



Cite this: *Phys. Chem. Chem. Phys.*,
2014, **16**, 23604

Kinetics of the NH_3 and CO_2 solid-state reaction at low temperature

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Ammonia and carbon dioxide play an important role in both atmospheric and interstellar ice chemistries. This work presents a theoretical and experimental study of the kinetics of the low-temperature NH_3 and CO_2 solid-state reaction in ice films, the product of which is ammonium carbamate ($\text{NH}_4^+\text{NH}_2\text{COO}^-$). It is a first-order reaction with respect to CO_2 , with a temperature-dependent rate constant fitted to the Arrhenius law in the temperature range 70 K to 90 K, with an activation energy of $5.1 \pm 1.6 \text{ kJ mol}^{-1}$ and a pre-exponential factor of $0.09_{-0.08}^{+1.1} \text{ s}^{-1}$. This work helps to determine the rate of removal of CO_2 and NH_3 , via their conversion into ammonium carbamate, from atmospheric and interstellar ices. We also measure first-order desorption energies of $69.0 \pm 0.2 \text{ kJ mol}^{-1}$ and $76.1 \pm 0.1 \text{ kJ mol}^{-1}$, assuming a pre-exponential factor of 10^{13} s^{-1} , for ammonium carbamate and carbamic acid, respectively.

Received 2nd June 2014,
Accepted 22nd August 2014

DOI: 10.1039/c4cp02414a

www.rsc.org/pccp

1 Introduction

Ammonia (NH_3) and carbon dioxide (CO_2) are ubiquitous constituents of the Earth's atmosphere and of the molecular interstellar medium.

On Earth, ammonia is considered to be the most important of all nitrogen-bearing species which are deposited onto vegetation and other receptors.¹ Ammonia originates from animal waste and the volatilisation of synthetic fertilizers, biomass burning, losses from soils bearing native vegetation or agricultural crops, and fossil fuel combustion.² Ammonia is a very important alkaline constituent in the atmosphere as it reacts readily with acidic substances, *e.g.* sulfuric acid (H_2SO_4) or nitric acid (HNO_3), to form ammonium (NH_4^+) salt aerosols.¹ The removal of gaseous NH_3 from the atmosphere by the formation of fine particulate NH_4^+ salts is a very efficient mechanism. The effects of NH_3 when combined with other air pollutants, such as the all-pervasive ozone (O_3) or the increasingly abundant carbon dioxide (CO_2), are poorly understood. Atmospheric CO_2 is of prime importance in plant and algal photosynthesis, as well as for the greenhouse effect. It originates from the respiration processes of living aerobic organisms, organic matter, and volcanic outgassing. Its increasing concentration contributes to global warming and ocean acidification.

Its chemical capture through conversion into non-volatile species is a vast field of research.³ Plants naturally fix the CO_2 they need for their growth in the form of carbamate using the ribulose 1,5-bisphosphate carboxylase/oxygenase enzyme in the first step of the Calvin cycle.³ It is therefore important to understand how the reactivity between NH_3 and CO_2 can lead to other non-methane volatile organic compounds (NMVOC) or refractory species on aerosols or in terrestrial ice. The reaction of carbon dioxide with Bronsted bases is of great importance in biology, geology, and for industrial applications.⁴ As an example, amines (RNH_2) are used to remove carbon dioxide from gas streams.⁵

In space, water, carbon dioxide, and ammonia are among the most abundant species present in interstellar ices. They are formed during the transition from the diffuse atomic medium to the dense molecular medium *via* simple atomic or diatomic reactions on the surface of bare interstellar grains. Ammonia is formed by the hydrogenation of the N atom.⁶ Carbon dioxide is thought to be formed from the HO-CO complex^{7–9} or by the $\text{CO} + \text{O}$ addition reaction.¹⁰ Water can be formed by the hydrogenation of the O atom, O_2 or O_3 molecules, or the OH radical.^{11–15} In molecular clouds and in solar system bodies, carbon dioxide and ammonia have abundances on the order of 20% and 5%, respectively.¹⁶ Under interstellar conditions, both molecules are transformed into other species either thermally^{17–20} or non-thermally, due to the effect of UV photon irradiation,²¹ proton or heavy ion bombardment,^{22,23} and/or electron bombardment.²⁴ Products will either enrich the gas-phase of the interstellar medium in complex organic molecules when the ice mantle is desorbed or be a constituent of the refractory organic residue.

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In this work we investigate the reaction mechanisms and the kinetics of the $\text{NH}_3:\text{CO}_2$ solid-phase system, with the reactants located on neighboring sites. Low-temperature $\text{NH}_3:\text{CO}_2$ thermal reactivity has been shown to lead to the formation of the ammonium carbamate salt ($[\text{NH}_4^+][\text{NH}_2\text{COO}^-]$), carbamic acid (NH_2COOH)^{17–20} and, in the presence of water, the ammonium bicarbonate salt ($[\text{NH}_4^+][\text{HCO}_3^-]$).²⁰ While these previous studies spectroscopically characterise the reaction products, the mechanisms and the kinetics of the reaction $\text{NH}_3 + \text{CO}_2$ have not yet been addressed experimentally. High level calculations on the solvation of CO_2 in water–ammonia clusters of four molecules are reported,²⁵ with barriers of solvation determined between 60 and 110 kJ mol^{-1} . Here, we present the results of dedicated isothermal laboratory experiments on $\text{NH}_3:\text{CO}_2$ ice films of different concentration ratios, measured using Fourier-transform infrared spectroscopy (FTIR). We measured the reaction barrier for the formation of ammonium carbonate to be $E_a^{\text{th}} = 5.1 \text{ kJ mol}^{-1} \pm 1.6 \text{ kJ mol}^{-1}$. The substitution of a NH_3 molecule by a H_2O molecule is also investigated. The question of the diffusion of the reactants within the ice has been purposefully separated from the reactivity of the reactants, and will be addressed in a future publication (Ghesquiere *et al.*, in preparation). We also performed calculations based on density functional theory to mimic the reaction of NH_3 and CO_2 in a water–ammonia cluster to aid the interpretation of experimental results and provide insight into the mechanism(s) of the formation of ammonium carbamate ($\text{NH}_4^+\text{NH}_2\text{COO}^-$) and carbamic acid (NH_2COOH) in a model $\text{NH}_3:\text{CO}_2:\text{H}_2\text{O}$ ice mixture.

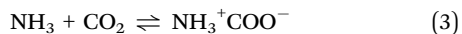
Reaction mechanisms

The formation of the products NH_2COOH (A) and $\text{NH}_4^+\text{NH}_2\text{COO}^-$ (C) from the reactants NH_3 and CO_2 can occur *via* three mechanisms.

In the first mechanism, NH_2COOH is a reaction intermediate, and $\text{NH}_4^+\text{NH}_2\text{COO}^-$ is the final product of a sequence of two successive reactions:

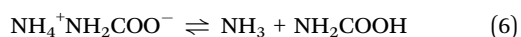


In the second mechanism, the reaction pathway proceeds *via* a zwitterion ($\text{NH}_3^+\text{COO}^-$, Z) intermediate, rather than carbamic acid:



If we are not able to observe the zwitterion intermediate, it cannot be included in the kinetic analysis and thus we cannot distinguish between reactions (1) and (3).

In the third mechanism, $\text{NH}_4^+\text{NH}_2\text{COO}^-$ is produced as a reaction intermediate (either directly or *via* a zwitterion, as in the second mechanism); NH_2COOH is the final product of a sequence of two successive reactions:



2 Methods

2.1 Experimental methods

The experiments were performed using our RING experimental set-up, as described elsewhere.²⁶ In a high-vacuum chamber (few 10^{-9} mbar) a gold-plated copper surface is held at low temperature using a closed-cycle helium cryostat (ARS Cryo, model DE-204 SB, 4 K cryogenerator). The sample temperature is measured using a DTGS 670 silicon diode with an uncertainty of 0.5 K. The temperature is controlled using a Lakeshore Model 336 temperature controller and a heating resistance. Infrared absorption spectra are recorded in reflection mode by means of Fourier-transform infrared reflection absorption spectroscopy (or FTIR) using a Vertex 70 spectrometer with either a DTGS detector or a liquid N_2 -cooled MCT detector. A typical spectrum has a resolution of 0.5 cm^{-1} and is averaged over a few tens of interferograms. Mass spectra of the gas-phase species are recorded using a Hiden HAL VII RGA quadrupole mass spectrometer (QMS). The ionization source is a 70 eV impact electronic source. Mass spectra are recorded between 1 and 60 amu.

$\text{NH}_3:\text{CO}_2(\text{H}_2\text{O})$ ice films are formed by vapour deposition. Gas-phase CO_2 and NH_3 are commercially available in the form of 99.9995% pure gas and obtained from Linde and Air Liquide, respectively. The H_2O vapour is obtained from deionised water which has been purified by several freeze–pump–thaw cycles, carried out under primary vacuum. The different gases are introduced and mixed together in a defined concentration ratio in a primary pumped vacuum line using standard manometric techniques at room temperature. The homogeneously mixed gas-phase mixture is then sprayed onto the cold gold-plated copper surface.

The morphology of the $\text{NH}_3:\text{CO}_2(\text{H}_2\text{O})$ ice film depends on the temperature of the gold surface on which the gas-phase mixture is deposited.²⁷ If the ice film is deposited below 60 K, the ice film is amorphous and porous. If deposited between 60 K and 150 K, the ice is amorphous and compact, with little or no porosity. If deposited above 150 K, the ice is crystalline. We deposit the homogeneous $\text{NH}_3:\text{CO}_2$ gas-phase mixture at 60 K in order to measure the $\text{NH}_3 + \text{CO}_2$ reactivity in compact amorphous ice. Such ice films are better defined and more reproducible than porous amorphous ice films. Pore collapse in the latter can change the overall kinetics by introducing additional reorganisation kinetics.²⁸

The column density (N , molecules cm^{-2}) of each molecular species is derived immediately after deposition from the IR spectra, an example of which is presented in Fig. 1(a), using the expression:

$$N = \frac{\int \tau_r d\tilde{\nu}}{A}, \quad (7)$$

where the optical depth (τ_r) is equal to $\ln(10)$ times the integrated absorbance and A is the band strength, in cm molecule^{-1} . Ammonia is identified *via* its umbrella mode at 1110 cm^{-1} , the band strength of which is $1.3 \times 10^{-17} \text{ cm molecule}^{-1}$.²⁹ Carbon dioxide is identified *via* its asymmetric stretching mode at 2339 cm^{-1} and its bending mode band at 667 cm^{-1} . The band strength of the CO_2 asymmetric stretching band was measured

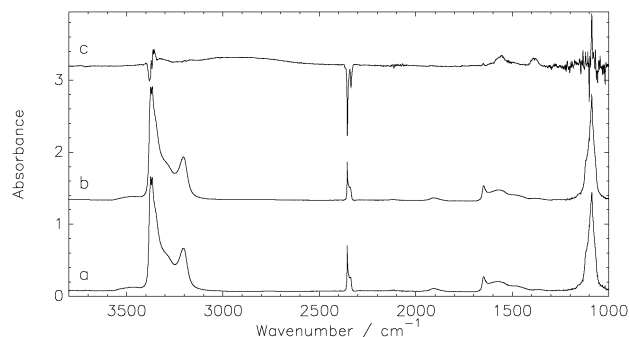


Fig. 1 Infrared absorption spectra of a homogeneously mixed $\text{NH}_3:\text{CO}_2$ ice film with an excess of NH_3 held at 80 K. Spectra shown are: (a) at $t = 0$, (b) after 11 hours at 80 K, and (c) the difference spectrum of (b) minus (a) magnified by a factor of 10. The CO_2 bands have decreased while the carbamate bands have appeared.

to be $7.6 \times 10^{-17} \text{ cm molecule}^{-1}$ for the pure solid,^{30,31} while in water ice, a value of $1.4 \times 10^{-17} \text{ cm molecule}^{-1}$ was found.³² Water ice has three characteristic bands at 3280, 1660, and 760 cm^{-1} corresponding to the OH stretching, HOH bending, and libration modes, respectively. The corresponding band strengths are 2.1×10^{-16} , 3.1×10^{-17} , and $3.1 \times 10^{-17} \text{ cm molecule}^{-1}$, respectively.³¹ The frequencies and band strengths of the carbamate are taken from Bossa *et al.*¹⁹ There is an approximately 30% uncertainty on the band strengths and therefore on the calculated column densities. The characteristic frequencies of the different products are listed in Table 1.

The ice film thickness is determined from the measured column density (N , molecule cm^{-2}), assuming $\rho = 0.94 \text{ g cm}^{-3}$ as the amorphous ice density, and using:

$$l_{\text{cm}} = \frac{N \times 17}{\rho \times N_A} \times \cos(18^\circ)/2, \quad (8)$$

where N_A is the Avogadro constant, 17 g mol^{-1} is the molar mass for NH_3 , and the $\cos(18^\circ)$ term comes from the 18° incidence angle between the FTIR beam and the normal to

Table 1 Infrared absorption bands and assignment of the products formed from the reaction of $\text{NH}_3 + \text{CO}_2$

Assignment	Wavenumbers (cm^{-1})
$\nu(\text{NH}_2) \text{ NH}_2\text{COOH dimer}$	3462
$\nu(\text{NH}_2)[\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	3428
$\nu(\text{NH}_2)[\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	3325
$\nu(\text{OH}) \text{ NH}_2\text{COOH}$	3140 ^a
$\nu(\text{C=O}) \text{ NH}_2\text{COOH}$	1691
$\delta(\text{NH}_2)[\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	1623
$\nu_{\text{as}}(\text{COO}^-)[\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	1553
$\delta(\text{NH}_4^+)[\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	1495
$\text{NH}_2\text{COOH dimer}$	1451
$\nu(\text{CN}) [\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	1393
$\text{NH}_2\text{COOH dimer}$	1320
$\nu_{\text{s}}(\text{COO}^-)[\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	1117
$\rho(\text{NH}_2) [\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	1037
$\delta_{\text{oop}}(\text{OCN}) [\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	829
$\delta(\text{COO}^-) [\text{NH}_4^+][\text{NH}_2\text{COO}^-]$	674

^a Broad band.

the ice film. The factor one half comes from the reflection mode, which probes double the column density.

We use two approaches to derive the relevant physical and chemical parameters of the $\text{NH}_3:\text{CO}_2$ system:

- During isothermal kinetic (IK) experiments, infrared spectra of the solid-phase molecules are recorded at regular time intervals at a fixed temperature.
- During temperature ramp experiments, IR spectra of the solid-state molecules are recorded at regular time (temperature) intervals, and mass spectra of the gas-phase molecules are recorded as they desorb during a temperature ramp.

2.1.1 Isothermal kinetic experiments. In isothermal kinetic (IK) experiments, immediately after deposition the ice film is heated as fast as possible to a fixed temperature (T), in typically a few tens of seconds. Once the temperature, T , is reached, we set the initial time, $t = 0 \text{ s}$, of our isothermal experiment. NH_3 and CO_2 react to form reaction products, as can be seen from the IR spectrum and the difference spectrum of the ice mixture at the end of the experiment, as displayed in Fig. 1(b) and (c), respectively. The kinetics of the $\text{NH}_3 + \text{CO}_2$ ice mixture at the fixed temperature, T , are monitored by measuring the disappearance of the reactants and appearance of the products from their characteristic IR absorption bands as a function of time, as illustrated for a typical isothermal experiment in Fig. 2. Isothermal kinetic experiments are performed at different temperatures to study the temperature dependence of the reactivity. These kinetics will determine the removal of NH_3 and CO_2 in atmospheric or interstellar ices. Since both in atmospheric and interstellar chemistry this reaction is competing with other reactions, such as $\text{NH}_3 + \text{HNCO}$,²⁸ $\text{NH}_3 + \text{H}_2\text{CO}$,³³ or $\text{CH}_3\text{NH}_2 + \text{CO}_2$,³⁴

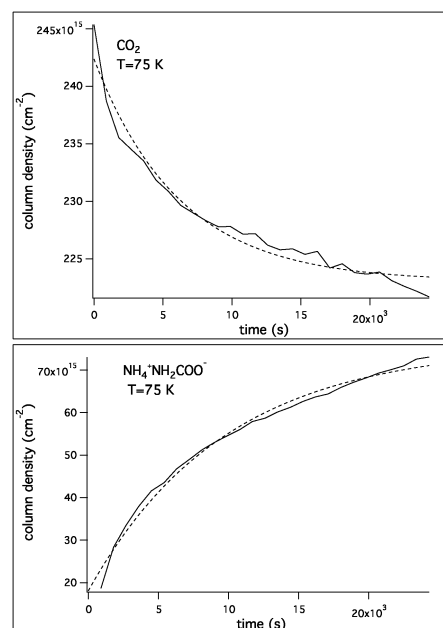


Fig. 2 Isothermal kinetic experiments at 75 K carried out on a homogeneously mixed $\text{NH}_3:\text{CO}_2$ ice film, deposited at 60 K with an excess of NH_3 (solid lines). The CO_2 column density exponentially decreases with time as the $\text{NH}_4^+\text{COO}^-$ (from its band at 1393 cm^{-1}) increases (dashed lines).

it is important to know its kinetic parameters in order to compare it with the other reactions.

The temperature range within which isothermal experiments can be performed is limited. The lowest temperature is constrained by the maximum time we can wait. This time is defined as the amount of background deposition onto the ice film from the vacuum chamber; at 10^{-8} mbar, *ca.* 360 monolayers are deposited in 10 hours. The highest temperature is constrained by desorption of our ice film. With pre-exponential factors of $5 \times 10^{13} \text{ s}^{-1}$ and $6 \times 10^{14} \text{ s}^{-1}$ and desorption energies of 25 and 23 kJ mol^{-1} for NH_3 and CO_2 , respectively,^{35,36} the desorption rates of NH_3 and CO_2 can be evaluated. For example, at 80 K, it takes approximately seven minutes to desorb one monolayer.

2.1.2 Temperature ramp experiments. In temperature programmed reactivity (TPR) experiments, the temperature is linearly increased at a ramp rate, β , from the deposition temperature, T_0 :

$$T = T_0 + \beta \times t. \quad (9)$$

The abundances of the solid-phase species during the temperature ramp are measured from FTIR spectra.

In temperature programmed desorption (TPD) experiments, the temperature is also linearly increased, as in eqn (9). During heating, the mass spectrum of the sublimating species is recorded; desorption parameters are derived from TPD experiments.

2.2 Computational methods

Energy profile calculations have been performed within the framework of density functional theory using the hybrid generalised gradient approximation (GGA) B3LYP functional^{37,38} in conjunction with a triple zeta atomic basis set extended by polarisation functions *i.e.*, 6-311G(d,p). Structures at minima and maxima (transition states) on the reaction paths have been located by total optimisation using analytical gradients. Harmonic vibrational analyses have been performed at the same levels of theory to confirm each stationary point as either an equilibrium structure (*i.e.*, all real frequencies) or a transition structure (TS) (*i.e.*, with one imaginary frequency). Intrinsic reaction coordinate calculations have been conducted in order to reliably link the transition states with the corresponding minima. All energies have been corrected for unscaled zero-point energies calculated at the same theoretical level. All calculations have been performed using the GAUSSIAN-09 package.³⁹

3 Results

3.1 Experimental results

We perform several IK and TPR experiments at different temperatures on several CO_2 : NH_3 ice mixtures with varying concentration ratios to investigate the reaction mechanism and measure the kinetics of the reaction. First we study the reactivity in a non-protic CO_2 dominated ice, and second in a protic NH_3 dominated ice. The possible influence of H_2O is addressed.

3.1.1 Reactivity of the NH_3 : CO_2 system with CO_2 in excess.

In an NH_3 : CO_2 ice mixture with a 1 : 20 concentration ratio, where NH_3 is diluted in a CO_2 ice, no reactivity is observed at

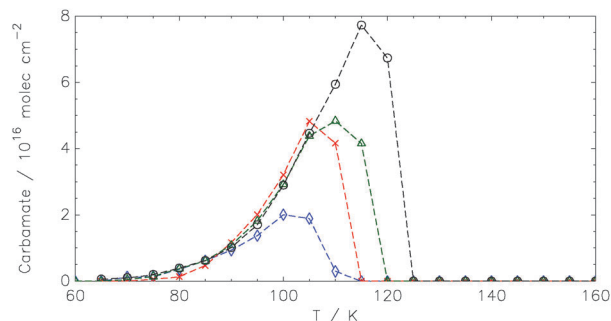


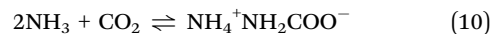
Fig. 3 $\text{NH}_4^+\text{NH}_2\text{COO}^-$ produced during temperature programmed reactivity experiments on NH_3 : CO_2 ice mixtures with an excess of NH_3 . The temperature is ramped between 60 K and 160 K at rates of 0.5 (diamonds), 1 (crosses), 2 (triangles) and 5 (circles) K min^{-1} . $\text{NH}_4^+\text{NH}_2\text{COO}^-$ abundances are monitored using the 1393 cm^{-1} band. IR bands corresponding to NH_2COOH are not observed when NH_3 is in excess. Although the initial quantity of matter (the curve area) is different in the four experiments, the slope of the curves is the same.

any temperature below the desorption temperature of CO_2 . This means that the reaction barriers are too high and, as a result, desorption of CO_2 is faster than any reaction. This case, where ice is dominated by a non-polar molecule such as CO_2 , is less usual in real ices, which are usually water-dominated. Thus we will focus on NH_3 : CO_2 where polar and hydrogen bonded molecules, such as NH_3 and H_2O , are dominant.

3.1.2 Reactivity of the NH_3 : CO_2 system with NH_3 in excess.

We perform TPR experiments on NH_3 : CO_2 ice films deposited at 60 K and heated at different temperature ramp rates, as shown in Fig. 3. The characteristic IR bands of $\text{NH}_4^+\text{NH}_2\text{COO}^-$ increase as it is produced and decrease as it sublimates. NH_2COOH is not identified in our spectra, either as a transitory species or as a final product, when NH_3 is in excess. Indeed, carbamic acid is observed in TPR experiments, at high temperatures, only when CO_2 is present in an equal concentration with NH_3 , as previously shown.^{19,20} The absence of NH_2COOH tends to validate either the second mechanism, with a non-observable zwitterion intermediate, where the activation energy of reaction (4) is lower than that of reaction (3), or the third mechanism, a serial formation pathway of NH_2COOH from $\text{NH}_4^+\text{NH}_2\text{COO}^-$, the second step (reaction (6)) having too large an energy to occur before carbamate desorption.

Thus, the experimental observations can be summarised as:



We assume that the reaction can be described using kinetic equations of the form:

$$\begin{aligned} \frac{d(\text{CO}_2)}{dt} &= -k(T) \times (\text{NH}_3)^\alpha \times (\text{CO}_2)^\beta \\ \frac{d(\text{NH}_4^+\text{NH}_2\text{COO}^-)}{dt} &= k(T) \times (\text{NH}_3)^\alpha \times (\text{CO}_2)^\beta \end{aligned} \quad (11)$$

where $k(T)$ is the temperature-dependent reaction rate constant, α and β are the partial orders of reaction, and (X) the molar fraction of the X species (with no dimension). In the case of

excess NH_3 , $(\text{NH}_3) \simeq 1$ and we measure the effective reaction rate constant $k' = k(T) \times (\text{NH}_3)^\alpha$.

In $\text{NH}_3:\text{CO}_2$ ice mixtures where CO_2 is diluted in an excess of NH_3 , each CO_2 molecule is surrounded by an NH_3 molecular environment and we can assume pseudo first-order kinetics for every reaction. The $\text{NH}_3:\text{CO}_2$ ice films are deposited at 60 K. The IR bands of reactants decrease and product bands increase as the temperature is increased, which implies that NH_3 and CO_2 react.

3.1.2.1 Determination of the partial orders of reaction. Isothermal kinetic experiments on $\text{NH}_3:\text{CO}_2$ ice films with an excess of NH_3 exhibit a time dependence, with CO_2 and $\text{NH}_4^+\text{NH}_2\text{COO}^-$ concentrations evolving as depicted in Fig. 2. The exponential decay of CO_2 and the corresponding growth of $\text{NH}_4^+\text{NH}_2\text{COO}^-$ exhibit pseudo first-order reaction kinetics, with a rate constant k' , i.e. $\beta = 1$. The system of kinetic eqn (11) is solved analytically as:

$$(\text{CO}_2)(t) = (\text{CO}_2)_0 \times e^{-k't} \quad (12)$$

$$(\text{NH}_4^+\text{NH}_2\text{COO}^-)(t) = (\text{CO}_2)_0(1 - e^{-k't}). \quad (13)$$

Fitting IK experiments with eqn (12) and (13) gives the pseudo first-order reaction constant, k' , at the fixed temperature T . To determine the partial reaction order, α , we measure k' at different (NH_3) molar fractions at the same temperature, as shown in Table 2 and in Fig. 4. The pseudo first-order reaction constant k' shows no dependence on the NH_3 molar fraction, which indicates that $\alpha = 0$ and therefore that $k' = k$. Due to the relatively large uncertainties on our measurements, the determination of α is tentative. In this particular case, the unit of k is s^{-1} .

3.1.2.2 Determination of the temperature dependence of the reaction rate. In order to determine the temperature dependence of the reaction rate constant $k(T)$, different IK experiments are performed at different fixed temperatures. They are summarised in Table 2.

The temperature dependence of the pseudo first-order reaction rate constant, k , is determined from the values of mixtures

Table 2 Reaction rate constants, k , from isothermal experiments with different $\text{NH}_3:\text{CO}_2$ concentration ratios. Uncertainties on the last digit of the rates are in parenthesis

$T(\text{K})$	Concentration ratio	Rate constant k' (s^{-1})
$\text{CO}_2:\text{NH}_3$ ice films		
70–95	Excess of CO_2	No reaction
70	Excess of NH_3	$9.6(2) \times 10^{-6}$
70	Excess of NH_3	$1.0(1) \times 10^{-5}$
75	Excess of NH_3	$4.8(3) \times 10^{-5}$
75	Excess of NH_3	$2.0(5) \times 10^{-5}$
80	Excess of NH_3	$4.9(3) \times 10^{-5}$
85	Excess of NH_3	$6.4(4) \times 10^{-5}$
90	Excess of NH_3	$6.4(4) \times 10^{-5}$
80	1:1	$6.8(5) \times 10^{-5}$
80	1:4	$4.9(4) \times 10^{-5}$
80	1:13	$7.8(5) \times 10^{-5}$
$\text{CO}_2:\text{NH}_3:\text{H}_2\text{O}$ ice films		
80	1:60:60	$5.8(4) \times 10^{-5}$
80	1:60:60	$9.0(4) \times 10^{-5}$

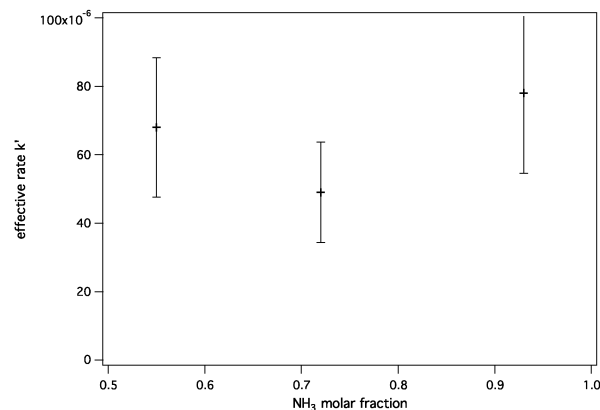


Fig. 4 Dependence of the pseudo first-order reaction constant $k' = k \times (\text{NH}_3)^\alpha$ on the (NH_3) molar fraction at $T = 80$ K. We limit (NH_3) to approximately 0.66, since we need at least two NH_3 molecules to react with one CO_2 molecule.

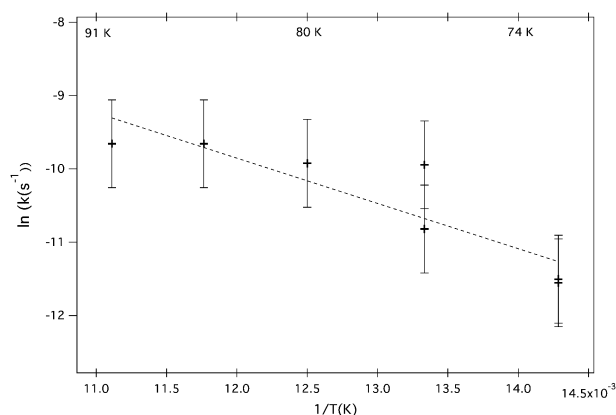


Fig. 5 Logarithm of the pseudo first-order reaction rate constant, k , as a function of the inverse of the temperature. The uncertainty on each point is estimated from both the fitting procedures for the CO_2 band and the four carbamate bands time decay, and from the dispersion between two measurements taken at 70 K and 75 K.

with an excess of NH_3 in Table 2, and is displayed in Fig. 5. The uncertainties are evaluated by (i) taking into account the fitting uncertainty on each fitting procedure, (ii) the dispersion on the rate constants obtained from the CO_2 band and from the four carbamate bands, and (iii) from the dispersion on two experiments performed at the same temperature. The uncertainty is dominated by the dispersion, which results from the pore collapse of the out-of-equilibrium ice.²⁸ The uncertainty on the temperature measurement is 0.5 K.

Fitting the experimental curve with the Arrhenius law gives an experimental activation energy of $5.1 \pm 1.6 \text{ kJ mol}^{-1}$ ($642 \pm 62 \text{ K}$) and a pre-exponential factor of $0.09_{-0.08}^{+1.1} \text{ s}^{-1}$ for a temperature interval between 70 K and 90 K. The small value of the pre-exponential factor can have two origins: either the measured pseudo first-order rate represents a sequence of elementary processes, or there is a contribution from quantum tunnelling between 70 K and 90 K.⁴⁰ Such a quantum tunnelling effect has been observed at lower temperature (8–15 K) in the $\text{HNCO} + \text{NH}_3$

system²⁸ (although not in the HNC₂ + H₂O system²⁶) and it contributes to the reaction rate in the 15–40 K range, along with the thermal reaction rate. The latter takes over as the reaction temperature increases.

3.1.3 Determination of the influence of H₂O. In order to investigate the change in reactivity induced by replacing a NH₃ molecule by a H₂O molecule, including its possible effect on the height of the reaction barrier, we perform IK experiments on CO₂:NH₃:H₂O ice films with different NH₃:H₂O ratios. We take care not to go below a 1:1 ratio, since we need at least two NH₃ molecules in the four closest neighbouring molecules of the first shell around CO₂ to form NH₄⁺NH₂COO[−]. If no NH₃ molecule is present in the first shell, it needs to diffuse toward CO₂ through the H₂O molecules, which alters the kinetic measurements. We see in Table 2 that the rates at 80 K are, within the dispersion uncertainty, similar or slightly higher if the NH₃ molecule is replaced by a H₂O molecule. This means that, within the dispersion of our experimental methods, NH₃ and H₂O have more or less the same effect on the reaction barrier.

In the presence of water, the formation of ammonium bicarbonate NH₄⁺HCO₃[−] can also take place.²⁵



We do not observe the formation of ammonium bicarbonate in our experiments, perhaps due to the limited range of temperature.

3.1.4 Reactivity of the CO₂:NH₃ system with equal amounts of CO₂ and NH₃. When CO₂ and NH₃ are present in comparable amounts in ice films, both ammonium carbamate and carbamic acid are formed.^{19,20}

We see in Fig. 6 that ammonium carbamate (NH₄⁺NH₂COO[−]) forms first, and that carbamic acid (NH₂COOH) forms later from the carbamate. Above 150 K, the initial reactants CO₂ and NH₃ have desorbed and are not present anymore. Part of the formed

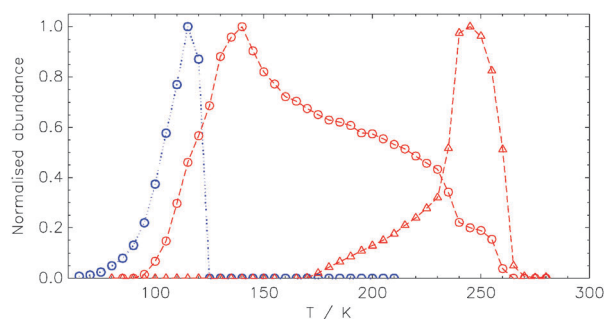
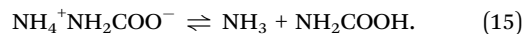


Fig. 6 A temperature programmed reactivity experiment performed at 5 K min^{−1} on a CO₂:NH₃ ice mixture in a 1:1.5 concentration ratio after an isothermal experiment at 80 K lasting 26.75 hours. The evolution of NH₄⁺NH₂COO[−] (circles, dashed line) and NH₂COOH (triangles, dashed line) is monitored via their bands at 1393 cm^{−1} and 3462 cm^{−1}, respectively, when the temperature is ramped between 60 K and 300 K. The (blue) dotted line (circles) is a TPR experiment performed immediately after the CO₂:NH₃ ice mixture deposition (data from Fig. 3, 5 K min^{−1}, circles). The desorption of reactants prevents the formation of large quantities of carbamate, and consequently of carbamic acid as well.

carbamate has co-desorbed with them. Above 150 K the ice film is made of carbamate only and carbamate is converted into carbamic acid, as seen in Fig. 6 between 150 K and 225 K. Above 225 K, both the carbamate and carbamic acid desorb. These experiments clearly show that we have an additional high-temperature mechanism of conversion of the carbamate into carbamic acid:



This is consistent with reaction (6) of the third reaction mechanism, although it could also be the reverse reaction of reaction (2).

3.1.5 Determination of the desorption energy of ammonium carbamate and carbamic acid. To determine the desorption parameters of ammonium carbamate, we perform a TPD experiment on a CO₂:NH₃ ice mixture with an excess of NH₃. The mixture was held at 75 K for 12 hours in an IK experiment, then the temperature was ramped at a rate of 5 K min^{−1}. The TPD profile of *m/z* 44 displayed in Fig. 7 shows three desorption features, which can be assigned from the correlation with IR bands. The first feature at 120 K corresponds to the desorption of CO₂^{36,41} which did not react with NH₃. The second feature at 240 K corresponds to the desorption of NH₄⁺NH₂COO[−]. The third feature at 265 K corresponds to the desorption of NH₂COOH.

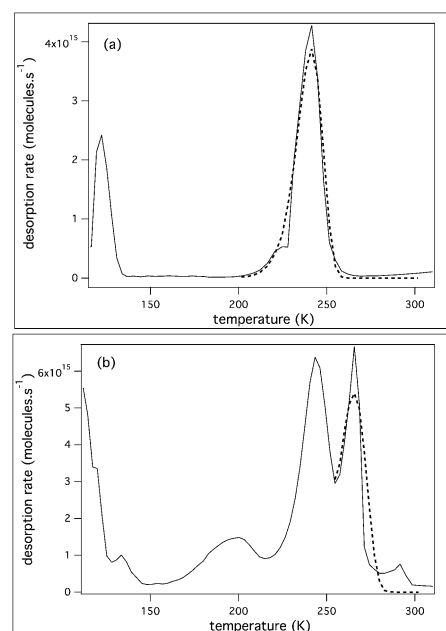


Fig. 7 Temperature programmed desorption experiment (*m/z* 44) at a 5 K min^{−1} temperature ramp of (a) a CO₂:NH₃ ice mixture with an excess of NH₃, and (b) an approximately equal amount of CO₂ and NH₃. The shoulder on the desorption feature is due to the crystallisation. The first desorption feature at 120 K corresponds to CO₂ desorption, the second one at 240 K to NH₄⁺:NH₂COO[−] desorption, and the third one at 265 K to NH₂COOH desorption, according to their correlation with IR bands. Fitting the experimental curve with a first-order Polanyi–Wigner equation (dashed line) gives the desorption parameters of NH₄⁺:NH₂COO[−] and of NH₂COOH.

Replacing time by temperature, using eqn (9), in the Polanyi-Wigner equation, we get:

$$\frac{N}{dT} = -\frac{\nu}{\beta} \exp(-E_{\text{des}}/RT) \times N^n, \quad (16)$$

where ν and E_{des} are the pre-exponential factor and desorption energy of the desorption rate constant, respectively, and n is the order of the desorption. Fitting the carbamate desorption feature at 240 K with a first-order Polanyi-Wigner equation while fixing the pre-exponential factor at a typical value of $\nu = 10^{13} \text{ s}^{-1}$, we get $E_{\text{des}} = 69.0 \pm 0.2 \text{ kJ mol}^{-1}$. Fitting the carbamic acid desorption feature at 265 K with a zeroth-order Polanyi-Wigner equation while fixing the pre-exponential factor at a typical value of $\nu = 10^{13} \text{ s}^{-1}$, we get $E_{\text{des}} = 76.1 \pm 0.1 \text{ kJ mol}^{-1}$. The higher desorption energy of carbamic acid is probably due to its ability to arrange into dimers.¹⁹

Fig. 8 shows the mass spectrum of ammonium carbamate and carbamic acid at their maximum desorption temperatures, *i.e.* 240 K and 265 K, respectively. For carbamic acid, the molecular ion at m/z 61 is weak but detectable and masses m/z 17, 18, and 44, corresponding to NH_3 and CO_2 , dominate. Carbamic acid decomposes into NH_3 and CO_2 either spontaneously or under electron impact, but is stable for at least some time since the molecular ion at m/z 61 is observed. For ammonium carbamate, the molecular ion at m/z 78 is not

observed, but rather m/z 61, corresponding to NH_2COOH , is weakly observed, and the masses corresponding to NH_3 and CO_2 dominate. The carbamate decomposes in the gas phase, either spontaneously or under the electron impact, into NH_3 and NH_2COOH and then into NH_3 and CO_2 .

3.2 Theoretical results

Three different clusters of eight molecules were constructed in order to study the reactivity of NH_3 and CO_2 in water:ammonia environments. These clusters were designed to provide a fully solvated first solvation layer (*i.e.* six molecules around the $\text{NH}_3\text{--CO}_2$ pair). Such cluster calculations are inherently gas phase calculations and thus resemble the energetics of the solid state reaction only approximately, independent of the quantum chemical method/DFT functional used.

The first cluster was designed to mimic the reactivity of CO_2 and NH_3 in a pure ammonia ice, and therefore it was constructed from one CO_2 and seven NH_3 molecules. This cluster is labeled “7:1:0”, derived from the $\text{NH}_3\text{:CO}_2\text{:H}_2\text{O}$ concentration ratio. The two other clusters were designed to mimic the reaction of NH_3 and CO_2 in a diluted, water-dominated environment. One was composed of one CO_2 , one NH_3 , and six H_2O molecules, hereafter denoted “1:1:6”. The other was composed of one CO_2 , two NH_3 , and five H_2O molecules, hereafter denoted “2:1:5”.

We would like to point out here that our goal with these calculations is not to provide accurate energy barriers, but rather to compare different mechanisms in order to assess the catalytic role of ammonia and water molecules in the formation of ammonium carbamate and carbamic acid in model ices, and thus to rationalise the present experimental results. The structures located in the following energy profiles are all obtained through an optimisation procedure allowing for the total relaxation of all eight molecules.

3.2.1 Reaction profile of the 7:1:0 cluster. The reaction of NH_3 and CO_2 is investigated in the presence of six surrounding ammonia molecules. The energy profile is shown in Fig. 9:

The energy profile shown in this figure reveals four stable structures. The first one, R, can be viewed as the solvation of CO_2 in an ammonia solvent. It is characterised by a CN bond of 2.8 Å, associated with a frequency of 119 cm^{-1} . This system has to overcome a barrier of 6.3 kJ mol^{-1} to produce the $\text{NH}_3^+\text{CO}_2^-$ zwitterion, Z, surrounded by six NH_3 molecules. The transfer of a proton from the zwitterion to a neighbouring ammonia molecule leads to the formation of the carbamate anion C (NH_2CO_2^-) stabilised by the ammonium cation NH_4^+ . This transformation involves a barrier that is 11 kJ mol^{-1} above R. Such a small barrier is consistent with the 5.1 kJ mol^{-1} barrier found experimentally. Structure C is very stable with respect to R, *i.e.* 42 kJ mol^{-1} below. One further hydrogen transfer can transform this carbamate anion into carbamic acid, A. This transformation involves barriers of 13 kJ mol^{-1} below R and 29 kJ mol^{-1} above C.

3.2.2 Reaction profile of the 1:1:6 cluster. The reaction of NH_3 and CO_2 is investigated in the presence of six surrounding water molecules. The energy profile is shown in Fig. 10:

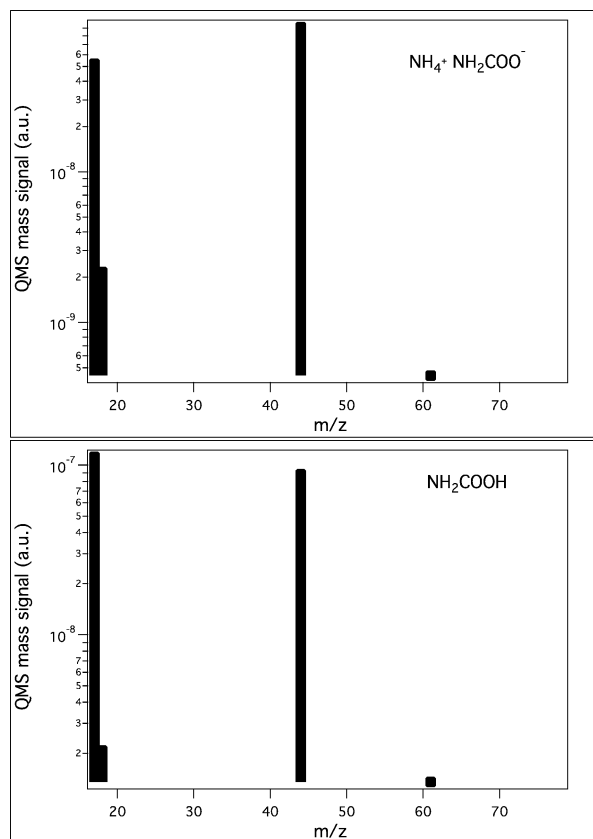


Fig. 8 Mass spectrum of ammonium carbamate ($\text{NH}_4^+ \cdot \text{NH}_2\text{CH}_2\text{COO}^-$) at $T = 240 \text{ K}$ (top) and of carbamic acid (NH_2COOH) at $T = 265 \text{ K}$ (bottom) obtained using a QMS spectrometer with a 70 eV electron impact source.

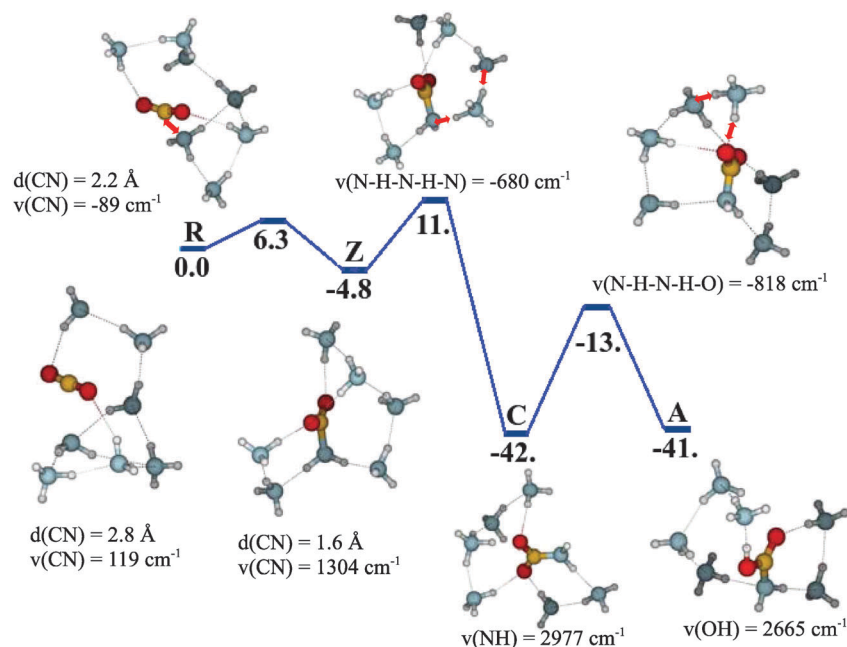


Fig. 9 B3LYP/6-311G(d,p) lowest energy profile for the formation of ammonium carbamate and carbamic acid in the 7 : 1 : 0 cluster. Energies are given in kJ mol⁻¹ and are corrected for unscaled zero-point energies. Green = carbon, red = oxygen, and white = hydrogen. The arrows indicate the atomic motion during the reaction. R, Z, C, and A stand for reactants, zwitterion, carbamate anion, and carbamic acid structures, respectively. All relative energies are given with respect to R.

The energy profile shown in Fig. 10 reveals three stable structures. As in the previous 7 : 1 : 0 structure, R can be viewed as CO₂ and NH₃ solvated in water. The CN bond of 2.6 Å, associated with a frequency of 160 cm⁻¹, is also consistent with the one obtained for R in the 7 : 1 : 0 structure. The second stable structure Z corresponds to the NH₃⁺CO₂⁻ zwitterion

surrounded by six H₂O molecules. A water-mediated proton transfer involving a high barrier of 55 kJ mol⁻¹ above R leads to the formation of carbamic acid. Such a high barrier for the formation of NH₂COOH is certainly large, but this formation pathway will dominate if H₂O is more abundant than NH₃, as long as the temperature is high enough.

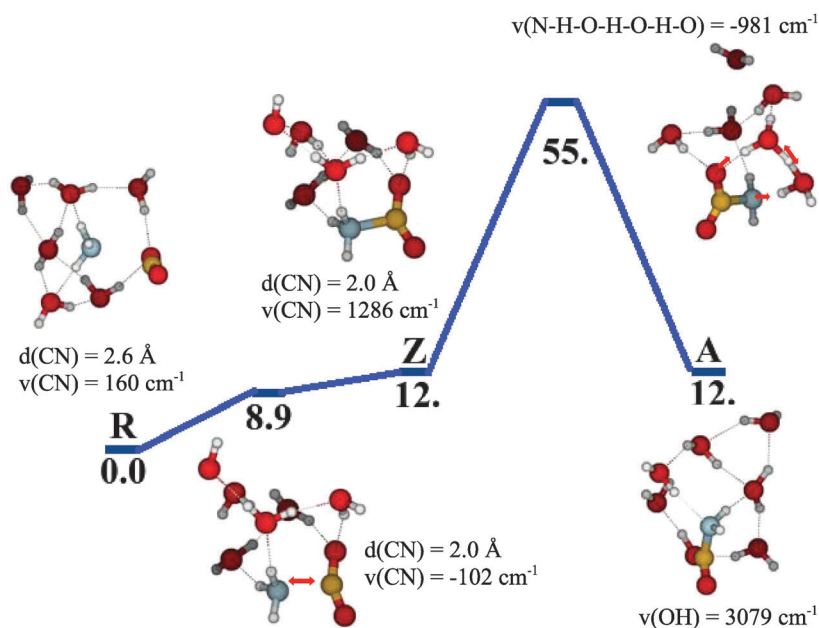


Fig. 10 B3LYP/6-311G(d,p) lowest energy profile for the formation of carbamic acid in the 1 : 1 : 6 cluster. Energies are given in kJ mol⁻¹ and are corrected for unscaled zero-point energies. Green = carbon, red = oxygen, and white = hydrogen. The arrows indicate the atomic motion during the reaction. R, Z, and A stand for reactants, zwitterion, and carbamic acid structures, respectively. All relative energies are given with respect to R.

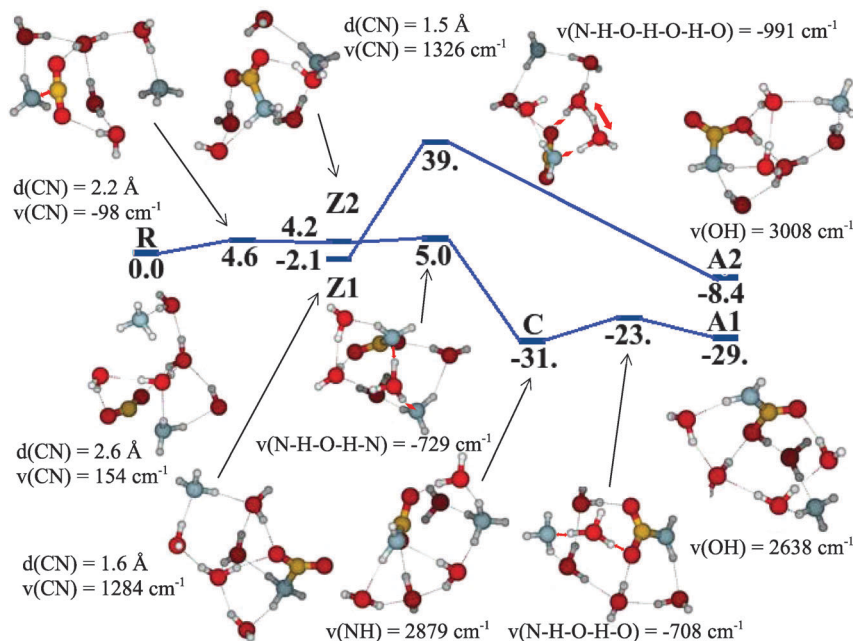


Fig. 11 B3LYP/6-311G(d,p) lowest energy profile for the formation of the carbamate anion and carbamic acid in the 2:1:5 cluster. Energies are given in kJ mol^{-1} and are corrected for unscaled zero-point energies. Green = carbon, red = oxygen, and white = hydrogen. The arrows indicate the atomic motion during the reaction. R, Z1, Z2, C and A stand for reactants, zwitterions 1 and 2, carbamate anion, and carbamic acid structures, respectively. All relative energies are given with respect to R.

3.2.3 Reaction profile of the 2:1:5 cluster. The reaction of NH_3 and CO_2 is investigated in the presence of five water molecules and one NH_3 molecule. The energy profile is shown in Fig. 11.

As for the previous energy profiles, structure R can be viewed as the solvation of CO_2 and NH_3 in a five water- and one ammonia-cluster. It is characterised by a CN distance of 2.6 \AA , with a frequency of 154 cm^{-1} , consistent with the two previous optimised R structures. The formation of Z2 from R, a $\text{NH}_3^+\text{CO}_2^-$ zwitterion surrounded by five water molecules and one ammonia molecule, involves a very small barrier of 4.6 kJ mol^{-1} . A water-mediated proton transforms this zwitterion into a carbamate anion stabilised by an NH_4^+ cation. The barrier for the transformation of Z2 into C is 5 kJ mol^{-1} above R. Structure C is very stable with respect to R, *i.e.* 31 kJ mol^{-1} below. This 5 kJ mol^{-1} barrier for a mixed $\text{NH}_3:\text{H}_2\text{O}$ solvation is lower than the 11 kJ mol^{-1} barrier for a pure NH_3 solvation. The formation of the carbamate anion seems to be better catalysed by water than ammonia, if water and ammonia are both present. This is due to higher efficiency of proton transfers. This phenomenon was not observed in the experiments in Section 3.1.3, but is clearly evident from the theoretical calculations.

A water-mediated proton transfer can allow for the transformation of this carbamate anion into the carbamic acid, A1. The transition state involved in the $\text{C} \rightarrow \text{A1}$ transformation is lower in energy with respect to R by 23 kJ mol^{-1} . This transition state is 8 kJ mol^{-1} above C.

An alternative pathway has been investigated for another zwitterionic structure, Z1, although Z1 being close enough to Z2 a simple relaxation can transform one into another. We found this zwitterion to transform into carbamic acid, A2,

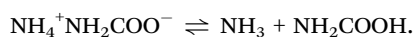
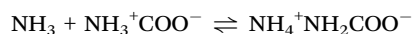
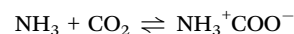
without going through the formation of a carbamate anion. This transformation does, however, involve a high barrier of 39 kJ mol^{-1} with respect to R. The barrier involved in the formation of A2 is much higher than the one involved in the formation of A1, both structures corresponding to carbamic acid but with a different arrangement of the solvent molecules. The reaction pathway *via* the carbamate anion structure should therefore be strongly favoured.

4 Discussion

On the basis of laboratory experiments and *ab initio* calculations we discuss the NH_2COOH and $\text{NH}_4^+\text{NH}_2\text{COO}^-$ formation mechanisms from a low temperature solid-phase NH_3 and CO_2 ice mixture. The mechanisms involved in the formation of the carbamate anion and carbamic acid are concentration dependent.

In a CO_2 -dominated ice, the proton transfer cannot take place and no reactivity occurs.

In a protic environment, *i.e.* a NH_3 - or H_2O -dominated ice, the less energetic pathway is the formation of the carbamate $\text{NH}_4^+\text{NH}_2\text{COO}^-$, *via* the formation of a zwitterion (scenario 2). The carbamate then transforms into carbamic acid, according to the following reactions:



The formation of carbamic acid involves lower energy barriers when formed from the carbamate anion. The direct formation of carbamic acid is possible but energetically unfavourable. However, in a H₂O dominated ice, where there is a shortage of NH₃ reactants, this energetic pathway is the only one available. Calculations show that carbamate seems to be better catalysed by water than by ammonia, although such a difference was not observed experimentally in kinetic experiments.

In a NH₃-dominated ice, the kinetics of the reaction are partial first-order with respect to CO₂ and partial zero-order with respect to NH₃ (for a NH₃ molar fraction between 0.5 and 1). The kinetic equation for the reaction can therefore be written as:

$$\frac{d(\text{NH}_4^+\text{NH}_2\text{COO}^-)}{dt} = -\frac{d(\text{CO}_2)}{dt} = k(T) \times (\text{CO}_2) \quad (17)$$

The temperature dependence of the first-order rate constant is experimentally determined to follow the Arrhenius law, $k(T) = 0.09_{-0.08}^{+1.1} \text{ s}^{-1} \times \exp(5.1 \pm 1.6 \text{ kJ mol}^{-1}/RT)$, in the 70 K to 90 K range, when the reactants are located on two neighbouring sites, *i.e.* for a NH₃:H₂O ratio greater than 1:1.

The determination of the reaction barrier of the two reactants located on two neighboring sites is very important for later studies of diffusion-limited reactions. Indeed, solid-phase reactions in water-dominated ice, in either interstellar or atmospheric environments, are diffusion-limited.⁴² The reaction will involve reactants either initially located on neighbouring sites (for a NH₃:H₂O ratio greater than 1) or brought to neighbouring sites by diffusion (NH₃:H₂O ratio lower than 1). The chemical reaction kinetics must be coupled with the diffusion kinetics of the reactants in order to fully describe such diffusion-limited reaction kinetics.

As shown in Fig. 12, the necessary diffusion of the reactants in H₂O-dominated ice ((NH₃:H₂O ratio lower than 1) slows down the kinetics of the NH₃ and CO₂ solid-state reaction. Very few studies exist on surface and volume diffusion in either crystalline^{43,44} or amorphous ice.^{45,46} Such studies on the diffusion of molecules in ice are a fundamental step toward the understanding of the kinetics of diffusion-limited reactions in ice. The coupling between solid-phase reactivity and diffusion in ice is therefore far from being understood.

We have also shown that NH₄⁺NH₂COO[−] has a zeroth-order desorption rate constant, $k_{\text{des}}(T) = 10^{13} \text{ s}^{-1} \times \exp(69.0 \pm 0.2 \text{ kJ mol}^{-1}/(R \times T))$, and is therefore more refractory than

water ice, which has a desorption energy of 46.6 kJ mol^{−1} (ref. 47)). This implies that some NH₄⁺NH₂COO[−] can stay on the substrate (silicate, carbon, aerosol) surface at high temperature when water ice has sublimated. Such refractory species enter the composition of a residue, where a water-free chemistry can take place at higher temperature than the water ice sublimation temperature. For example, the reaction between amines and CO₂ produces alkyl-ammonium alkyl-carbamates which, under (solar or interstellar) ultraviolet irradiation, can lead to the formation of amino acid salts, such as ethyl-ammonium glycinate.³⁴

More generally, carbamates are CO₂ reservoirs. They can store CO₂, which can be released at higher temperatures when the carbamate sublimates, as seen in Fig. 7. The rate of carbamate formation is important when calculating the overall rate of CO₂ removal. Carbamates can also be reaction intermediates in the synthesis of urea from NH₃ and CO₂ carried out in industrial plants.⁴⁸ Industrial research is presently carried out on methods of CO₂ removal in aqueous ammonia solutions.⁴⁹ At middle latitudes, the tropopause temperature ranges from an average of 15 °C at the sea level to about −55 °C at the top of the tropopause. The NH₃ to NH₄⁺ conversion rates have been estimated between 10^{−3} s^{−1} (ref. 50) and 5 × 10^{−5} s^{−1}.⁵¹ Upon extrapolating the rate we have measured to these temperatures, we find reaction rates between 0.01 s^{−1} and 5 × 10^{−3} s^{−1}, with an average of 7 × 10^{−3} s^{−1}. This extrapolation is tentative since the temperature ranges are different. However, as long as diffusion is not involved, the amorphous or crystalline state of the ice should not be an issue. Our results are slightly higher than the previous estimates of the rate of removal of atmospheric gas-phase NH₃ and its transformation into (NH₄⁺) salt aerosols. This can be explained by the effect of the diffusion on the overall reaction rate, as shown in Fig. 12.

5 Conclusion

We studied, both theoretically and experimentally, the low temperature solid-phase reactivity of the CO₂:NH₃ system. While NH₃ and CO₂ do not react in the gas-phase, we have shown that once in the solid-phase, the molecular environment can lower the reaction barrier, enabling the reaction between frozen CO₂ and NH₃ to occur. In a CO₂ dominated environment, the reaction is not possible. In a hydrogen bonded environment, such as in the presence of NH₃ or H₂O, the reaction barrier is lowered and the reaction is possible. The reaction produces both carbamic acid (NH₂COOH) and ammonium carbamate (NH₄⁺NH₂COO[−]). However, the formation of NH₄⁺NH₂COO[−] precedes the formation of NH₂COOH. The reaction can occur at temperatures below the desorption of the reactants, and their kinetic parameters can be measured using isothermal kinetic experiments and temperature programmed reactivity experiments on CO₂:NH₃ ice films. We concluded that the reaction rate constant follows the Arrhenius law $k(T) = 0.09_{-0.08}^{+1.1} \text{ s}^{-1} \times \exp(5.1 \pm 1.6 \text{ kJ mol}^{-1}/(RT))$ between 70 K and 90 K. The product of this reaction, ammonium carbamate (NH₄⁺NH₂COO[−]), is

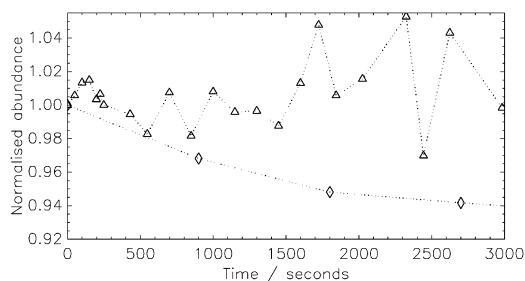


Fig. 12 Isothermal decay at 80 K of CO₂ in a CO₂:NH₃ ice film (diamonds) and in a CO₂:NH₃:H₂O ice film where H₂O is in excess with respect to NH₃ (triangles). The need for reactants to diffuse before reacting dramatically slows down the reaction.

more refractory than water ice and has $69.0 \pm 0.2 \text{ kJ mol}^{-1}$ first-order desorption energy for a 10^{13} s^{-1} pre-exponential factor. Carbamic acid (NH_2COOH) has $76.1 \pm 0.1 \text{ kJ mol}^{-1}$ first-order desorption energy for a 10^{13} s^{-1} pre-exponential factor. Real ices are water dominated, and thus solid-phase thermal reactions are diffusion-limited. The next steps are therefore to investigate the kinetics of the diffusion of each reactant and the kinetics of the reactivity of the $\text{CO}_2:\text{NH}_3:\text{H}_2\text{O}$ mixture where H_2O is dominant. Understanding how the reactivity is limited by the diffusion of the reactants is the key to understand ice chemistry.

Acknowledgements

We thank the PCMI (Physique et Chimie du Milieu Interstellaire) program and the CNES (Centre National d'Etudes Spatiales) for financial support, and the HPC resources from GENCI-[CCRT/CINES/IDRIS] (grant 2014 [x2014085116]) for computing time. J.A.N. is a Royal Commission for the Exhibition of 1851 Research Fellow.

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