is a key process for changing physical-chemical properties, including diffusion and migration. This charge switching and also the literature on the role of bicarbonate in processes involving spermatozoa suggest an association in living organisms and give support the hypothesis, presented in the Introduction, about the formation of MACs from biologically important compounds such as cholesterol. The hypothesis, as well as its relevance for transport through membranes need experimental demonstration. As seen, there are a growing number of recent contributions to the rediscovered field of MAC chemistry, advancing the knowledge of these ubiquitous compounds, while many research questions and rich

opportunities for further investigation and understanding remain open, with potential impact on various processes and products.

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