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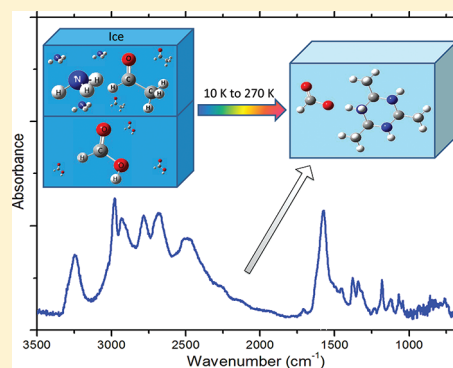
Acetaldehyde Solid State Reactivity at Low Temperature: Formation of the Acetaldehyde Ammonia Trimer

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ABSTRACT: We focus on low temperature reactivity from 25 to 300 K, in ice containing acetaldehyde, ammonia, and formic acid. We show that the warming of this ice mixture forms the acetaldehyde ammonia trimer (2,4,6-trimethyl-1,3,5-hexahydrotriazine, $C_6H_{15}N_3$) after five steps. The reaction is monitored by FTIR spectroscopy and mass spectrometry. We propose a mechanism for its formation that differs from the one proposed in the liquid phase. The reaction intermediates, α -aminoethanol (from 80 K) and ethanimine (formed at 180 K), have been identified by a mechanistic approach: each step of the reaction has been treated separately. The chemical implications and the astrophysical relevance of the study are also discussed.



INTRODUCTION

Acetaldehyde ammonia trimer is a cyclic molecule that can be formed easily at room temperature in the liquid phase from acetaldehyde, CH_3CHO , and ammonia, NH_3 .¹ The reaction goes directly to the acetaldehyde ammonia trimer formation, but this molecule is unstable at room temperature and the product has to be maintained in methanol or water. Nowadays, the acetaldehyde ammonia trimer has various roles in chemistry. It has been used as a scavenger for sulfhydryl compounds, for example, in the petroleum industry,² as a reactant in organic chemistry,³ and also for its capability to generate ammonia from 313 K.⁴

The reaction to form the 2,4,6-trimethyl-1,3,5-hexahydrotriazine ($C_6H_{15}N_3$) from acetaldehyde and ammonia was studied by Hull et al. in 1973 by NMR spectroscopy.⁵ They predicted a reaction scheme based on addition of RNH_2 to a carbonyl group shown by several studies^{6,7} to form the corresponding amino alcohol. They tried to identify the intermediates expected but neither the α -aminoethanol ($CH_3CH(OH)NH_2$) nor the corresponding imine were observed or isolated. The reaction in the liquid phase at room temperature is too fast to permit the isolation of the intermediates even by NMR spectroscopy, and they predicted a lot of intermediate species coming from the reaction between the amino alcohol and the corresponding imine. In this article, we focus on the acetaldehyde ammonia trimer (2,4,6-trimethyl-1,3,5-hexahydrotriazine, $C_6H_{15}N_3$) formation at low temperature from an ice mixture containing acetaldehyde (CH_3CHO), ammonia (NH_3), and formic acid ($HCOOH$) in the solid state. Experimental low temperature chemistry (10–200 K) is an

important tool for the understanding of reaction mechanisms and the isolation of reaction intermediates, as well as for organic, industrial, or interstellar chemistry applications. The chemistry of interstellar grains inside the interstellar clouds consists of thermal, photochemical, and cosmic-ray energetics processes that can trigger chemical reactions. The icy mantles of the interstellar grains (10–100 K) are mainly composed of amorphous water ice and some other constituents, such as NH_3 , CO , H_2CO , and CO_2 , that surround a silicate core.^{8,9} Among energetic processes that trigger reactions in the icy mantle, the thermal reactions that occur at low temperature (10–100 K) start to be studied and can be a source of the complex molecules observed in the interstellar medium. Those reactions can be classified into three types: acid–base reactions,^{10,11} nucleophilic additions,^{12–14} and isomerization.^{15,16} Gas phase acetaldehyde was detected in the interstellar medium from its rotational transitions and is suspected to be present into ice mantles. The presence of this molecule in ices should not exceed 1% with respect to water.¹¹ Ammonia and formic acid have been detected both in gas and in ice mantles.

The thermal reactions between amines and aldehydes have been the subject of several studies.^{6,17–19} One example of this reactivity is the ammonia and formaldehyde condensation in liquid phase leading to the formation of hexamethylenetetramine (HMT; $C_6H_{14}N_4$), while its reaction with aliphatic

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aldehydes leads to 2,4,6-trialkyl-1,3,5-hexahydrotriazine.⁶ Recently, Vinogradoff et al. have shown that the HMT (hexamethylenetetramine) can be formed in astrophysical conditions (i.e., low temperature and pressure) from a formaldehyde–ammonia–formic acid ice mixture in the solid state.²⁰ This molecule is also a good ammonia generator and has the same base structure as the acetaldehyde ammonia trimer. However, there are still unanswered questions about the reaction mechanism and the nature of the intermediates.¹⁷ Nielsen et al. in 1973 suggested the intermediacy of amino alcohol in the reaction to form the HMT and the acetaldehyde ammonia trimer, but until now, there are no direct experimental evidence of such intermediates.^{6,17} Next to the amino alcohol, Hull et al. in 1973 also suggest that the imine can be an intermediate, but no experimental evidence has been found.

In the present work, we put in evidence a complex mechanism for the formation of the acetaldehyde ammonia trimer from acetaldehyde and ammonia, where several intermediates such as α -aminoethanol [$\text{NH}_2(\text{CH}_3)\text{CHOH}$] and iminium ($\text{HCOO}^-\text{CH}_3\text{CH}=\text{NH}_2^+$) are experimentally observed in situ for the first time. We show that acetaldehyde and ammonia thermally react around 90 K, giving α -aminoethanol,¹⁴ which dehydrates in the presence of HCOOH , giving the corresponding protonated imine, $\text{CH}_3\text{CH}=\text{NH}_2^+$. This latter species leads to the formation of the protonated acetaldehyde ammonia trimer ($\text{C}_6\text{H}_{15}\text{N}_3\text{H}^+$) during the sample warming. The solid state allows to put in evidence the intermediates supposed to be in liquid phase. The astrophysical implications of these results are discussed in the last part of this manuscript.

RESULTS AND DISCUSSION

Thermal Reaction of Acetaldehyde Ammonia Trimer and Formic Acid at Low Temperature. *Infrared and Mass Spectra of Acetaldehyde Ammonia Trimer.* In this section, we present the infrared and mass spectra of the acetaldehyde ammonia trimer. The infrared spectrum of the solid acetaldehyde ammonia trimer has already been studied by Novak in 1960,¹ but its vibrational assignment was approximated. We used quantum calculations at the B3LYP/6-31G** level to give a more accurate assignment. The optimized geometry used for the vibrational calculations has a C_{3v} symmetry, with the methyl groups in an equatorial position (Figure 1), while the hydrogen atoms carried by the nitrogen atoms are in an axial position.⁶

Moreover, we present its mass spectrum for the first time. Acetaldehyde ammonia trimer is known as a trihydrate of 2,4,6-trimethylhexahydro-1,3,5-triazine, $(\text{CH}_3\text{CHNH})_3 \cdot 3\text{H}_2\text{O}$.¹ Figure 1a displays the infrared spectrum of the hydrated form of the acetaldehyde ammonia trimer from Aldrich, deposited and recorded at 115 K, to remove the impurity (NH_3). The infrared bands as well as the calculated frequencies are listed in Table 1 with their vibrational assignments, established from previous work as well as from the comparison with theoretical and experimental frequencies (Table 1). We observe a good agreement between the experimental and the B3LYP frequencies, except in the $3500\text{--}3000\text{ cm}^{-1}$ for the NH stretching modes. This difference could be due to the fact that the NH stretching modes are sensitive to the environment, which is not taken into account in our calculations. Four bands are not assigned. They are located at 2816, 2779, 2680, and 2525 cm^{-1} and can be due to harmonic or combination bands

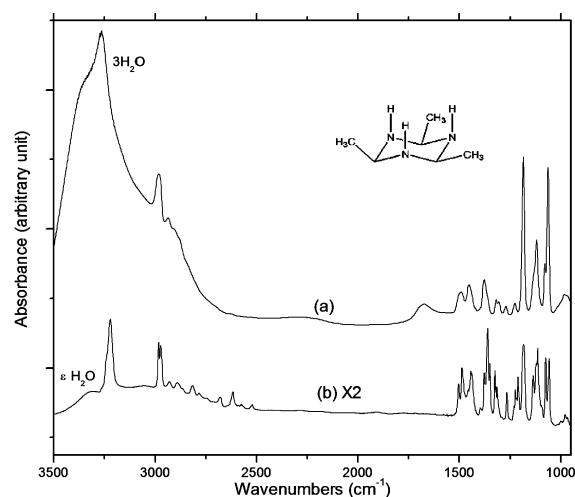


Figure 1. Characterization of acetaldehyde ammonia trimer: FTIR spectrum deposited at 115 K and recorded at (a) 115 K in its hydrated form and (b) 230 K in its dehydrated form (a small amount of water molecules may be still present).

(Table 1). In the NH and OH stretching region ($3500\text{--}3100\text{ cm}^{-1}$), there is a strong and broad band due to both NH stretching of the trimer and the OH stretching of water, Figure 1a. The OH bending mode of water molecules is also observed at 1674 cm^{-1} . The most intense bands of the hydrated species are observed at 1184 and 1064 cm^{-1} due to C–N stretching modes. As water molecules sublime around 200 K, the infrared spectrum of the trimer is drastically changed (Figure 1b). The spectrum of the dehydrated species is now dominated by a strong NH band at 3218 cm^{-1} . The region between 1600 and 1000 cm^{-1} is more complicated, with new bands and shifted bands (Table 1). The trimer fully sublimated at 230 K. The mass spectrum of the acetaldehyde ammonia trimer is displayed in Figure 2a. The molecular ion is observed at m/z 129. The most characteristic peaks are observed at m/z 115 and 86. Nevertheless, the intensity of the $(M + 1)$ peak at m/z 130 is relatively high if we compare with the intensity of the molecular ion. According to the molecular formula, the intensity of the $(M + 1)$ peak should be around 8% of the intensity of the molecular peak at m/z 129, while 50% is experimentally observed. This variation could be due to an ion–molecule reaction in the ionization chamber of the mass spectrometer.²¹ These results will serve as benchmarks for the reactivity of the acetaldehyde ammonia trimer with HCOOH , and the peaks observed at m/z 86 and 115 will be used in this manuscript as a probe for the acetaldehyde ammonia trimer formation.

Thermal Reaction of Acetaldehyde Ammonia Trimer and Formic Acid. Figure 3 displays the FTIR spectrum of a pure ice of HCOOH deposited at 25 K (bottom layer) on which we added a second layer of the acetaldehyde ammonia trimer hydrated (top layer). We chose to work with separated layers instead of a mixed ice to prevent any reaction between them in the gas phase during the gas deposition. This bilayered ice is then slowly warmed to 300 K. Before 140 K, the spectrum is the combination of the FTIR spectra of pure HCOOH , Figure 3c, and pure acetaldehyde ammonia trimer, Figure 3d, as shown in Figure 3a, which indicates the absence of reaction between the two layers. The bands of acetaldehyde ammonia trimer are marked by stars. As the HCOOH starts to diffuse ($T > 160\text{ K}$) and gets through the acetaldehyde ammonia trimer, the FTIR

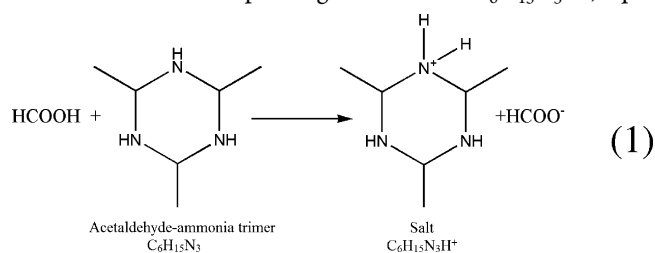
Table 1. Comparison of the Experimental Infrared Spectrum of the Acetaldehyde Ammonia Trimer in Its Hydrated, Dehydrated, and Protonated Forms with the B3LYP/6-31G** Calculated Infrared Spectrum^a

assignment	wavenumbers (cm ⁻¹)				
	acetaldehyde ammonia trimer		ice HCOOH/C ₆ H ₁₅ N ₃	B3LYP/6-31G** (cm ⁻¹)	
	C ₆ H ₁₅ N ₃ ·3H ₂ O 140 K	C ₆ H ₁₅ N ₃ 230 K	HCOO ⁻ /C ₆ H ₁₅ N ₃ H ⁺ 260 K	C ₆ H ₁₅ N ₃	C ₆ H ₁₅ N ₃ H ⁺
ν(OH)	3267 (s)				
ν(NH)			3300 (w)		3399 (13)
ν(NH)		3218 (s)	3246 (w)	3318 (5)	3360 (24)
ν(NH)					3280 (18)
ν(CH)	2980 (s)	2982 (s)		3024 (13)	3043 (1)
ν(CH)		2972 (s)		2990 (30)	3030 (1)
ν(CH)			2983 (s)		3008 (16)
ν(CH)	2934 (w)	2927 (w)	2927 (s)	2917 (57)	2957 (15)
ν(CH)		2887 (w)		2908 (6)	2937 (15)
		2816 (w)			
		2779 (w)	2782 (s)		
		2680 (w)	2686 (s)		
		2525 (w)	2448 (s)		
δ(OH)	1674 (w)				
ν _{as} (COO ⁻)			1571 (s)		
δ(NH ₂)			1571 (s)		1567 (6)
δ(CH)	1493 (m)	1484 (m)	1456 (w)	1461 (11)	1448 (6)
δ(NH)	1453 (w)	1444 (m)	1456 (w)	1446 (4)	1469 (12)
δ(NH)					1425 (25)
δ(CH)	1380 (w)	1380 (m)	1373 (m)	1380 (3)	1380 (12)
δ(CH)	1360 (m)		1373 (m)	1363 (4)	1367 (9)
δ(CH)	1350 (m)	1350 (w)		1350 (4)	
ν _s (COO ⁻)			1342 (m)		
δ(CH)	1324 (m)	1317 (w)	1314 (w)	1334 (<1)	1325 (31)
δ(CH)	1268 (m)	1268 (w)	1314 (w)	1277 (8)	1293 (27)
δ(NH)	1212 (m)	1224 (w)	1241 (w)	1233 (<1)	1230 (50)
ν(CN)	1184 (s)	1184 (s)		1175 (33)	
ρ(CH)			1181 (w)		1152 (41)
ν(CN)	1116 (m)	1113 (m)	1120 (w)	1090 (30)	1135 (11)
ν(C–N)			1085 (w)		1084 (31)
δ _{o.o.p.} (NH)			1073 (w)		1063 (21)
ν(CC)	1064 (s)	1076 (s)		1032 (36)	
ν(CN)		1058		1063 (<1)	
ρ(CH)			1039 (w)		1033 (33)
ρ(CH)					988 (37)
ν(CC)	980 (w)	980 (w)		914 (3)	926 (6)
δ _{o.o.p.} (NH)	921 (m)	921 (m)	865 (12)		
δ _{o.o.p.} (CH)			847 (w)		847 (4)
δ _{o.o.p.} (NH)	813 (m)	813 (m)		763 (100)	654 (100)
δ _{o.o.p.} (NH)			760 (w)		696 (7)

^aHarmonic frequencies are scaled with a factor of 0.96. Only calculated frequencies with intensity higher than 0.5% are presented in this table. Vibration mode: stretching (ν), bending (δ), out of plane deformation (δ_{o.o.p.}), rocking (ρ), antisymmetric mode (as), and symmetric mode (s). Experimental and calculated intensities are given between brackets: strong (s), medium (m), and weak (w).

spectrum changes, indicating a thermal reaction between the two compounds. Around 180–200 K, water sublimates and the acetaldehyde ammonia trimer in its dehydrated form is still observed, along with the formic acid and a new species. At 260 K, the starting materials (HCOOH and trimer) have fully sublimated, and we observe the FTIR spectrum of the newly formed molecule (Figure 3b). The structure of this compound has been elucidated by FTIR spectroscopy and mass spectrometry as well as by quantum calculation. The FTIR spectrum of the compound at 260 K exhibits very characteristic features located at 1571 and 1342 cm⁻¹ due to the antisymmetric and symmetric C–O stretching modes of the

HCOO⁻,¹¹ which indicates an acid–base reaction between HCOOH and acetaldehyde ammonia trimer leading to the formation of the corresponding salt: HCOO⁻C₆H₁₅N₃H⁺, eq 1.



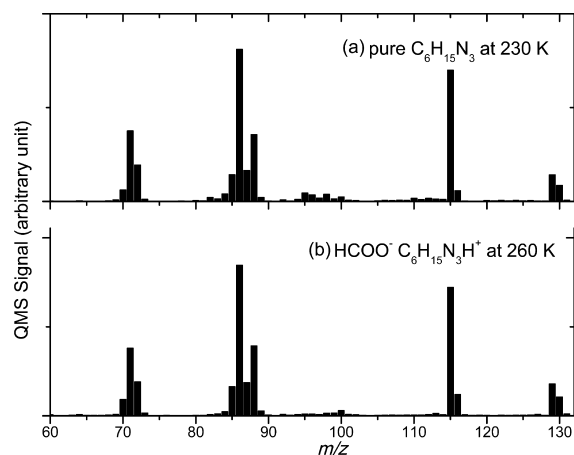


Figure 2. Mass spectrum using a quadrupole mass spectrometer with a 70 eV impact electronic source of (a) the acetaldehyde ammonia trimer ($\text{C}_6\text{H}_{15}\text{N}_3$, $3\text{H}_2\text{O}$) obtained at 230 K and (b) $\text{HCOO}^-\text{C}_6\text{H}_{15}\text{N}_3\text{H}^+$ at 260 K.

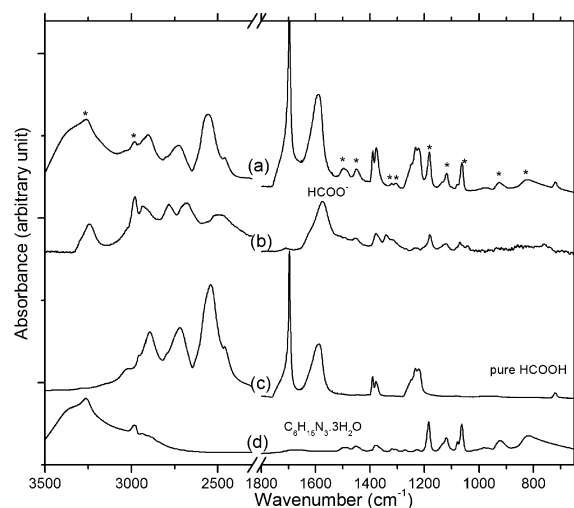


Figure 3. Formation of acetaldehyde ammonia trimer salt: FTIR spectrum of (a) bilayered ice $\text{HCOOH}/\text{acetaldehyde ammonia trimer}$ at 140 K, (b) bilayered ice $\text{HCOOH}/\text{acetaldehyde ammonia trimer}$ at 260 K, compare with (c) pure HCOOH at 140 K, and (d) pure acetaldehyde ammonia trimer at 140 K. The stars show the bands of acetaldehyde ammonia trimer in the mixture with HCOOH .

Position of the salts infrared bands and their vibrational assignments are given in Table 1 with the calculated B3LYP frequencies. $\text{HCOO}^-\text{C}_6\text{H}_{15}\text{N}_3\text{H}^+$ formation from HCOOH and acetaldehyde ammonia trimer is also supported by mass spectrometry. At a temperature higher than 260 K, this salt sublimates and its mass signature is recorded. The mass spectrum of the salt at 260 K is the same as the one recorded at 230 K for pure acetaldehyde ammonia trimer (Figure 2a,b), which indicates the reverse reaction, leading to the release of HCOOH and the free base of acetaldehyde ammonia trimer in the gas phase. This kind of decomposition has been already observed in ice for different salts at low temperature.^{12,22}

Warming of an Ice Mixture $\text{CH}_3\text{CHO}/\text{NH}_3/\text{HCOOH}$.

Figure 4a displays the FTIR spectrum of a pure ice of HCOOH deposited at 25 K (bottom layer) on which we added a second layer of an acetaldehyde (CH_3CHO) and ammonia in excess (top layer), and the mixture deposited at 25 K, with a 1/3 ratio between CH_3CHO and NH_3 .

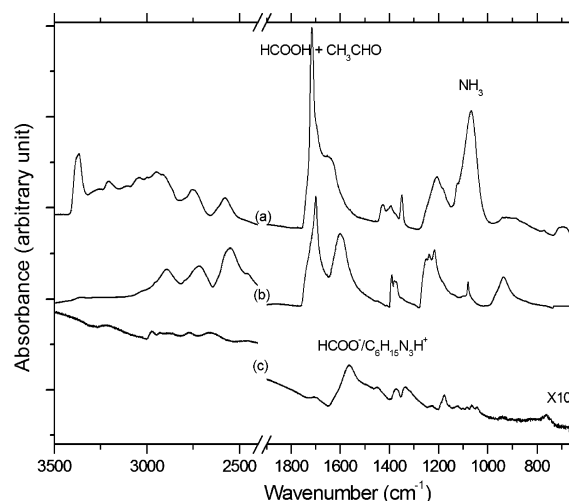
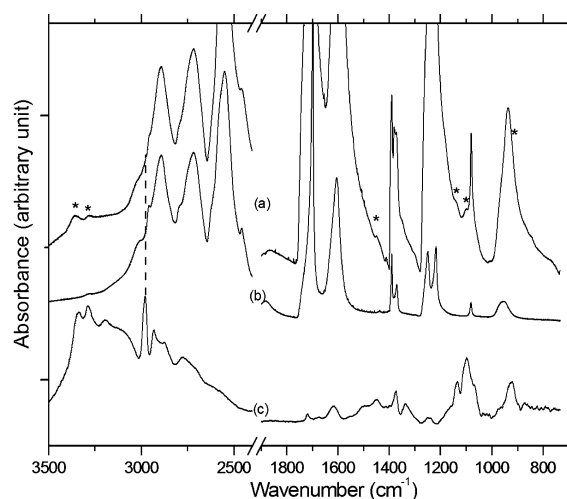


Figure 4. Formation of α -aminoethanol and acetaldehyde ammonia trimer salt: FTIR spectra recorded during the warming of a bilayered ice, $\text{HCOOH}/\text{CH}_3\text{CHO} + \text{NH}_3$; spectrum recorded at (a) 25, (b) 150, and (c) 260 K.

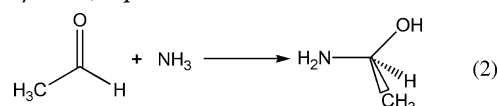
As previously, we chose to work with separated layers instead of a mixed ice to prevent any reaction between formic acid and ammonia. Indeed, those two molecules are known to react spontaneously at low temperature (40 K) leading to ammonium formate ($\text{HCOO}^-\text{NH}_4^+$).¹¹ Furthermore, the composition of the bottom and top layers is dictated by the sublimation temperatures, or the reaction temperature of the molecules present in each layer. For example, HCOOH is known to sublimate under our vacuum condition at around 160 K. Pure acetaldehyde and pure ammonia fully sublimate around 130 K. The reaction between ammonia and acetaldehyde was shown by Duvernay et al., giving from 90 K the α -aminoethanol that sublimates at 210 K.¹⁴ Thus, the most refractory starting material (i.e., HCOOH) is within the bottom layer, while acetaldehyde and ammonia are within the top layer. The IR spectrum of the sample at 25 K is now dominated by strong absorption bands in the $\text{C}=\text{O}$ stretching region due to both acetaldehyde and formic acid. Ammonia gives strong bands at 3370 and 1067 cm^{-1} due to NH stretching and NH wagging modes, respectively.²³ At 25 K, the IR spectrum of the sample is the sum of the individual spectrum of HCOOH , NH_3 , and CH_3CHO , which indicates the absence of reactivity at 25 K. The assignment of each band is well-known and reported in Table 2.^{14,23} The bilayered sample is then warmed up from 25 to 300 K at a rate of 4 K/min. At 150 K, changes are observed on the IR spectrum (Figure 4b). The spectrum is dominated by the IR bands of HCOOH , while the most volatile compounds (i.e., NH_3 and CH_3CHO) sublimate at 130 K. Most features of HCOOH are different from the spectrum recorded at 25 K and consist of multiple components. The $\nu(\text{C}=\text{O})$, $\delta(\text{OH}/\text{CH})$, and $\nu(\text{CO})$ modes at around 1700 and 1379 cm^{-1} split into two components. The splitting of those bands is assigned to the out-of-phase and in-phase motions of different HCOOH molecules within the crystal structure²⁴ which complicate the spectrum of HCOOH when it is warmed. Besides the bands due to HCOOH , small bands are also observed at 3354 , 3276 , 1447 , 1134 , and 1098 cm^{-1} marked on the IR spectrum by stars (Figure 5a) at 150 K (see also Table 2). We compared these new bands with pure α -aminoethanol ($\text{NH}_2(\text{CH}_3)\text{CHOH}$; Figure 5c) and pure HCOOH (Figure 5b). The spectra of pure α -aminoethanol ($\text{NH}_2(\text{CH}_3)\text{CHOH}$), realized in the same

Table 2. Infrared Absorption Bands and Vibrational Assignments of HCOOH/NH₃ and CH₃CHO Ice Mixture at 25 and 150 K^a

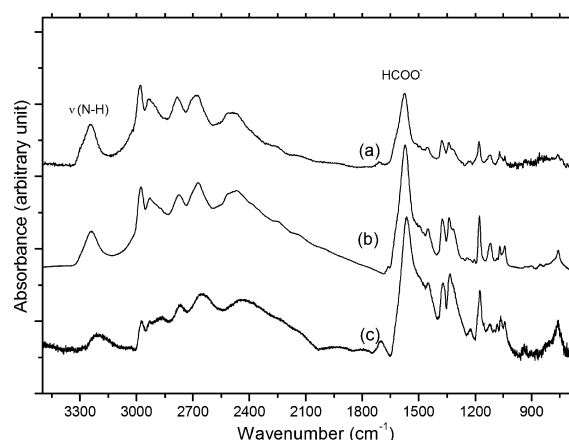
assignment	wavenumbers (cm ⁻¹)		ref.
	HCOOH/NH ₃ /CH ₃ CHO		
	at 25 K	at 150 K	
NH ₃			
$\nu(\text{NH})$	3370		23
$\nu(\text{NH})$	3210		23
$\delta(\text{NH})$	1631		23
$\omega(\text{NH})$	1067		23
Acetaldehyde			
$\nu(\text{CH})$	3001		25
$\nu(\text{CH})$	2958		25
$\nu(\text{CH})$	2915		25
$\nu(\text{CH})$ (aldehyde)	2860–2764		25
$\nu(\text{C=O})$	1715		25
$\delta(\text{CH})$	1426		25
$\delta(\text{CH})$	1348		25
$\nu(\text{C–C})$	1123		25
Formic Acid			
$\nu(\text{CH})$		2893	26
$\nu(\text{OH})$	2758	2717	26
$\nu(\text{OH})$	2572	2547	26
$\nu(\text{C=O})$	1700	1697–1595	26
$\delta(\text{OH}) + \delta(\text{CH})$	1379	1391–1376	26
$\nu(\text{C–O})$	1206	1227	26
$\delta_{\text{o.o.p.}}(\text{OH})$		954	26
$\delta_{\text{o.o.p.}}(\text{OCO})$		707	26
α -Aminoethanol			
$\nu(\text{NH})$		3354	14
$\nu(\text{NH})$		3276	14
$\delta(\text{CH})$		1447	14
$\nu(\text{C–O}) + \nu(\text{C–N})$		1134	14
$\nu(\text{C–N}) + \nu(\text{C–C})$		1098	14

^aVibration mode: stretching (ν), bending (δ), wagging (ω).**Figure 5.** Characterization of α -aminoethanol: FTIR spectra of (a) an ice mixture CH₃CHO + NH₃/HCOOH deposited at 25 K and recorded at 150 K (same as Figure 4b), (b) pure HCOOH at 150 K, and (c) pure NH₂CH(CH₃)OH at 150 K. The stars are relative to the α -aminoethanol.

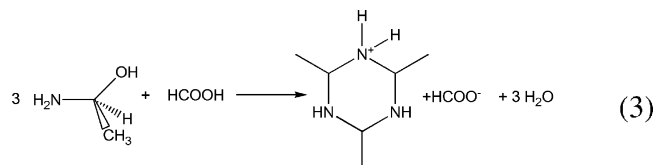
experimental conditions, was enlarged for clarity. The band at 2980 cm⁻¹ is not visible on the spectra, Figure 5a, due to the broad and strong features of HCOOH in this region (dash line). Even if the features, shown by stars, are weak in regard to HCOOH, those bands are clearly assigned to the α -aminoethanol (NH₂(CH₃)CHOH) formed from the thermal reaction in ice between acetaldehyde and ammonia, studied by Duvernay et al., eq 2.¹⁴



Thus, at 150 K, the sample can be described as a bottom layer of pure HCOOH and a top layer of pure α -aminoethanol. After 150 K, the IR spectrum shows a decrease of the bands of HCOOH, and α -aminoethanol, while new bands located at 1562, 1367, 1333, 1175, and 764 cm⁻¹ are observed (Figure 4c). Those new bands are easily assigned to HCOO⁻C₆H₁₅N₃H⁺ from the comparison with a mixture of pure HCOO⁻C₆H₁₅N₃H⁺ as seen in Figure 6a,c. The

**Figure 6.** Characterization of acetaldehyde ammonia trimer salt: FTIR spectra of (a) pure HCOO⁻C₆H₁₅N₃H⁺ at 260 K (same as Figure 4c), (b) warming of a CH₃CH=NH/HCOOH bilayered ice at 260 K, and (c) warming of a HCOOH/CH₃CHO + NH₃ bilayered ice at 260 K.

wavenumbers are slightly different from the one shown in Table 1 due to the environment. The infrared detection is also confirmed by mass spectrometry and gives the same masses as shown in Figure 2. After 260 K, when this compound sublimates, the mass spectrum indeed shows peaks at m/z 86 and 115, characteristic of this product. Between 150 and 260 K, the decrease of the bands of HCOOH can be explained by its sublimation and its reaction with the α -aminoethanol into the top layer. Indeed, at temperatures higher than 160 K, HCOOH starts to sublime and diffuses through the top layer of α -aminoethanol, initiating the formation of HCOO⁻C₆H₁₅N₃H⁺, as represented in eq 3.



Recently, Vinogradoff et al. suggested that formic acid was able to dehydrate the aminomethanol (NH₂CH₂OH) in ice at low temperature, leading to the formation of methanimine

(CH₂NH).²⁰ This imine in the presence of HCOOH forms, in their experimental conditions, the hexamethylenetetramine (HMT). Thus, the intermediate species, in our reaction, could be the corresponding imine, the ethanimine (CH₃CH=NH), due to the presence of HCOOH in the reaction. To strengthen and prove this hypothesis, we investigate the reactivity of CH₃CH=NH with HCOOH at low temperature and high vacuum condition. This is described in the next section.

Acetaldehyde Ammonia Trimer Formation from CH₃CH=NH and HCOOH. *Reference Spectra, FTIR, and Mass of CH₃CH=NH.* In this section, we present the reference spectra (FTIR and mass spectra) of pure ethanimine. Pure ethanimine is kept at 77 K in a pyrex tube connected directly to the cryostat, because of its instability at room temperature. The tube is gently warmed in order to sublimate the ethanimine and allows its deposition onto the substrate cooled down at 25 K inside the cryostat. The IR spectrum of ethanimine deposited at 25 K is displayed in Figure 7a. The spectrum shows strong

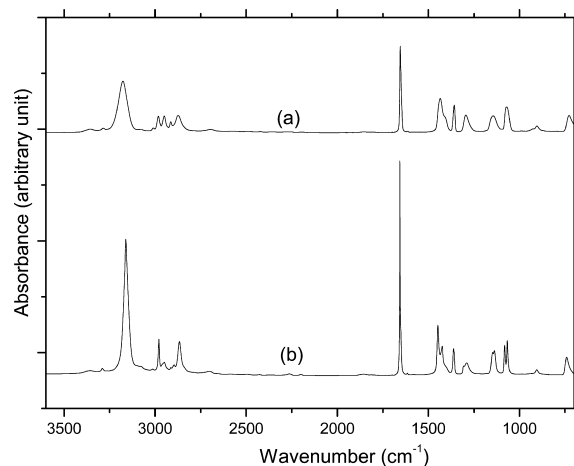


Figure 7. FTIR spectrum of ethanimine (CH₃CH=NH) at (a) 50 and (b) 140 K.

bands at 3174 and 1654 cm⁻¹ assigned to the NH and C=N stretching modes, respectively. All the observed absorption bands are listed in Table 4 with their corresponding assignments. The vibrational assignments have been done with the help of previous work on IR studies of this species in the gas phase and with the IR spectrum of methanimine (CH₂NH) recorded at 25 K.^{27–29} In addition, B3LYP calculations have been performed to help in the infrared band assignments (Table 4). At 140 K, the IR bands of ethanimine narrow because it crystallizes (Figure 7b). Finally, it starts to sublimate around 160 K. The warming from 25 to 200 K of the solid ethanimine has also been followed by mass spectrometry. Figure 8 displays the corresponding mass spectrum recorded at 175 K during the sublimation of the ethanimine. The base peak is observed at *m/z* 28, corresponding to the loss of CH₃ fragment from an alpha fragmentation of the ethanimine. It is interesting to note the base peak for the methanimine is also observed at *m/z* 28, which corresponds in this case to the loss of H.²⁸ Thus, it seems that the most common means of fragmentation of small imine is the CX bond cleavage in α position of the nitrogen. Assignments of some other peaks are given in Figure 8. At 200 K, both IR and mass spectra do not show any spectroscopic evidence of ethanimine, indicating that

Table 3. Infrared Absorption Bands and Vibrational Assignments of a Warming Ice CH₃CHNH/HCOOH from 115 to 300 K^a

assignment	bilayered ice CH ₃ CHNH/HCOOH at 200 K	
	wavenumbers (cm ⁻¹)	
	HCOO ⁻ CH ₃ CHNH ₂ ⁺	B3LYP/6-31G**
ν (NH)	3346 (s)	3469 (92)
ν (NH)	3260 (s)	3362 (100)
ν (CH)		3061 (3)
ν (CH)		3034 (1)
ν (CH)	2967 (s)	2966 (8)
ν (CH)	2921 (s)	2941 (20)
ν (CH)	2853 (s)	
ν (C=N)	1659 (m)	1654 (100)
δ (NH) + ν (COO ⁻)	1580 (m)	1547 (14)
δ (CH)	1434 (m)	1408 (11)
δ (CH)	1434 (m)	1392 (14)
δ (CH)	1363 (m)	1373 (11)
δ (CH)	1308 (w)	1326 (40)
δ (CH)	1135 (m)	1208 (7)
$\delta_{\text{o.o.p.}}$ (CH)		978 (10)
ν (C–C)	871 (m)	892 (11)

^aHarmonic frequencies are scaled with a factor of 0.96. Vibration mode: stretching (ν), bending (δ), and out of plane deformation ($\delta_{\text{o.o.p.}}$). Intensities are given between brackets: strong (s), medium (m), and weak (w).

it has fully sublimated from the substrate. In addition, in our experimental conditions, there is no evidence either by IR or by mass spectrometry of the formation of acetaldehyde ammonia trimer. Pure ethanimine (CH₃CHNH) is known to polymerize into 2,4,6-trimethyl-1,3,5-hexahydrotriazine (C₆H₁₅N₃) at temperatures higher than 200 K in a sealed tube.^{5,30} These results indicate that pure ethanimine under high vacuum conditions in the solid state sublimates before its own trimerization. Another way to say it is that the activation barrier for the trimerization is higher than the desorption energy of ethanimine. In the next section, we will see that the formation of the acetaldehyde ammonia trimer from ethanimine under high vacuum conditions can be activated by formic acid.

Acetaldehyde Ammonia Trimer Formation in Ice at Low Temperature. The ethanimine and HCOOH are deposited separately to avoid any gas phase reaction. Pure ethanimine is first deposited (because it has the lower temperature of desorption) at 115 K and then HCOOH is introduced at 115 K, forming a bilayered ice. The spectrum of this ice is displayed in Figure 9a. No reaction is observed at this temperature. The sample is slowly warmed up from 115 to 300 K. Around 190 K, ethanimine sublimates and diffuses through the HCOOH top layer, leading to the formation of a new species, since new bands are observed (Figure 9b). They are located in the NH stretching region at 3346 and 3260 cm⁻¹ and in the C=N stretching region at 1659 cm⁻¹ (Table 3). Those bands keep growing until the ethanimine has been fully consumed and finally decrease around 230 K (Figure 9e, dash lines). The position of the observed bands could be related to the iminium CH₃CH=NH₂⁺ formed from the acid–base reaction between HCOOH and CH₃CH=NH. We performed B3LYP/6-31G** calculation on CH₃CH=NH₂⁺ in order to get the calculated infrared spectrum of the ethaniminium and be able to compare it with the experimental data. The experimental and theoretical frequencies are given in Table 3. The good agreement between

Table 4. Infrared Absorption Bands and Vibrational Assignments of Ethanamine (CH_3CHNH) at 25 and 140 K^a

assignment	wavenumbers (cm^{-1})			
	CH_3CHNH at 25 K	CH_3CHNH at 140 K	CH_3CHNH (gas)	B3LYP/6-31G**
$\nu(\text{NH})$	3175 (s)	3159 (s)	3264 (vw)	3297 (7)
$\nu_{\text{as}}(\text{CH}_3)$	2983 (m)	2983 (m)	2990 (m)	3027 (16)
$\nu_{\text{as}}(\text{CH}_3)$	2949 (m)	2949 (w)	2954 (m)	2969 (26)
$\nu_{\text{s}}(\text{CH}_3)$				2917 (17)
$\nu(\text{CH})$	2872 (m)	2866 (m)	2885 (m)	2883 (100)
$\nu(\text{C}=\text{N})$	1654 (s)	1656 (s)	1652 (s)	1675 (97)
$\delta(\text{CH}_3)$	1435 (m)	1447–1422 (m)	1438 (s)	1432 (12)
$\delta(\text{CH}_3)$				1424 (16)
$\delta(\text{HCN})$	1358 (m)	1358 (m)	1358 (s)	1389 (32)
$\delta_{\text{o.o.p.}}(\text{CH})$				1342 (13)
$\delta(\text{HCC})$	1289 (m)	1294 (m)	1252 (s)	1231 (53)
$\delta_{\text{o.o.p.}}(\text{C}=\text{N})$	1142 (m)	1149–1138 (m)	1160 (w)	1084 (12)
$\delta_{\text{o.o.p.}}(\text{NH})$				1037 (17)
$\delta(\text{CNH})$	1070 (m)	1079–1065 (m)	1045 (s)	1021 (25)
$\nu(\text{CC})$	906 (w)	906 (w)	920 (w)	890 (12)
$\delta_{\text{o.o.p.}}(\text{CH})$	723 (w)	738 (w)	668 (s)	655 (66)
$\rho(\text{CH}_3)$				470 (23)

^aHarmonic frequencies are scaled with a factor of 0.96. Vibration mode: stretching (ν), bending (δ), out of plane deformation ($\delta_{\text{o.o.p.}}$), rocking (ρ), antisymmetric mode (as), and symmetric mode (s). Experimental and calculated intensities are given between brackets: strong (s), medium (m), and weak (w)

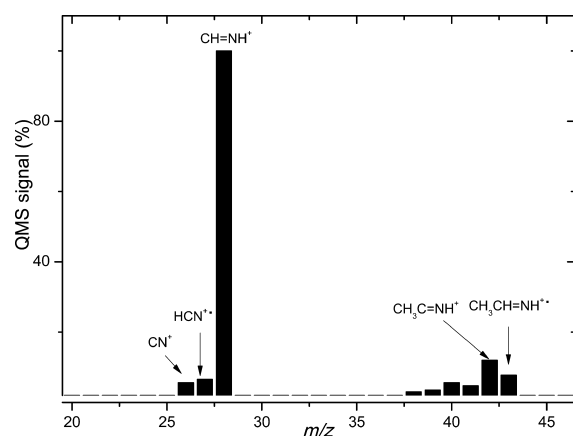
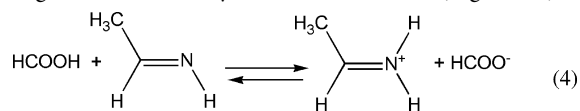


Figure 8. Mass spectrum of $\text{CH}_3\text{CH}=\text{NH}$ obtained at 175 K using a quadrupole mass spectrometer with a 70 eV impact electronic source.

the experimental and theoretical values allows us to conclude in the formation of the iminium from the reaction between HCOOH and $\text{CH}_3\text{CH}=\text{NH}$ according to the eq 4. The formation of the iminium salt is likely a reversible reaction. To form the acetaldehyde ammonia trimer, both neutral and protonated forms of ethanimine are needed. Experimentally, from 215 K, the iminium salt starts to decrease and releases the neutral form of ethanimine, allowing the trimerization process, leading to the acetaldehyde ammonia trimer (Figure 10).



At 230 K, the bands due to the iminium disappear, while at the same time, the acetaldehyde ammonia trimer bands appear at 1574, 1181, and 1057 cm^{-1} . In addition, a new band labeled with a star in Figure 9 is observed at 770 cm^{-1} . Finally, at 270 K, it remains on the gold substrate the salt of the acetaldehyde ammonia trimer $\text{HCOO}^- \text{C}_6\text{H}_{15}\text{N}_3\text{H}^+$ (Figure 10), as seen in Figure 6c. As previously, the frequencies depend on the

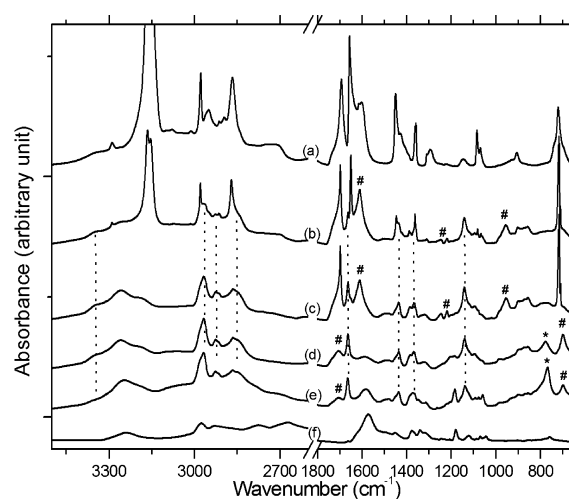


Figure 9. Formation of iminium and acetaldehyde ammonia trimer salt: warming of a bilayered ice $\text{CH}_3\text{CHNH}/\text{HCOOH}$ at (a) 115, (b) 190, (c) 200, (d) 215, (e) 230, and (f) 272 K. Dashed lines refer to the most intense bands, assigned to $\text{HCOO}^- \text{CH}_3\text{CHNH}_2^+$. Star refers to the unknown intermediate between the iminium and the acetaldehyde ammonia trimer salt. Hash signs refer to the remaining formic acid, which evolves during the heating before its sublimation.

environment but are close to the wavenumbers of $\text{C}_6\text{H}_{15}\text{N}_3\text{H}^+$ seen in Table 1. Thus, the new observed band from 215 to 230 K labeled with a star at 770 cm^{-1} in Figure 9 can be tentatively assigned to an intermediate species between the iminium and the trimer. However, we cannot determine a structure of this intermediate from its vibrational bands. Indeed, only one band is observed at 770 cm^{-1} , which is not significant enough. Nevertheless, we suppose that it can be a dimer of ethanimine or the linear protonated trimer, followed by an intramolecular cyclization (Figure 10).

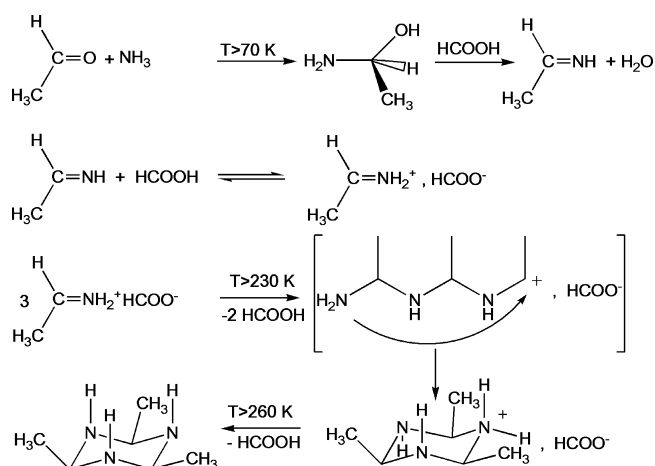


Figure 10. Acetaldehyde ammonia trimer formation from $\text{CH}_3\text{CHO}/\text{NH}_3/\text{HCOOH}$ ice mixture.

DISCUSSION

The reaction of amines and aldehydes has been the subject of several studies.^{6,17–19} Formaldehyde is known to form HMT, in presence of ammonia, while aliphatic aldehydes lead to the aldehyde–ammonia trimer (2,4,6-trialkyl-1,3,5-hexahydrotriazine).⁶ Nevertheless, there are unanswered questions about the mechanism.¹⁷ This work gives evidence in the formation mechanism of acetaldehyde ammonia trimer at low temperature. Due to the cryogenic conditions, we are able to observe intermediates such as α -aminoethanol [$\text{NH}_2\text{CH}(\text{CH}_3)\text{OH}$] and ethanimine ($\text{CH}_3\text{CH}=\text{NH}$) for the first time, in the reaction acetaldehyde ammonia trimer formation. Nielsen et al. and Hull et al., in 1973, suspected that α -aminoethanol could be an intermediate in the formation of acetaldehyde ammonia trimer from acetaldehyde and ammonia. However, they could not give any direct experimental evidence. According to our results, we can draw a formation mechanism of acetaldehyde ammonia trimer in ice at low temperature starting from acetaldehyde, ammonia, and HCOOH ice mixture (Figure 10). The first step consists of the nucleophilic addition of ammonia on acetaldehyde leading to α -aminoethanol. The later, in the presence of HCOOH , dehydrates, forming the ethanimine and then the corresponding iminium. It evolves around 220 K to form the protonated acetaldehyde ammonia trimer. Finally, at a temperature higher than 260 K, the free base of the acetaldehyde ammonia trimer is released in the gas phase along with HCOOH .

Performing a chemical study at low temperature is very interesting and useful to identify and isolate the intermediate products, which eases the elaboration of the reaction mechanism. In our study, we clearly identify two intermediates, namely, α -aminoethanol and ethanimine/iminium, in the reaction between CH_3CHO and NH_3 with HCOOH . The presence of HCOOH is essential for the dehydration of the alcohol and stabilizes the iminium species during the trimerization. This study can be compared with the formation of HMT from formaldehyde and ammonia. These two molecules react together to form at room temperature or in cryogenic conditions (with formic acid) the HMT, which is a four-cycles molecule ($\text{C}_6\text{H}_{12}\text{N}_4$). However, unlike our results obtained previously for the reactivity of formaldehyde with ammonia and formic acid, where HMT was detected, we do not detect in our study a molecule derivative from HMT with

methyl groups. This indicates the impossibility to continue the cyclization to a molecule such as HMT, due to the presence of methyl groups in the acetaldehyde ammonia trimer, which lock the molecule. From an astrophysical point of view, acetaldehyde (CH_3CHO), ammonia (NH_3), and formic acid (HCOOH) are three interstellar molecules, and the intermediates α -aminoethanol and ethanimine/iminium are astrophysically relevant. Considering the conditions of its formation, α -aminoethanol is expected to be formed in warm astrophysical environments such as cometary nucleus or hot cores environments. Ethanamine has never been detected in the interstellar medium, but it could be a good candidate for observation since its homologue, methanimine, has been detected in 1976.³¹ Acetaldehyde ammonia trimer can be formed on a reasonable time-scale in relevant interstellar conditions and, thus, may be a plausible candidate for further investigation of cometary material. Moreover, acetaldehyde ammonia trimer may be observed from its rotational transitions in cometary environments when the solid material desorbs in the gas phase.

EXPERIMENTAL SECTION

Ammonia is commercially available as a 99.9995% pure gas from Air Liquide. Acetaldehyde is bought under its liquid form from Aldrich and is gently heated up to be evaporated. Formic acid (Acros, 99% purity) is distilled under vacuum before utilization. Acetaldehyde ammonia trimer is bought under its hydrate form from Aldrich. The ethanimine was synthesized from the dehydrocyanation of the 2-aminopropionitrile.³⁰ The acetaldehyde ammonia trimer product was bought under its hydrated form from Aldrich with 96% of purity. The $\text{NH}_3/\text{CH}_3\text{CHO}$ gas mixtures are prepared at room temperature into two primary vacuum-pumped mixing lines, the first one for the NH_3 mixture and the second one for CH_3CHO , to prevent any gas phase reaction. They are then codeposited with a chosen ratio onto a copper surface cooled to 10 K by a Model 21 CTI cold head within a high vacuum chamber (ca. 10^{-8} mbar). Products with low vapor pressure (acetaldehyde ammonia trimer) or unstable at room temperature (ethanimine) are gently heated and injected from a tube directly connected to the cryostat.

The IR spectra are recorded between 4000 and 650 cm^{-1} in transmission mode using a FTIR spectrometer. A typical spectrum has a 1 cm^{-1} resolution and is averaged over 100 interferograms. The sample is warmed using a heating resistance and the temperature is controlled using a Lakeshore Model 331 temperature controller. The mass spectra are recorded using a MKS quadrupole mass spectrometer as the products are being sublimated. The ionization source is a 70 eV impact electronic source and the mass spectra are recorded between 1 and 200 amu. The concentration ratio of the different mixtures is first set before deposition using standard manometric techniques and then derived after deposition from the IR spectra by integrating vibrational bands to estimate the column density of NH_3 and CH_3CHO according to their band strengths provided by the literature. For NH_3 , the band strengths of the wagging mode at 1070 cm^{-1} varies from 1.3×10^{-17} to $1.7 \times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$ in its pure solid form.^{32,33} We use the value $1.3 \times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$, given by Kerkhof et al.,³² as usually done in the literature. For CH_3CHO , we use the values given by Schutte et al. and Wexler of $1.3 \times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$ for the CO stretch mode at 1715 cm^{-1} and $1.5 \times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ for the CH bending mode at 1350 cm^{-1} . Calculations on vibrational frequencies, for the different

molecules (acetaldehyde ammonia trimer and ethanimine), are performed using the Gaussian 03 package^{34,35} at the B3LYP/6-31G** level, which is known to supply reliable predictions of vibrational wavenumbers for isolated molecules. Nevertheless, the calculated harmonic frequencies are usually overestimated, with respect to the experimental anharmonic values; therefore, they have been scaled by a standard factor of 0.96.³⁶ In the case of the ionic species, only the cation is taken into account for the calculation. In all calculations, the environment is not taken into account and molecules are supposed to be isolated.

CONCLUSION

Our study has shown that acetaldehyde reacts thermally (above 70 K) with ammonia in the presence of formic acid, forming a cyclic molecule, the acetaldehyde ammonia trimer. We succeed in controlling the reactivity using a bilayered ice to observe the reaction intermediates, namely, α -aminoethanol and ethanimine, by means of infrared spectroscopy and mass spectrometry. This mechanism would allow a better understanding in the HMT formation, which probably has a cyclic intermediate molecule, such as the formaldehyde ammonia trimer. In addition, this study shows that the molecular complexity is possible, even in cold environments such as astrophysical environments.

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Notes

The authors declare no competing financial interest.

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