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Formation of Neutral Methylcarbamic Acid ($CH_3NHCOOH$) and Methylammonium Methylcarbamate $[CH_3NH_3^+][CH_3NHCO_2^-]$ at Low Temperature

Jean-Baptiste Bossa, Fabien Borget, Fabrice Duvernay, Patrice Theulé, and Thierry Chiavassa*

Physique des Interactions Ioniques et Moléculaires, UMR 6633, Université de Provence et CNRS, Centre de St Jérôme, case 252, 13397 Marseille Cedex 20, France

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We study low temperature reactivity of methylamine (CH_3NH_2) and carbon dioxide (CO_2) mixed within different ratios, using FTIR spectroscopy and mass spectrometry. We report experimental evidence that the methylammonium methylcarbamate $[CH_3NH_3^+][CH_3NHCO_2^-]$ and methylcarbamic acid ($CH_3NHCOOH$) are formed when the initial mixture CH_3NH_2:CO_2 is warmed up to temperatures above 40 K. An excess of CH_3NH_2 favors the carbamate formation while an excess of CO_2 leads to a mixture of both methylammonium methylcarbamate and methylcarbamic acid. Quantum calculations show that methylcarbamic acid molecules are associated into centrosymmetric dimers. Above 230 K, the carbamate breaks down into CH_3NH_2 and $CH_3NHCOOH$, then this latter dissociates into CH_3NH_2 and CO_2. After 260 K, it remains on the substrate a solid residue made of a well-organized structure coming from the association between the remaining methylcarbamic acid dimers. This study shows that amines can react at low temperature in interstellar ices rich in carbon dioxide which are a privileged place of complex molecules formation, before being later released into "hot core" regions.

Introduction

Amine and CO_2 are well-known to lead to the synthesis of alkylammonium alkylcarbamates $[RNH_3^+][RNHCO_2^-]$[1,2] according to reaction 1, and this is proposed as an attractive method for CO_2 removal in various industrial processes.[3]

$$CO_2 + 2RNH_2 \rightleftharpoons [RNH_3^+][RNHCO_2^-] \qquad (1)$$

The formation of alkylcarbamates can result from a two step mechanism proceeding through a transient species which can be either an alkylcarbamic acid, RNHCOOH,[4,5] or a zwitterionic species, $RNH_2^+COO^-$.[6–9] However, other studies suggest a single step mechanism.[10,11] Alkylammonium alkylcarbamates are generally stable at room temperature as they contain a long alkyl chain, but they decompose into amine and carbon dioxide when heated.[12]

Using infrared spectroscopy, alkylammonium alkylcarbamates are characterized[13] by the most typical absorption bands assigned to alkylcarbamate anion, NH stretching (3440−3290 cm^{-1}), COO^- asymmetric stretching (1570−1550 cm^{-1}), OCN out of plane bending (815−810 cm^{-1}), and to alkylammonium cation, RNH_3^+ bending (1645−1610 cm^{-1}).

The simplest of these systems NH_3:CO_2 has been studied by Frasco[14] et al. from low temperature condensation of these molecules using IR spectroscopy. They reported that NH_3 and CO_2 can react to yield ammonium carbamate, $[NH_4^+][NH_2CO_2^-]$, under two solid forms, amorphous and crystalline, depending on the sample temperature. Later, Hisatsune[15] assigns this former form to a pre reactive complex $(NH_3)_2CO_2$. There was no evidence of neutral carbamic acid (NH_2COOH) formation in these studies.

The formation of carbamic acid derivatives is also possible from energetic proton bombardment,[16] ultraviolet/extreme ultraviolet photon irradiation[17] or electronic bombardment[18] performed at 10 K on mixed ices involving NH_3:CO_2 or CH_3NH_2:CO_2 systems which are interesting for the interstellar medium physical chemistry. Nevertheless, in each of these works, carbamic acid derivatives are identified once the sample is heated at 250 K in order to sublimate the most volatile species. Results from the present study indicate that these latter identifications must be reconsidered. Indeed, during the warming up, it is possible that carbamates are thermally produced from the species of the initial mixtures which have not reacted upon irradiation. That is why it is important in these kinds of studies to correctly separate the thermally induced effects from the irradiation effects.

In this paper, we study the formation of the most simple alkylcarbamic acid, methylcarbamic acid, $CH_3NHCOOH$, resulting from the thermal reaction between CH_3NH_2 and CO_2. These reactants are mixed in different ratios, condensed at 10 K, and then progressively warmed up until room temperature. The evolution and characterization of the different formed species are performed using FTIR and mass spectroscopy. We also use theoretical calculations to interpret our experimental data. Carbon dioxide is one of the main constituents of the astrophysical ices, and methylamine has already been detected in the gas phase of the interstellar medium[19] as in "hot cores"[20] and is expected to exist on interstellar grains. Methylamine can be formed from UV irradiation of CH_4 and NH_3,[18,21] two of the main precursor molecules identified within the interstellar ices. Carbon dioxide and methylamine can reacts into the interstellar ices giving products such as methylcarbamic acid, $CH_3NHCOOH$, which is an isomer of the smallest proteinaceous amino acid, glycine NH_2CH_2COOH.

Experimental Methods

Carbon dioxide (CO_2) and methylamine (CH_3NH_2) are commercially available as 99.9995% pure gas from Linde and

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* Corresponding author. Telephone: +33 491-289-195. Fax: +33 491-639-194. E-mail: Thierry.Chiavassa@univ-provence.fr.

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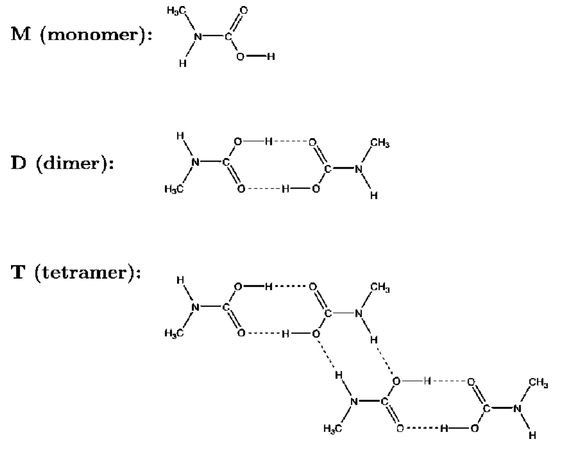
SCHEME 1: Structures of the Methylcarbamic Acid: M (monomer as the most stable conformer), D (dimer), and T (tetramer)



Air−Liquide. These gases are directly mixed at room temperature into a primary vacuum pumped glass mixing ramp. The gas mixture is deposited onto a gold plated metal surface, cooled at 10 K by a model 21 CTI cold head within a high vacuum chamber (10^{-7} mbar). Pure CO_2, pure CH_3NH_2, and CH_3NH_2:CO_2 mixtures within 5:1, 1:5, 1:20, and 1:50 ratios are prepared and deposited at 10 K. The relative concentrations are obtained from the IR spectra by estimating the column density of methylamine and carbon dioxide,[18,22,23] using the procedure described by Bennett[24] et al. By following this latter procedure, we can also estimate the thickness of the deposited solid films using densities of CO_2 (1.7 g.cm^{-3})[25] and CH_3NH_2 (0.85 g.cm^{-3}).[26] These thicknesses are estimated between 0.30 and 0.75 μm.

The IR spectra are recorded between 4000 and 650 cm^{-1} by reflection onto the gold platted surface using a NICOLET Magna 750 FTIR spectrometer. The angle between the surface normal and the infrared beam is 7°. A typical spectrum has 1 cm^{-1} resolution and is averaged over 100 interferograms.

Mass spectra are recorded using a RGA quadrupole mass spectrometer (MKS Microvision-IP Plus) as the products are desorbed during the temperature ramp. The mass spectra are recorded between 1 and 80 amu (atomic mass units) with 13 amu·s^{-1} scanning rate. The ionization source is a 70 eV electronic impact thus only single charged fragments are observed. The IR and mass analysis are not made simultaneously because of our experimental configuration; as a consequence, we doubled each experiment in order to get both the IR spectra and the mass spectra. The sample is warmed up with a constant rate of 4 K·min^{-1} during infrared acquisitions and 8 K·min^{-1} during mass analysis. These rates are different in both experiments in order to get a better detectivity of the species in mass spectrometry. We record an infrared spectrum every 10 K.

In order to characterize the carbone dioxide−methylamine reaction products, we compute each methylcarbamic acid conformer, dimer, and tetramer species using Gaussian 03,[27] with the B3LYP level of theory associated with the 6−311G** basis set. The most stable conformer is displayed in Scheme 1. Structures, relative energies, and calculated vibrational frequencies are reported in Supporting Information. The frequencies are scaled by a single factor (0.9613) to correct them from the basis set limitation effects and anharmonicity.[28]

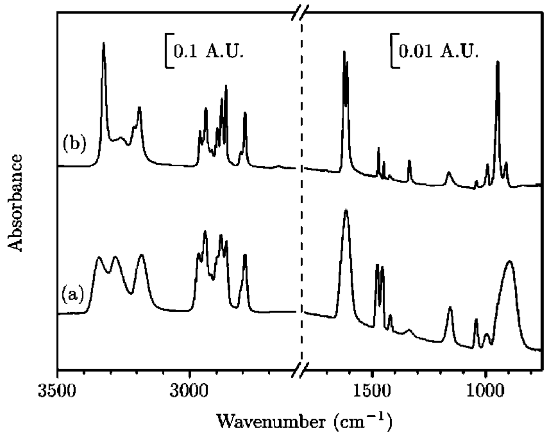


Figure 1. Infrared spectrum of a pure CH_3NH_2 ice film deposited at 10 K then recorded (a), after heating to 120 K (b).

TABLE 1: Infrared Band Positions (cm^{-1}) with Their Assignments of Pure Methylamine and Carbon Dioxide Ices at 10 K[a]

wavenumber $\bar{\nu}$ (cm^{-1})	molecules		assignment[b]
3708	CO_2^-		$(\nu_1 + \nu_3)$ CO_2
3600	CO_2^-		$(2\nu_2 + \nu_3)$ CO_2
3334		CH_3NH_2	(ν_{10}) ν_{as} NH_2
3282		CH_3NH_2	(ν_1) ν_s NH_2
3182		CH_3NH_2	H bonding
2967, 2942, 2920		CH_3NH_2	(ν_{11}) ν_d CH_3 and Fermi resonance
2897, 2883, 2862		CH_3NH_2	(ν_2) ν_d CH_3 and Fermi resonance
2808, 2792		CH_3NH_2	(ν_3) ν_s CH_3
2327	CO_2^-		(ν_3) ν_{as} CO_2
2282	CO_2^-		(ν_3) ν_{as} $^{13}CO_2$
1615		CH_3NH_2	(ν_4) δ NH_2
1477, 1455		CH_3NH_2	(ν_{12}) (ν_5) δ_d CH_3
1420		CH_3NH_2	(ν_6) δ_s CH_3
1339		CH_3NH_2	(ν_{13}) twist NH_2
1156		CH_3NH_2	(ν_{14}) (ν_7) ω CH_3
1042		CH_3NH_2	(ν_8) ν CN
997, 896		CH_3NH_2	(ν_9) ω NH_2
654	CO_2^-		(ν_2) δ CO_2

[a] Vibration mode: stretching (ν), bending (δ), rocking (ρ), wagging (ω), torsion (τ) and twisting (twist). Indication: asymmetric (as), symmetric (s) and degenerated (d). [b] Reference: Durig, 1968.

Results

Thermal Desorption of CH_3NH_2 and CO_2 Pure Solid. The infrared spectrum of pure methylamine deposited at 10 K, then heated to 120 K, is displayed in Figure 1, the frequency assignment is reported in Table 1. The CH_3NH_2 infrared spectrum[29] is characterized by two prominent features with multiplets located in the 3400−3100 cm^{-1} and 3000−2750 cm^{-1} ranges assigned to NH_2 and CH_3 stretching vibration modes, respectively. Weaker bands are also observed for the NH_2 bending and wagging modes at 1615 and 896 cm^{-1} and for the CH_3 bending and wagging modes at 1477 and 1156 cm^{-1}. When the sample is heated above 90 K (Figure 1b), a change occurs in the IR spectrum; the vibration bands become sharper, and some modes, such as the NH_2 bending mode, splits into two components. These changes are consistent with a higher organization of the CH_3NH_2 molecules. Above 110 K, CH_3NH_2 begins to sublimate from the gold substrate, and the resulting mass spectrum of this molecule shows significant peaks corresponding to the $CH_3NH_2^{+\bullet}$ molecular ion (m/z = 31), the most intense fragment assigned to $CH_2NH_2^+$ (m/z = 30) and the radical cations $CH_2NH^{+\bullet}$ and $CHN^{+\bullet}$ (m/z = 29 and m/z = 27, respectively). A complete sublimation of CH_3NH_2 from the gold platted surface occurs at 130 K.

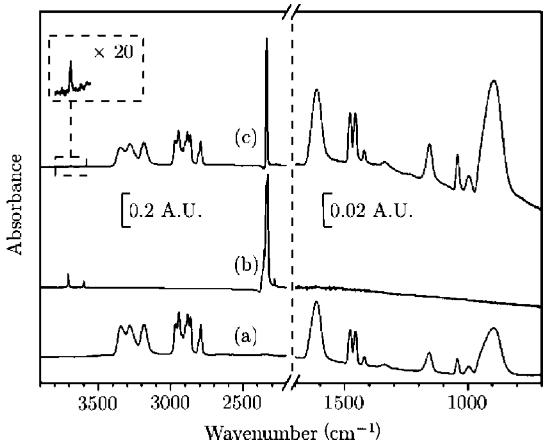


Figure 2. Infrared spectrum of a CH_3NH_2 ice film (a), a CO_2 ice film (b) and a CH_3NH_2:CO_2 = 5:1 ice film deposited at 10 K (c).

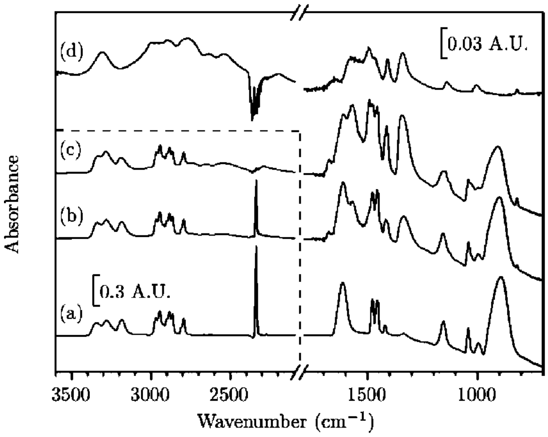


Figure 3. Infrared spectrum of a CH_3NH_2:CO_2 = 5:1 ice film deposited at 10 K then recorded (a), after heating to 50 (b), 80 (c), and 230 K (d). The spectrum (d) is relative to the methylammonium methylcarbamate (C) before desorption.

TABLE 2: Infrared Band Positions (cm^{-1}), Assignments and Measured Band Strengths of Pure Methylammonium Methylcarbamate (C) at 230 K[a]

wavenumber $\bar{\nu}$ (cm^{-1})	ion	assignment[b]	band strength[c], A (10^{-17} cm molecule^{-1})
3302	CH_3NHCOO^-	ν NH	
2989	$CH_3NH_3^+$	(ν_1) ν_s NH_3	
2959	$CH_3NH_3^+$	(ν_8) ν_{as} CH_3	
2934	$CH_3NH_3^+$	(ν_2) ν_s CH_3	
2771	$CH_3NH_3^+$	($\nu_{10} + \nu_{11}$)	
2635	$CH_3NH_3^+$	($\nu_4 + \nu_{11}$)?	
2536	$CH_3NH_3^+$	($\nu_9 + \nu_{12}$)	
2202	$CH_3NH_3^+$	($\nu_{11} + \nu_5$)?	
1652	$CH_3NH_3^+$	(ν_9) δ_{as} NH_3	0.14
1575	CH_3NHCOO^-	ν_{as} COO^-	1.67
1496	CH_3NHCOO^-	δ NH	
1471	$CH_3NH_3^+$	(ν_{10}) δ_{as} CH_3	0.57
1409	CH_3NHCOO^-	ν_s COO^-	0.50
1340	CH_3NHCOO^-	δ CH_3	3.03
1273 (sh)	$CH_3NH_3^+$	(ν_{11}) ρ NH_3	
1141	CH_3NHCOO^-	ν CN	
1005	$CH_3NH_3^+$	(ν_5) ν CN	
945	$CH_3NH_3^+$	(ν_{12}) ρ CH_3	
819	CH_3NHCOO^-	δ_{oop} OCN	0.03

[a] Vibration mode: stretching (ν), bending (δ), rocking (ρ), wagging (ω), torsion (τ). Indication: asymmetric (as), symmetric (s), out-of-plane (oop), and shoulder (sh). [b] Reference. Aresta, 1992; Holas, 2006; Waldron, 1953; Cabana, 1962, and Frasco, 1964. [c] Derived by the total number of CO_2 and CH_3NH_2 consumed in the thermal reaction.

A pure solid infrared spectrum of CO_2 is displayed in Figure 2b and the well-known[22] assignment of these bands is reported in Table 1. The sublimation of CO_2 occurs between 75 and 95 K, that is, before the sublimation of pure CH_3NH_2, and it is monitored in mass spectrometry by the intense molecular ion $CO_2^{+\bullet}$ (m/z = 44).

Methylammonium Methylcarbamate Formation from a CH_3NH_2:CO_2 Solid Film with an Excess of CH_3NH_2. Infrared spectra of a CH_3NH_2:CO_2 binary ice mixture within a 5:1 ratio deposited at 10 K (Figures 2c and 3a) is found to be the contribution of solid CH_3NH_2 (Figure 2a) and CO_2 (Figure 2b) spectra, indicating that no reaction occurs at this temperature. When the sample is warmed up above 40 K (Figure 3b), new features are increasing until the CO_2 is entirely consumed in the reaction around 80 K (Figure 3c). After the complete sublimation of the remaining CH_3NH_2 (130 K), the infrared spectrum is in agreement with the formation of methylammonium methylcarbamate, [$CH_3NH_3^+$][$CH_3NHCO_2^-$] (noted C), and the absorption bands of the spectrum recorded at 230 K (Figure 3d) are reported in Table 2 along with their assignments. By comparison with the most typical bands expected for an alkylcarbamate anion,[12,13] we observe features located at 3302, 1575, and 819 cm^{-1} assigned to the NH stretching, COO^- aymmetric stretching, and OCN out of plane bending, respectively. The most typical vibrational bands of the methylammonium ion are observed at 1652 and 1471 cm^{-1} assigned to NH_3 and CH_3 asymmetric bending, respectively, and between 3000 and 2000 cm^{-1}, which can be explained[30-32] as combinations or overtones of lower modes of $CH_3NH_3^+$. No change in the infrared spectrum of the carbamate (C) is observed until it decomposes above 230 K and totally disappears at 260 K.

The integrated band strength, A (cm·molecule^{-1}), corresponding to the most typical bands of the methylammonium methylcarbamate (C), can be determined by measuring the optical depth, τ_v at a frequency v by means of the following equations where N (absorbing molecule·cm^{-2}) is the total column density of carbamate (C) molecules.

$$A = \int \tau_v \mathrm{d}(\nu)/N$$

This column density N is determined by measuring the amount of CO_2 and CH_3NH_2 molecules having reacted in order to produce the carbamate (C). To evaluate the amount of consumed product, we use the NH_2 wagging mode of CH_3NH_2 at 892 cm^{-1} (1.10×10^{-17} cm·molecule^{-1}) and the C=O asymmetric stretching mode of CO_2 at 2337 cm^{-1} (7.60×10^{-17} cm·molecule^{-1}) before sublimation. The methylammonium methylcarbamate (C) band strengths are listed in Table 2. These values will be useful to determine the column density of the carbamate (C) formed during the thermal or subsequent irradiation processes.

It is interesting to correlate the infrared observations with a mass spectrometry analysis while the sample is warmed up to room temperature. The resulting mass spectrum of the molecules which are released between 230 and 260 K is reported in Figure 4. The molecular ion peak detected at m/z = 75, contains an odd number of nitrogen atoms, and its low intensity suggests instability during the analysis time scale. The resulting fragments for this species are observed at m/z = 45 and m/z = 58 which are assigned to the $COOH^+$ and CH_3NHCO^+ ions, respectively. This set of peaks is consistent with the mass spectrometry detection of neutral methylcarbamic acid ($CH_3NHCOOH$) in the gas phase. From this result, we deduce that, during this

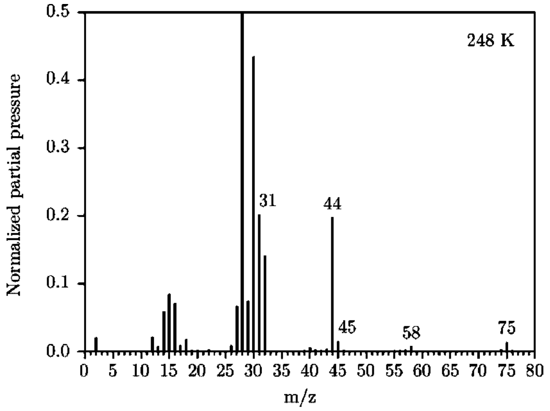


Figure 4. Electronic impact mass spectra (70 eV) of the released molecules at 248 K (CH_3NH_2:CO_2 = 5:1).

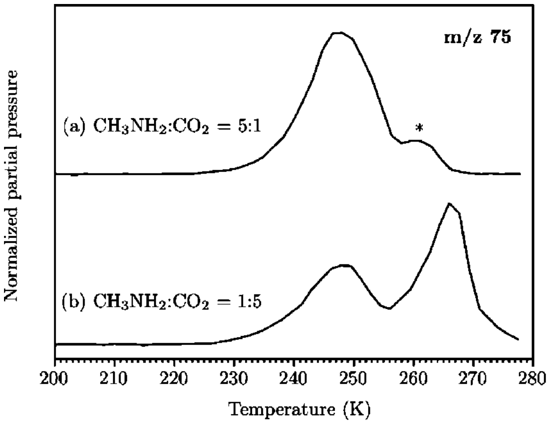


Figure 5. Temperature dependency of methylcarbamic acid detected by mass spectrometry during the annealing phase of different CH_3NH_2:CO_2 ice mixtures. The peak at $m/z = 75$ is relative to $CH_3NHCOOH^{+\bullet}$ molecular ion. The peak * can be explained by the recondensation of molecules onto the cold shield as seen by Bennett[23] et al.

releasing phase, methylammonium methylcarbamate (C) breaks down into $CH_3NHCOOH$ and consequently into CH_3NH_2. The carbamate (C) decomposition (230−260 K) can be followed in Figure 5a, which displays the peak at $m/z = 75$ versus temperature trend. This peak is relative to the methylcarbamic acid molecular ion. By comparison with carbamic acid, NH_2COOH, which is known to be unstable in the gas phase giving CO_2 and NH_3,[15,33−35] we also suggest a partial decomposition of the methylcarbamic acid, $CH_3NHCOOH$ into CO_2 and CH_3NH_2 under our analysis conditions. The result is that the peaks detected at $m/z = 44$ and $m/z = 31$ (Figure 4) must contain a sizable contribution of $CO_2^{+\bullet}$ and $CH_3NH_2^{+\bullet}$ parent radical ions, respectively.

Methylcarbamic Acid Formation from a CH_3NH_2:CO_2 Solid Film with an Excess of CO_2. We study the thermal evolution of several mixtures of CH_3NH_2:CO_2 within different ratios: 1:5, 1:20, and 1:50. The results are pretty similar, with the same products obtained, as long as CO_2 is in excess. We choose to describe here the results related to the CH_3NH_2:CO_2 ice mixture in a 1:5 ratio, deposited at 10 K, and then warmed up until room temperature. At 10 K (Figure 6a), no reaction occurs between these molecules; however, we observe that the NH_2 and CH_3 group vibration modes of CH_3NH_2 and those of CO_2 are perturbed by the new existing interaction between methylamine and carbon dioxide. This one induces a slight frequency shift of NH_2, CH_3 and CO_2 stretching modes. A change in the relative intensity of the NH_2 and CH_3 stretching modes is also observed. As the sample is heated above 40 K (Figure 6b), a drastic change is observed in the infrared spectrum compared to the 10 K one. A decrease of methylamine and CO_2 absorption bands is going along with the increase of several bands. These bands are sorted out according to their differentiation during the thermal process into three sets corresponding to three species.

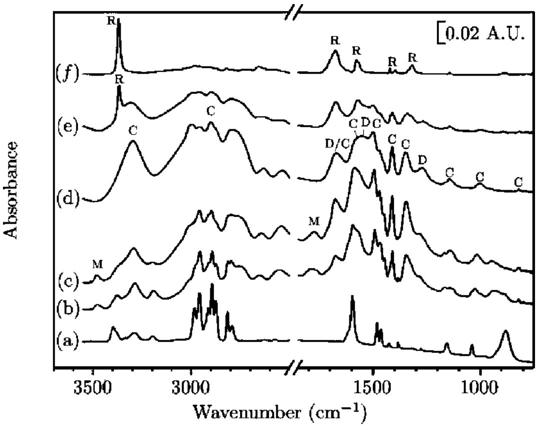


Figure 6. Infrared spectrum of a CH_3NH_2:CO_2 = 1:5 ice film deposited at 10 K then recorded (a), after heating to 60 (b), 80 (c), 110 (d), 240 (e), and 250 K (f). The C abbreviation refers to methylammonium methylcarbamate; M refers to monomer; D refers to dimer; and R refers to residue.

As the first species noted, M is mainly characterized by one band at 3480 cm^{-1} and another one at 1775 cm^{-1}. They are weakly intense, but they increase until 80 K (Figure 6c), then decrease until they fully disappear at 110 K (Figure 6d). M species has the typical behavior of an intermediate. The two observed frequencies for this latter are in good agreement with the theoretical values:[36] 3467 and 1778 cm^{-1} assigned to the NH and C=O stretching mode for the methylcarbamic acid monomer. According to our calculations, we estimated these bands at 3508 and 1756 cm^{-1}, respectively, using a single scaling factor (0.9613).[28]

The second set of bands is similar to the bands observed during the warming up of the CH_3NH_2:CO_2 within a 5:1 ratio sample, and it is therefore consistent with the formation of methylammonium methylcarbamate (C). The IR absorption features of the carbamate (C) increase until the CH_3NH_2 is entirely consumed at 90 K. The CO_2 desorption occurring between 75 and 95 K induces a loss of material. As a result, the carbamate (C) bands decrease as this latter is going away with carbon dioxide. Only the band at 3302 cm^{-1} seems to be differently affected because of the environment effect. Between 120 and 220 K, no change in the spectra is observed.

A third species is observed, noted D in the spectrum (Figure 6d). Its features are obtained by substracting the carbamate (C) vibrational bands to the 230 K spectrum (Figure 7a). We find similarities with the infrared spectrum of sarcosine, CH_3NHCH_2COOH as a dimer[37] such as the broad and weak band located at 3062 cm^{-1} and the intense bands at 1679 cm^{-1} and 1263 cm^{-1} (Figure 7a) which can correspond to the υOH, υC=O, and δOH + υC−O modes, respectively. This is consistent with a hydrogen-bonded pair of molecules as encountered in carboxylic acid. The weak number of vibrational bands observed in the IR spectrum suggests the formation of a centrosymetric carboxylic acid dimer-like organization for methylcarbamic acid. Our results are also in agreement with those of Jamróz[38] et al. who have reported such a centrosymmetric structure for dibenzyl carbamic acid dimer.

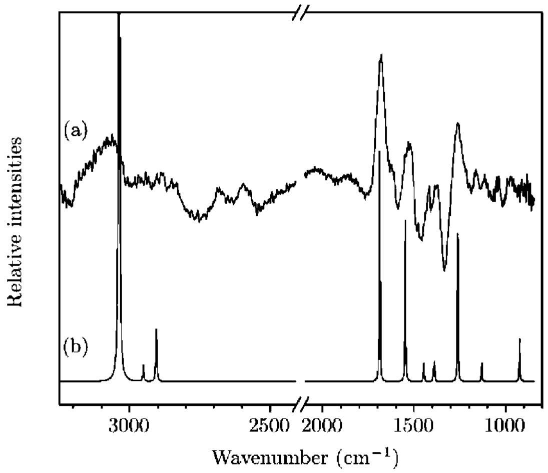


Figure 7. Comparison between the experimental spectrum of the dimer (a), recorded upon heating the CH_3NH_2:CO_2 mixture within a 1:5 ratio at 230 K and then subtracted to the methylammonium methylcarbamate (Figure 3d), and the theoretical infrared spectrum of methylcarbamic acid dimer (b). Calculation is performed with the B3LYP/6−311G** level of theory, and the frequencies are scaled with a single factor (0.9613).

As expected, the carbamate (C) breaks down above 230 K until it totally disappears at 260 K. In this temperature range, new features appear in the 3500−2800 cm^{-1} range and in the 1700−1200 cm^{-1} range (Figure 6f), showing strong similarities with dimer (D) IR spectrum (Figure 7a). One of the most typical bands is located at 3369 cm^{-1} in the NH stretching region. This species fully desorbs above 270 K. We suggest from these observations that carbamate (C) decomposition allows the association between the remaining dimer (D) species. Thus, we observe a decrease of dimer (D) vibrational bands. This aggregation of dimers (D) gives a more organized structure noted (R) as residue.

As for the mixture CH_3NH_2:CO_2 in a 5:1 ratio, we determine the nature of the molecules released during the thermal process using mass spectrometry. In Figure 5b, two distinct peaks are observed, and they are assigned to the methylcarbamic acid molecular ion. The first peak (248 K) fits nicely with the one observed in the CH_3NH_2:CO_2 = 5:1 experiment, because of the carbamate (C) decomposition. The second peak (266 K) is consistent with the neutral methylcarbamic acid coming from the residue (R) desorption. The mass spectrum obtained at 266 K is noticeably the same as the spectrum recorded at 248 K (Figure 4).

Characterization of the Neutral Forms of Methylcarbamic Acid. Our experimental results show that methylcarbamic acid can be thermally produced on different neutral forms: monomer (M), dimer (D), and also a more organized structure obtained as a residue (R). The most stable structure for the monomer (M) has been calculated[36] as seen in Scheme 1. Except for the H of the methyl group, all other atoms are in the same plane. The only two vibrational frequencies observed for this molecule are in excellent agreement with those calculated from the geometry described above. The other modes are not observed because they are overlapped with the carbamate (C) absorption bands as they continuously grow within this temperature range. Considering that the dimer (D) formation results from the association between two methylcarbamic acid molecules with the most stable geometry, we obtain the neutral centrosymmetric methylcarbamic acid dimer (D) as displayed in Scheme 1. This dimer (D) is the most stable dimer configuration among all of the possibilities that we calculated (see Supporting Information). This dimer (D) displays interactions similar with those observed into carboxylic acids, each monomer being bonded by two OH•••O=C hydrogen bonds related by an inversion center. We observe that the dimer (D) infrared spectrum calculated at the B3LYP/6−311G** level of theory and scaled with a single coefficient (0.9613) fits nicely the experimental data (Figure 7a,b), and thus, the assignment of the different modes is straightforward. The dimer (D) vibrational frequencies and modes are summed up in Table 3. The IR inactivity of the symmetric modes in the dimer (D) structure gives a very simple spectrum. The νOH and νC=O asymmetric stretching modes appear at lower frequencies than for the monomer, whereas the δOH + νC−O mode is observed at higher frequency. Note that the νOH stretching mode is also very broad and weak. The difference between experimental and calculated νOH intensity modes underlines the importance of anharmonic effects, which are not taken into account in our calculations. The νNH stretching mode, weakly intense, is not observed in the dimer (D) spectrum.

The residue (R) infrared spectrum obtained after the carbamate (C) disappeared is very similar to the dimer (D) infrared spectrum and suggests that this residue (R) could be the result of the association between the dimers (D). Taking into consideration an association between two of these dimers, we obtain a centrosymmetric tetramer structure, noted (T), displayed in Scheme 1. The comparison of the calculated infrared spectrum for this new structure with the spectrum of the residue (Figure 8a,b) strengthens the existence of a well-organized structure. The frequency shifts between the bands of the dimer (D) and those of the tetramer (T) are in accordance with our observations. The most striking effects are a downshift of the νOH and νNH stretching modes (this latter one at 3369 cm^{-1} becoming more intense) and an upshift of the νCN + δNH and νOH + δC−O modes. The νC=O mode appears at the same frequency for the dimer (D) and tetramer (T) structures. Our results show that we could represent the residue (R) as a ramified centrosymmetric structure, built from dimers (D), as seen in Scheme 1. Table 4 lists the residue (R) bands along with their assignments.

Discussion

Our investigations show that, for temperature above 40 K, a methylamine and excess carbon dioxide mixture gives methylcarbamic acid monomer (M) and dimer (D) as well as methylammonium methylcarbamate (C), according to the process summarized in Scheme 2. The monomer (M) is an intermediate leading to methylammonium methylcarbamate (C) and to dimer (D). The ratio between these two forms is very sensitive to the environment. A methylamine excess leads to the formation of carbamate (C) exclusively whereas a CO_2 excess increases the production of dimer (D). Between 50 and 80 K, we estimated the ratio D/C to be lower than 1 in the CH_3NH_2:CO_2 = 1:5 experiment, using the carbamate (C) band strengths and the column density evolution of both methylamine and carbon dioxide. This estimation can be done only before the CO_2 sublimation which induces a loss of material preventing any further quantification.

Our results are in good agreement with several theoretical studies[4,39,40] showing that carbamic, methylcarbamic, and dimethyl carbamic acid monomers can be produced from the reaction between ammonia, methylamine, and dimethylamine and carbon dioxide, respectively. By modeling the reaction in the presence of a second amine molecule, a lower activation enthalpy is obtained. For the dimethylamine/carbon dioxide reaction, this value is estimated to 40 kJ/mol. This low value is

TABLE 3: Experimental and Calculated (B3LYP/6-311G) Frequencies (cm^{-1}) with Their Assignments and Potential Energy Distribution (PED) of Methylcarbamic Acid Dimer (D)[a]**

Experimental IR (D)		Calculated IR (D)			
assignment	frequencies (cm^{-1})	frequencies (cm^{-1})	intensities (km mol^{-1})	scaled (cm^{-1})	PED (%)
		3647	76	3506	ν NH (100)
ν OH	3062	3159	4125	3037	ν OH (100)
ν_{as} CH_3	2942	3069	73	2950	ν_{as} CH_3 (100)
ν_s CH_3	2889	3021	237	2904	ν_s CH_3 (100)
	2850				
	2680				
	2595				
ν C=O	1679/1628 (sh)	1757	1028	1689	ν C=O (90), δ OH (10)
ν CN + δ NH	1533	1611	740	1548	ν CN (60), δ NH (20)
	1478				
δ_d CH_3	1441/1417	1507	84	1449	δ_d CH_3 (100)
δ_s CH_3 + δ OH	1388	1451	61	1395	δ_s CH_3 (80), δ OH (20)
δ OH	1374	1445	86	1389	δ OH (100)
δ OH + ν C—O	1263	1313	669	1262	δ OH (80), ν C—O (10)
δ_{as} CH_3	1163	1176	86	1130	δ_{as} CH_3 (85), δ NH (10)
		1160	3	1115	ν N-CH_3 (100)
		961	190	924	δ_{oop} OH (100)
		781	20	750	τ H bonding (100)

[a] Vibration mode: stretching (ν), bending (δ), rocking (ρ), wagging (ω), torsion (τ). Indication: asymmetric (as), symmetric (s), degenerated (d), out-of-plane (oop) and shoulder (sh).

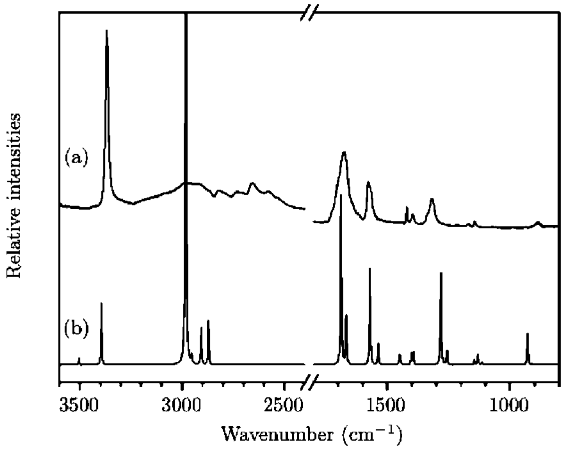


Figure 8. Comparison between the experimental spectrum of the residue (R) recorded upon heating the CH_3NH_2:CO_2 mixture within a 1:5 ratio at 250 K (a) and the theoretical (b) infrared spectrum of methylcarbamic acid tetramer (T). Calculation is performed with the B3LYP/6−311G** level of theory, and the frequencies are scaled with a single factor (0.9613).

consistent with the ability to form dimethylcarbamic acid at low temperature. The methylcarbamic acid dimers (D) formation results from the aggregation between monomers (M) during the thermal activation of the sample.

The methylammonium methylcarbamate (C) can be produced by an acid−base reaction that transfers the methylcarbamic acid carboxylic group hydrogen atom to the methylamine nitrogen. It is likely that the methylcarbamic acid solvation by methylamine is the driving factor of this reaction, and we plan further quantum calculations to check it. Our results do not exclude forming carbamate (C), directly from the reaction between CH_3NH_2 and CO_2 without any neutral methylcarbamic acid intermediate (M).

The carbamate (C) decomposition above 230 K gives $CH_3NHCOOH$ and CH_3NH_2 as clearly evidenced by mass spectrometry and the self-association of the remaining dimers (D) leading to a residue (R). Indeed the infrared spectrum of the residue (R) is consistent with a well-organized centrosymmetric structure. The peaks at $m/z = 44$ and $m/z = 31$ show that methylcarbamic acid can be fragmented into carbon dioxide and methylamine radical cations either under electronic impact source or by neutral dissociation due to its instability. The mass spectrum of the desorbed methylcarbamic acid coming from the residue (R) shows that the former can be partially dissociated into CH_3NH_2 and CO_2.

Our results lead us to a comment on the study performed by Holtom[18] et al. dealing with the formation of glycine and methylcarbamic acid induced by proton irradiation of a methylamine and carbon dioxide binary ice mixture. First, it is clear that the spectrum obtained at 10 K before irradiation for this mixture is mainly due to the methylammonium methylcarbamate spectrum. Second, the infrared spectrum which is obtained in the 1800−1200 cm^{-1} range, after irradiation by energetic electron and annealing of the sample, displays strong similitude with the spectrum of the neutral methylcarbamic acid and also methylammonium methylcarbamate. They assigned these bands to glycine under an anionic and zwitterionic form. No band in their spectrum show clear evidence of glycine formation. However, it is true that the formation of glycine in the Holtom's experiment cannot be ruled out, but if it is produced, it is not the main product.

Conclusions

Our infrared study shows that the CH_3NH_2 and CO_2 can react at low temperature to yield methylammonium methylcarbamate $[CH_3NH_3^+][CH_3NHCO_2^-]$ and methylcarbamic acid ($CH_3NHCOOH$). The carbamate is mainly formed when CH_3NH_2 is in excess with respect to CO_2. When CO_2 is in excess, the carbamate is still the main product, but methylcarbamic acid monomer and dimer are also observed. The dimer is centrosymmetric and involves intermolecular H bonds between the C=O and OH groups. It results from the association between previously formed methylcarbamic acid monomers. At higher temperature, the methylammonium methylcarbamate breaks down into methylcarbamic acid and methylamine, which gives a residue resulting from the association between methylcarbamic acid dimers.

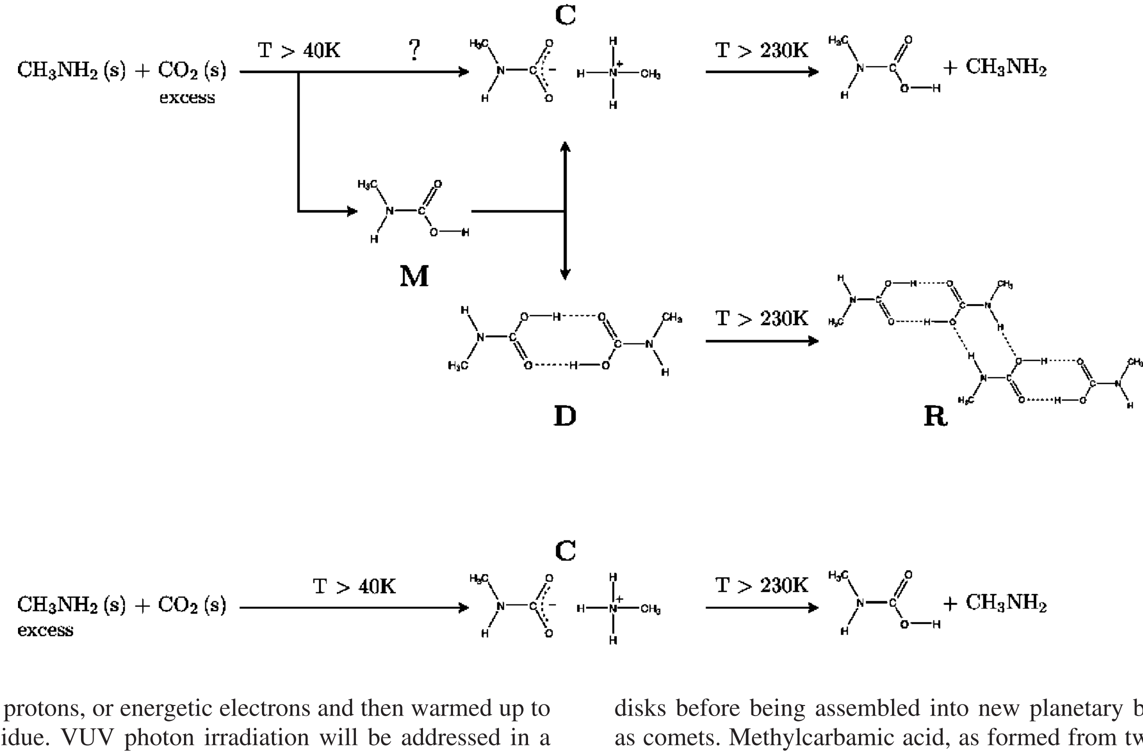
This study will help to a better understand the processes occurring between CH_3NH_2 and CO_2 when irradiated by

TABLE 4: Experimental Frequencies (cm^{-1}) with Their Assignments of Residue (R) and Calculated (B3LYP/ 6-311G) Frequencies (cm^{-1}) of Methylcarbamic Acid Tetramer (T)[a]**

Experimental IR (R)		Calculated IR (T)		
assignment	frequencies (cm^{-1})	frequencies (cm^{-1})	intensities ($km \cdot mol^{-1}$)	scaled (cm^{-1})
ν NH free		3646	80	3505
ν NH H bonding	3369	3532	736	3395
	3070			
ν OH H bonding	2985	3103	8764	2983
ν_{as} CH_3	2959	3074	60	2955
ν_s CH_3	2919	3022	393	2905
ν OH H bonding	2867	2987	529	2871
	2820/2802			
	2723			
	2658			
	2581			
	2534			
ν C=O	1672/1619 (sh)	1755/1733	2023/561	1687/1666
ν CN + δ NH	1578	1633/1598	1110/252	1570/1536
δ_d CH_3	1421	1508	115	1450
δ OH	1396	1458	129	1402
δ_s CH_3 + δ OH	1396	1450	146	1394
δ OH + ν C−O	1318	1333/1307	1069/164	1281/1256
δ_{as} CH_3	1170	1191	64	1145
δ_{as} CH_3	1144	1176	125	1131
ν N-CH_3		1160	35	1115
δ_{oop} OH	884	965	372	928
τ H bonding	786	780	29	750

[a] Vibration mode: stretching (ν), bending (δ), rocking (ρ), wagging (ω), torsion (τ). Indication: asymmetric (as), symmetric (s), out-of-plane (oop) and shoulder (sh).

SCHEME 2: Reactions Occurring during the Thermal Process



photons, protons, or energetic electrons and then warmed up to get a residue. VUV photon irradiation will be addressed in a forthcoming paper.

From an interstellar medium physical chemistry point of view, our results show that methylcarbamic acid can be formed thermally in the interstellar ices once the icy mantle of dust grains is heated up, as by a newly formed star. When this star warms the ices up, methylcarbamic acid sublimates into the gas phase, the so-called "hot core" region ($T > 200$ K) in the immediate vicinity of massive protostars. A part of the gas phase and icy material can also be incorporated into the circumstellar disks before being assembled into new planetary bodies such as comets. Methylcarbamic acid, as formed from two detected molecules, would be an interesting candidate for radio astronomy detection toward hot core sources or comets. If both reactants are the main way toward glycine formation, methylcarbamic acid is formed in much more abundance than glycine. However, because of its poor gas phase stability, it may possibly be detected in the solid phase ISM.

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Supporting Information Available: Structures, relative energies and calculated vibrationnal frequencies of methylcarbamic acid conformers and dimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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