DOI: 10.1002/ejic.200500622

On the Existence of the Elusive Monomethyl Ester of Carbonic Acid [$CH_3OC(O)OH$] at 300 K: ^{1}H- and ^{13}C NMR Measurements and DFT Calculations

Angela Dibenedetto,*[a] Michele Aresta,[a] Potenzo Giannoccaro,[a] Carlo Pastore,[a] Imre Pápai,*[b] and Gábor Schubert[b]

Keywords: Carbon dioxide / Density functional calculations / Methylation / NMR spectroscopy

The elusive monomethyl ester of carbonic acid [$CH_3OC(O)OH$] has been prepared at 300 K by protonation of the sodium salt $NaOC(O)OCH_3$ with anhydrous HCl or water and characterized by ^{1}H- and ^{13}C NMR spectroscopy. The stability of the acid and its reactivity towards hydroxo ions and methylating agents under ambient conditions are discussed. The energetics and the mechanism of the investigated reactions are examined on the basis of density functional calculations. For kinetic and thermodynamic reasons $CH_3OC(O)OH$ is unlikely to be formed by insertion of CO_2 into the O–H bond of methanol.

Introduction

Carbonic acid (H_2CO_3, **1**) and its amino [$RR'NC(O)OH$, **2**] and monoalkyl derivatives [$ROC(O)OH$, **3**] are elusive species. Their isolation as pure compounds is not trivial as they easily decompose to afford CO_2 plus water [Equation (1)], amine [Equation (2)], or alcohol [Equation (3)].

$$\underset{\mathbf{1}}{H_2CO_3} \rightleftharpoons H_2O + CO_2 \qquad (1)$$

$$\underset{\mathbf{2}}{RR'N\text{-}C(O)OH} \rightleftharpoons RR'NH + CO_2 \qquad (2)$$

$$\underset{\mathbf{3}}{ROC(O)OH} \rightleftharpoons ROH + CO_2 \qquad (3)$$

In particular, **1** has never been isolated pure (only its water solutions are known), and **2** was only very recently isolated and characterized as a dimer in the solid state. The X-ray structure shows the existence of H-bonding through the carboxylic moieties [$R = C_6H_5CH_2$, $R' = H$; or $R,R' = PhP(OCH_2CH_2)_2$].[1,2] For **3** only a report of its low-temperature IR spectrum can be found in the literature;[3] no report of its existence at room temperature or information about its stability/reactivity are available. Conversely, the salts of **1** [$MHCO_3$, M_2CO_3, $M'CO_3$; M = group 1 metal or ammonia; M′ = group 2 metal], **2** [$RR'NC(O)OR''$; R″ = ammonium or metal cation], and **3** [$ROC(O)OM$] or the organic esters of **2** and **3** (R, R′, R″ = alkyl or aryl group) have been known for a long time to be stable compounds at room temperature.

Despite their instability, compounds **1**–**3** are often proposed to be intermediates in reactions in which carbon dioxide is implied. Thus, **2** has been suggested to exist in solutions containing amines and carbon dioxide[4] and **3** has been proposed to be formed by direct interaction of alcohols and CO_2,[5] a reaction relevant to the synthesis of organic carbonates by direct carboxylation of alcohols that occurs at temperatures ranging from 330 to 450 K and at a CO_2 pressure of 0.1–20 MPa.[7]

In the course of our research on carbon dioxide chemistry, we have synthesized and characterized the first examples of the elusive species **2**.[1,2] We wish to report here the first evidence of the existence of $CH_3OC(O)OH$ at room temperature and describe its reactivity. Density functional calculations have also been carried out to provide a rationale for our experimental findings.

Results and Discussion

Although it has been suggested that **3** could be formed by direct reaction[5] of ROH with CO_2, our ^{1}H- and ^{13}C NMR measurements run on pressurized (5 MPa) solutions of CO_2 in pure, freshly distilled, and absolutely anhydrous methanol did not give any evidence of CO_2 insertion into

---

[a] Department of Chemistry, University of Bari and CIRCC,
Via Celso Ulpiani 27, 70126 Bari, Italy
Fax: +39-080-544-2430
E-mail: a.dibenedetto@chimica.uniba.it
[b] Chemical Research Center, Hungarian Academy of Sciences,
P.O.B. 17, 1525 Budapest, Hungary
Fax: +36-1-325-7554
E-mail: papai@chemres.hu

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

the O–H bond of methanol to afford $CH_3OC(O)OH$ [**4**; Equation (4)].

$$CH_3OH + CO_2 \rightleftharpoons \underset{\mathbf{4}}{CH_3OC(O)OH} \tag{4}$$

One can argue that reaction 4 may either occur through a direct bimolecular insertion [Equation (4)] or through the generation of a CH_3O^- anion by autoprotolysis of methanol [Equation (5a)], which may attack the electrophilic carbon of CO_2 with formation of $CH_3OC(O)O^-$ [Equation (5b)]. The protonation of this latter species would afford **4** [Equation (5c)].

$$CH_3OH + CH_3OH \rightleftharpoons CH_3O^- + CH_3OH_2^+ \tag{5a}$$

$$CH_3O^- + CO_2 \longrightarrow CH_3OC(O)O^- \tag{5b}$$

$$CH_3OC(O)O^- + CH_3OH_2^+ \rightleftharpoons \underset{\mathbf{4}}{CH_3OC(O)OH} + CH_3OH \tag{5c}$$

The abundance of CH_3O^- is very low in pure anhydrous methanol as it is generated by the autoprotolytic dissociation of methanol [Equation (5)], which has an equilibrium constant, K_{dis}, of 10^{-16}.[6] The lack of formation of **4** under these conditions can be explained by taking into consideration the thermodynamics of reaction 4 and its kinetic aspects, as discussed below.

It is worthwhile mentioning that previous theoretical studies[8–11] on the mechanism of carbonic acid formation from H_2O and CO_2, a reaction that is analogous to Equation (4), have excluded the possibility of a direct bimolecular insertion because the activation energy predicted for this step is about 50 kcal mol^{-1},[8–10] while the energy barrier decreases substantially (to about 15 kcal mol^{-1})[8] if an additional water molecule is assumed to participate in the hydration process. Our calculations carried out at the B3LYP/6-311++G** level of density functional theory for $CH_3OC(O)OH$ formation involving two CH_3OH molecules (see Figure 1) predict a relatively high energy barrier for this process ($\Delta G^{\ddagger}_{gas} = 28.9$ and $\Delta G^{\ddagger}_{solv} = 22.7$ kcal mol^{-1} if solvent effects due to the methanol environment are included), indicating that reaction 4 is likely to be kinetically hindered. Furthermore, $CH_3OC(O)OH$ is found to be thermodynamically unstable with respect to its dissociation products, since the calculations give $\Delta G_{gas} = +9.9$ kcal mol^{-1} for the gas-phase reaction shown in Figure 1, which decreases to $\Delta G_{solv} = +4.4$ kcal mol^{-1} in the solvated model [for the isolated $CH_3OC(O)OH$ molecule the calculated dissociation free-energy values are $\Delta G_{gas} = +15.1$ and $\Delta G_{solv} = +11.6$ kcal mol^{-1}].

Accordingly, **4** has been reported to be a labile species and has only been characterized so far by IR spectroscopy at low temperature.[3] Therefore, it is not likely that it will exist for a long time at temperatures above 273 K. These results suggest that the direct insertion of CO_2 into the O–H bond of methanol is quite unlikely to occur under reaction conditions such as those used for the synthesis of organic carbonates,[7] and $CH_3OC(O)OH$ is unlikely to be an intermediate in such a reaction.

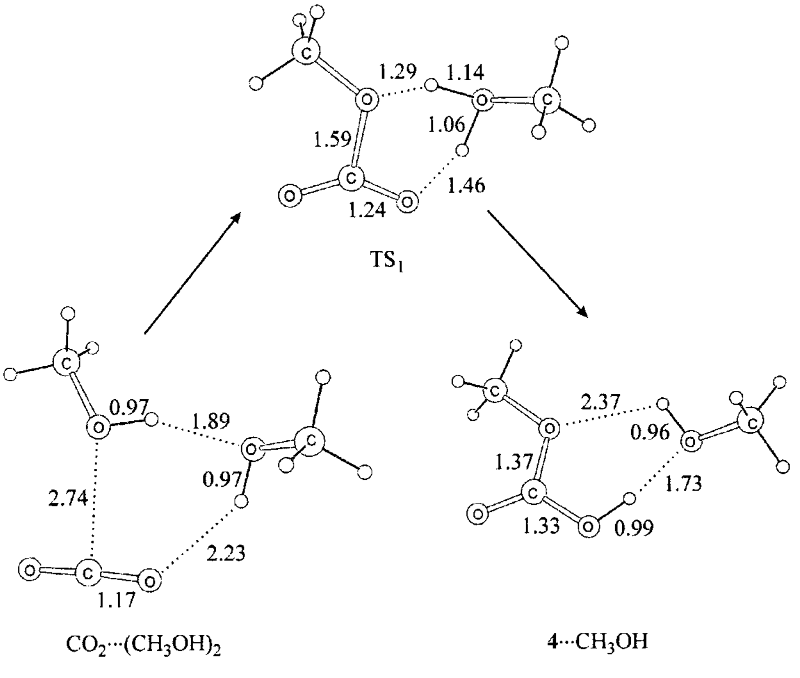


Figure 1. Formation of $CH_3OC(O)OH$ from CO_2 and two molecules of methanol. Selected bond lengths obtained from B3LYP/6-311++G** calculations are given in Ångstroms.

We generated **4** by treating the sodium salt $NaO^{13}C(O)OCH_3$ (**5**) with either anhydrous HCl/CD_2Cl_2 or water in a biphasic system. $NaO^{13}C(O)OCH_3$ is easily formed by reaction of sodium methoxide with $^{13}CO_2$ [Equation (6)].

$$\underset{}{CH_3ONa} + {}^{13}CO_2 \rightleftharpoons \underset{\mathbf{5}}{NaO^{13}C(O)OCH_3} \qquad (6)$$

Compound **5** is a stable, white solid that has already been described.[12] Its IR spectrum shows strong bands at 1631 and 1381 cm^{-1} for the $\nu_{C=O}$ absorption of the carbonate moiety. The reaction of **5** with anhydrous HCl/CD_2Cl_2 or water was monitored by carrying out a detailed NMR (^1H and ^{13}C) study. $^{13}CO_2$ was used in the synthesis of **5** in order to reduce the acquisition time of the ^{13}C NMR spectrum, thereby minimizing the risk of decomposition of **4**.

When **5** was suspended in CD_2Cl_2 under 0.1 MPa of $^{13}CO_2$, the ^1H- and ^{13}C NMR spectra of the solution did not show any signal that could be attributed to **5** due to its very poor solubility in the solvent. The addition of a substoichiometric amount of either anhydrous HCl/CD_2Cl_2 or water to the suspension at 295 K caused the immediate appearance of new signals in the ^1H- and ^{13}C NMR spectra.

The ^1H NMR spectrum shows a singlet (1 H) at $\delta = 4.76$ and a second signal at $\delta = 3.38$ ppm (3 H; Table 1), which are attributed to the CD_2Cl_2-soluble $HO^{13}C(O)OCH_3$ species formed according to reaction 7.

Table 1. Spectroscopic properties of labile $CH_3OC(O)OH$.

Compound	νCO	νOH	^1H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
$CH_3OC(O)OH$	1779	3484	4.76 (1 H, O*H*)	50.58 (*C*H$_3$)
	1730		3.38 (3 H, C*H$_3$*)	159.92 (*C*=O)

$$\underset{\mathbf{5}}{CH_3OC(O)ONa} + HCl\ (H_2O) \rightleftharpoons \underset{\mathbf{4}}{CH_3OC(O)OH} + NaCl\ (NaOH) \qquad (7)$$

The ^{13}C NMR spectrum confirms the formation of **4**, as demonstrated by the appearance of a signal at δ = 159.92 ppm due to the carbon atom of the hemicarbonate moiety. Continuing the addition of anhydrous HCl up to a stoichiometric amount produced an increase of the intensity of the signals mentioned above (Figure 2a). The addition of water produces broader peaks (Figure 2b), although they are located at the same positions.

If the NMR tube is left under the same conditions after the addition of the HCl/CD_2Cl_2 solution to NaO(O)$COCH_3$ at 295 K, the ^1H- and ^{13}C NMR spectra change: the signals due to **4** slowly disappear while the signals of CH_3OH [δ = 4.81 (1 H) and 3.42 ppm (3 H)] appear (Figure 2). When $CH_3O^{13}C(O)OH$ is generated using sub-stoichiometric amounts of anhydrous HCl/CD_2Cl_2 it has a longer lifetime than when it is generated with water. Therefore aged solutions of **4** show a different behavior according to their preparation. In fact, when anhydrous HCl is used the signal of free CO_2 generated by conversion of **4** is found at δ = 121.4 ppm. Conversely, when water is used a second signal appears at δ = 159.62 ppm in the ^{13}C NMR spectrum besides the signal at δ = 159.92 ppm that is attributed to $NaH^{13}CO_3$. In the latter case, the formation of methanol and $NaH^{13}CO_3$ can occur according to two mechanisms:

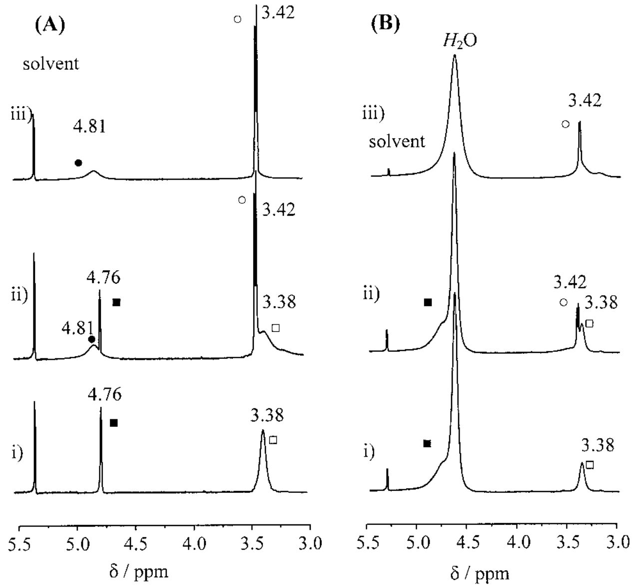


Figure 2. Evolution of the ^1H NMR spectrum of $CH_3OC(O)OH$ formed upon addition of (A) HCl/CD_2Cl_2 and (B) H_2O to $CH_3OC(O)ONa$ suspended in CD_2Cl_2. i) soon after the addition; ii) after 10 min; iii) after 60 min. ■ $CH_3OC(O)O$*H*; □ *C*H$_3$OC(O)OH; ● CH_3O*H*; ○ *C*H$_3$OH.

i) decomposition of $CH_3O^{13}C(O)OH$ into methanol and $^{13}CO_2$ [Equation (8a)] and subsequent reaction [Equation (8b)] of $^{13}CO_2$ with the NaOH formed in reaction 7.

$$CH_3O^{13}C(O)OH \rightarrow CH_3OH + {}^{13}CO_2 \qquad (8a)$$

$$^{13}CO_2 + NaOH \rightarrow NaH^{13}CO_3 \qquad (8b)$$

ii) direct interaction of the hydroxy moiety OH^- with $CH_3O^{13}C(O)OH$ [Equation (9a)] by attack at the methyl group with formation of methanol and concurrent formation of $NaH^{13}CO_3$ [Equation (9b)].

$$CH_3O^{13}C(O)OH + OH^- \rightarrow CH_3OH + H^{13}CO_3^- \qquad (9a)$$

$$H^{13}CO_3^- + Na^+ \rightarrow NaH^{13}CO_3 \qquad (9b)$$

The energy barrier obtained for the decomposition of $CH_3OC(O)OH$ via the reverse reaction shown in Figure 1 is $\Delta G^{\ddagger}_{solv}$ = 18.3 kcal mol^{-1} ($\Delta G^{\ddagger}_{gas}$ = 19.0 kcal mol^{-1}), whereas the calculations carried out for the methyl-transfer reaction between $CH_3OC(O)OH$ and OH^- (see Figure 3) give a much smaller barrier ($\Delta G^{\ddagger}_{solv}$ = 11.3 and $\Delta G^{\ddagger}_{gas}$ = 4.4 kcal mol^{-1}). Moreover, the S_N2-type nucleophile substitution depicted in Figure 3 is predicted to be highly exergonic (ΔG_{solv} = –39.4 and ΔG_{gas} = –49.5 kcal mol^{-1}). These data indicate that reaction 9a is both kinetically and thermodynamically more feasible than the direct decomposition of $CH_3OC(O)OH$. This agrees with the experimental observation of the stability of **4** in the absence and presence of hydroxy ions.

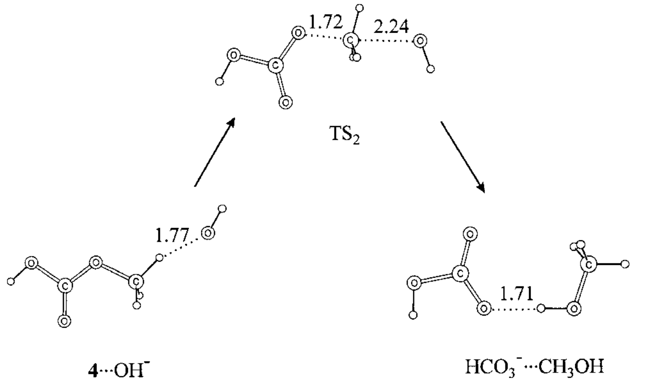
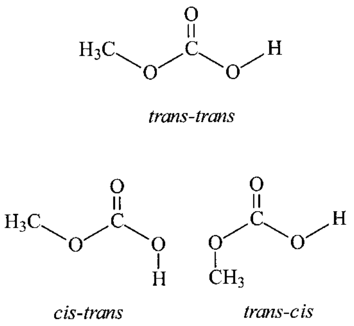


Figure 3. Stationary points located for the methyl-transfer reaction from $CH_3OC(O)OH$ to OH^- forming HCO_3^- and CH_3OH. Selected bond lengths obtained from B3LYP/6-311++G** calculations are given in Ångstroms.

The rate of conversion of **4** into methanol and CO_2 in the presence of OH^- is affected by the solvent: an apolar solvent slows the reaction as it does not favor the formation of hydroxy ions in solution from insoluble NaOH. Conversely, when a polar organic solvent or a stoichiometric amount of water is added to CD_2Cl_2 containing **5**, **4** is transformed so rapidly that it cannot be detected and only the final products (CH_3OH and $NaHCO_3$) are observed. These experimental data support the direct interaction of **4** with OH^- more than the dissociation of **4** into CH_3OH and CO_2 and the subsequent reaction of the latter with NaOH. However, this study gives thermodynamic and kinetic information about **4** and allows us to complete, with the ^1H- and ^{13}C NMR spectra, the characterization of the labile species **4** for which only the low-temperature IR spectrum had been reported so far.

As noted in a previous theoretical study,[13] the global energy-minimum of the $CH_3OC(O)OH$ molecule corresponds to the *trans*-*trans* orientation of the CH_3 and OH groups (see Scheme 1). Our present calculations predict two other conformations that lie only 1.3 (*cis*-*trans*) and 3.2 $kcal\,mol^{-1}$ (*trans*-*cis*) above the most stable isomer to be local minima on the gas-phase potential energy surface. We also estimated the acidity of $CH_3OC(O)OH$ by computing the aqueous pK_a value for the *trans*-*trans* isomer (see Computational Details) and found that $CH_3OC(O)OH$ is slightly less acidic than H_2CO_3. In fact, we calculated a pK_a for $CH_3OC(O)OH$ of 1.7 and for H_2CO_3 of 1.1; the experimental pK_a value for H_2CO_3 is 3.6. The difference between calculated and experimental pK_a values for H_2CO_3 is within the range of typical errors obtained with similar calculations[14] and can be attributed to the simplified solvation model.



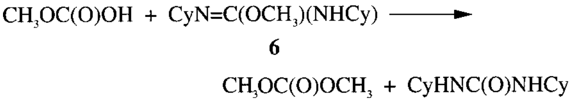
Scheme 1. Conformations of $CH_3OC(O)OH$.

Besides the conversion of **4** into methanol and CO_2, we also investigated the reactivity of **4** towards a methylating agent. The interest of reaction 10 lies in the fact that the product is an organic carbonate.

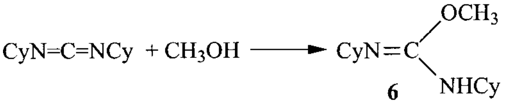
$$CH_3OC(O)OH + SubOR \rightarrow CH_3OC(O)OR + SubOH \qquad (10)$$

If $CH_3OC(O)OH$ could be formed from methanol and CO_2, reaction 10 would be an effective way to produce DMC, a chemical that has several industrial applications as an alkylating[15] or methoxycarbonylating[16] agent, a precursor of pharmaceuticals and agrochemicals,[17] a solvent,[18] and as an additive to gasoline.[19]

In particular, we investigated the reaction of **4** with the methylating agent *O*-methylisourea (**6**)[20,21] [Equation (11)], which is obtained by treating dicyclohexylcarbodiimide (DCC) with methanol [Equation (12)]. This reagent was preferred to other classical methylating systems (e.g. BF_3/CH_3OH) as the latter may carry Brønsted acids that decompose **4**.



$$CH_3OC(O)OH + \underset{\textbf{6}}{CyN{=}C(OCH_3)(NHCy)} \longrightarrow CH_3OC(O)OCH_3 + CyHNC(O)NHCy \qquad (11)$$



$$CyN{=}C{=}NCy + CH_3OH \longrightarrow \underset{\textbf{6}}{CyN{=}C\begin{matrix}\diagup OCH_3\\ \diagdown NHCy\end{matrix}} \qquad (12)$$

When isourea **6** was added to a CH_2Cl_2 solution containing $HOC(O)OCH_3$ generated from $NaOC(O)OCH_3$ dimethyl carbonate was immediately formed according to reaction 11. Both products (urea and DMC) were isolated and identified from their NMR spectra (^1H and ^{13}C) and GC-MS profiles compared with those of authentic samples. When the reaction was carried out in an NMR tube it was possible to follow the disappearance of the signals of **4** and the appearance of new signals due to DMC ($\delta = 3.69$ ppm, CH_3). This reaction both confirms the existence of **4** in solution and underlines the role of **6** as a methylating agent, as already reported in the literature.[20,21] If the isourea is treated with NaOC(O)OMe no methylation reaction occurs, although the addition of a small amount of water allows the reaction to proceed to form urea and DMC as $CH_3OC(O)OH$ is formed.

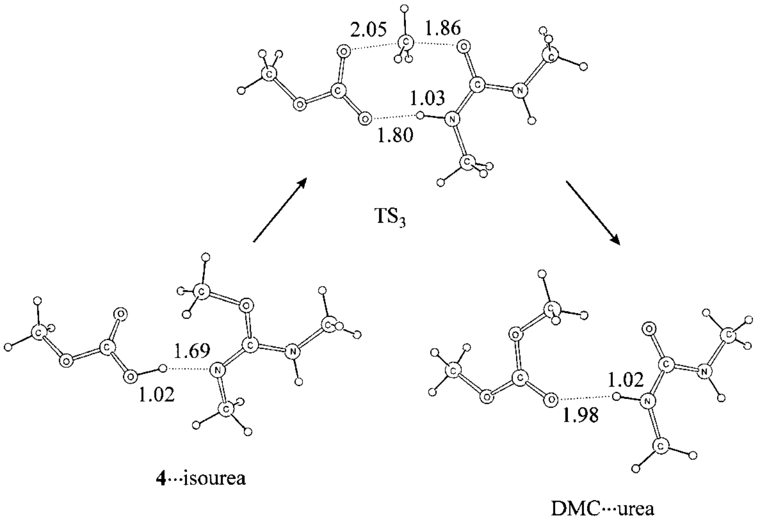


Figure 4. Stationary points located for the $CH_3OC(O)OH + CH_3N{=}C(OCH_3)(NHCH_3) \rightarrow CH_3OC(O)OCH_3 + CH_3HNC(O)NHCH_3$ model reaction. Selected bond lengths obtained from B3LYP/6-311++G** calculations are given in Ångstroms.

In order to explain the mechanism of reaction 12 we carried out DFT calculations on the reaction of **4** with a simplified model of **6** where the cyclohexyl groups have been replaced by methyl moieties (see Figure 4).

The transition state located for the model reaction describes a methyl transfer from isourea to **4**, while the O–H proton of **4** is already transferred to the iminic nitrogen of the isourea. IRC calculations indicate that the reaction takes place in a single step because the H-bonded **4**···isourea minimum is reached directly from the transition state in the reverse direction. The reaction is thermodynamically favored (ΔG_{solv} = –12.4, ΔG_{gas} = –11.8 kcal mol^{-1}) and the energy barrier is predicted to be $\Delta G^{\ddagger}_{\text{solv}}$ = 19.9 kcal mol^{-1} ($\Delta G^{\ddagger}_{\text{gas}}$ = 25.5 kcal mol^{-1}), which is slightly higher than that found for reaction 13 ($\Delta G^{\ddagger}_{\text{solv}}$ = 14.5 kcal mol^{-1}).[20]

$$2\ ROH + CO_2 + DCC \rightarrow (RO)_2CO + CyNHC(O)NHCy \qquad (13)$$

It is worthwhile noting that the concentration of **4** in the system generated from **5** and HCl/CD_2Cl_2 or water decreases rapidly with an increase of temperature, and above 310 K we were not able to detect the formation of **4** at all. This agrees with the lability of **4**, which converts into methanol and CO_2 according to Equation (3), and makes it unlikely that $CH_3OC(O)OH$ is an intermediate in the synthesis of carbonates from alcohols and CO_2.

Conclusions

Our work has demonstrated for the first time the existence of $CH_3OC(O)OH$ (**4**) at room temperature and its stability/lability under the same conditions. Although **4** is very labile, it exists in solution at room temperature for the time necessary to record its ^{1}H- and ^{13}C NMR spectra and to study its conversion with characterization of the products. It can be easily methylated to afford DMC, which is a reaction of potential practical importance. Nevertheless, **4** is not stable at temperatures above 300 K and is not formed for kinetic and thermodynamic reasons at room temperature from alcohols and CO_2 [nor in alcohol under 30 MPa of CO_2 nor in supercritical CO_2 (30 MPa) with added alcohol]. In order for **4** to play a role in the formation of DMC from methanol and CO_2, very high pressures of CO_2 should most probably be used (likely >>100 MPa).

Experimental Section

All solvents and starting reagents were RP Aldrich products. Alcohols and solvents were dried, distilled,[22] and stored under dinitrogen. Carbon dioxide was purchased from Rivoira IP (99.999% purity). NMR experiments were carried out with a 300-MHz Bruker apparatus using deuterated CIL solvents. IR spectra were recorded with a FTIR Perkin–Elmer 1710 apparatus. GC-MS analyses were carried out with a Shimadzu 17 A gas chromatograph (capillary column: 30 m; MDN-5S; Ø 0.25 mm, 0.25 µm film) coupled to a Shimadzu QP5050A mass spectrometer. Quantitative determinations on the reaction solutions were recorded using a Hewlett–Packard 6850 GC-FID (capillary column: 30 m; MDN-5S; Ø 0.25 mm, 0.25 µm film).

Methylisourea was prepared as reported in the literature.[20,21]

Synthesis of the Monomethyl Ester of Carbonic Acid [$CH_3OC(O)OH$] and NMR Studies: NaOC(O)OMe [or NaO^{13}C(O)OMe] (35.0 mg, 0.36 mmol) freshly prepared from MeOH and Na under a CO_2 atmosphere was placed in an NMR tube in 0.7 mL of anhydrous CD_2Cl_2 and the tube was closed with a silicone stopper. ^{1}H- and ^{13}C NMR spectra were recorded for this sample: no signals were evident besides that of the solvent. Anhydrous HCl in CD_2Cl_2 was injected through the stopper in different amounts until the stoichiometric ratio was reached and the ^{1}H- and ^{13}C NMR spectra were recorded after each addition. NMR spectroscopic data are presented and discussed in the main text. Similarly, the reaction was monitored when water was added instead of anhydrous HCl.

Reaction of 4 with Methylisourea: $HOC(O)OCH_3$ was generated as described above from sodium methyl carbonate (78.0 mg, 0.8 mmol) and anhydrous HCl/CD_2Cl_2 (or water). Once the ^{1}H NMR signals of **4** had reached their maximum intensity methylisourea (200 mg, 0.8 mmol) was added to the solution. After one hour at room temperature the ^1H NMR signal (δ = 3.69 ppm) of dimethyl carbonate became evident. The solution was dried under vacuum and the resulting solid suspended in diethyl ether. The ether solution was filtered from the solid. The latter was shown to be urea [CyHNC(O)NHCy]. DMC was isolated from the solution by evaporating the solvent.

Computational Details: DFT calculations were carried out at the B3LYP/6-311++G** level[23] in order to obtain information about the structures and relative energies of energy minima and transition states relevant to the reactions investigated. The nature of the stationary points obtained from the geometry optimizations was verified by subsequent vibrational frequency analysis. Intrinsic Reaction Coordinate (IRC) calculations were performed from the located transition states in order to check whether these structures indeed connect the appropriate minima on the proposed reaction pathways. Most of the investigated reactions in the present work involve charged species, therefore we estimated the solvation free-energies using a recent implementation[24] of the Polarizable Continuum Model (PCM).[25] In these calculations, the cavities of the solute molecules were constructed using the atomic radii of the universal force field (UFF)[26] model with individual hydrogen spheres to be able to describe transition states for hydrogen-transfer reactions. The dielectric constant was always chosen according to the solvent used in the experiments (ε = 8.93 for CH_2Cl_2 and 32.63 for methanol). The Gibbs free-energies calculated for the gas phase and solvated models are denoted ΔG_{gas} and ΔG_{solv}, respectively, in the text, and include the thermal corrections as well. The aqueous pK_a of $CH_3OC(O)OH$ was estimated according to the procedure described by Takano and Houk[14] and using the UAHF cavity model in the PCM calculations to obtain the solvation free-energies. All these calculations were carried out using the Gaussian 03 software package.[27]

Supporting Information (see the footnote on the first page of this article): Cartesian coordinates and total energies of located structures.

Acknowledgments

The Italian authors wish to thank the Ministry of Education, University and Research (COFIN grants MM03027791 and 2003039774) and the EU Project TOPCOMBI for financial support, and Dr. Paride Papadia for experimental assistance in NMR studies. The Hungarian authors acknowledge the support of the Hungarian Research Foundation (OTKA grants T037345 and T034547).

---

[1] M. Aresta, D. Ballivet-Tkatchenko, M. C. Bonnet, R. Faure, H. Loiseleur, *J. Am. Chem. Soc.* **1985**, *107*, 2994–2995.

[2] M. Aresta, D. Ballivet-Tkatchenko, D. Belli Dell'Amico, M. C. Bonnet, D. Boschi, F. Calderazzo, R. Faure, L. Labella, F. Marchetti, *Chem. Commun.* **2000**, 1099–1100.

[3] a) G. Gattow, W. Von Behrendt, *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 534–535; b) G. Gattow, W. Von Behrendt, *Z. Anorg. Allg. Chem.* **1973**, *398*, 198–206.

[4] M. H. Jamroz, J. C. Dobrowolski, J. E. Rode, M. A. Borowiak, *J. Mol. Struct. (Theochem)* **2002**, *618*, 101–108.

[5] K. N. West, C. Wheeler, J. P. McCarney, K. N. Griffith, D. Bush, C. L. Liotta, C. A. Eckert, *J. Phys. Chem. A* **2001**, *105*, 3947–3948.

[6] a) P. Ballinger, F. A. Long, *J. Am. Chem. Soc.* **1960**, *82*, 795–798; b) J. Hine, M. Hine, *J. Am. Chem. Soc.* **1952**, *74*, 5266–5271.

[7] M. Aresta, A. Dibenedetto, C. Pastore, *Inorg. Chem.* **2003**, *42*, 3256–3261.

[8] M. T. Nguyen, T. K. Ha, *J. Am. Chem. Soc.* **1984**, *106*, 599–602.

[9] C. A. Wight, A. I. Boldyrev, *J. Phys. Chem.* **1995**, *99*, 12125–12130.

[10] K. R. Liedl, S. Sekušak, E. Mayer, *J. Am. Chem. Soc.* **1997**, *119*, 3782–3784.

[11] P. Ballone, B. Montanari, R. O. Jones, *J. Chem. Phys.* **2000**, *112*, 6571–6575.

[12] M. Kunert, P. Wiegeleben, H. Gorls, E. Dinjus, *Inorg. Chem. Commun.* **1998**, *1*, 131–133.

[13] H. Sun, S. J. Mumby, J. R. Maple, A. T. Hagler, *J. Phys. Chem.* **1995**, *99*, 5873–5882.

[14] Y. Takano, K. N. Houk, *J. Chem. Theory Comput.* **2005**, *1*, 70–77.

[15] Y. Ono, *Appl. Catal., A* **1997**, *155*, 133–166.

[16] M. Aresta, A. Dibenedetto, E. Quaranta, *Green Chem.* **1999**, *1*, 237–242.

[17] S. C. Stinson, *Chem. Eng. News* **2001**, *79*, 15–16.

[18] A. A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951–976.

[19] M. A. Pacheco, C. L. Marshall, *Energy Fuels* **1997**, *11*, 2–29.

[20] M. Aresta, A. Dibenedetto, E. Fracchiolla, P. Giannoccaro, I. Pápai, C. Pastore, G. Schubert, *J. Org. Chem.* **2005**, *70*, 6177–6186.

[21] E. Dabritz, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 470–477.

[22] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, England, **1986**.

[23] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[24] M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* **2002**, *117*, 43–54.

[25] S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129.

[26] A. K. Rappi, C. J. Casewit, K. S. Colwell, W. A. Goddard III, W. M. Skid, *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.

[27] *Gaussian 03, Revision C.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr.,T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

Received: July 13, 2005