Interstellar complex organic molecules are commonly observed during star formation, and are proposed to form through radical chemistry in icy grain mantles. Reactions between ions and neutral molecules in ices may provide an alternative cold channel to complexity, as ion-neutral reactions are thought to have low or even no-energy barriers. Here we present a study of the kinetics and mechanisms of a potential ion-generating, acid-base reaction between NH3 and HCOOH to form the salt NH$_3^+HCOO^−$. We observe salt growth at temperatures as low as 15 K, indicating that this reaction is feasible in cold environments. The kinetics of salt growth are best fit by a two-step model involving a slow “pre-reaction” step followed by a fast reaction step. The reaction energy barrier is determined to be 70 ± 30 K with a pre-exponential factor 1.4 ± 0.4 × 10$^{−3}$ s$^{−1}$. The pre-reaction rate varies under different experimental conditions and likely represents a combination of diffusion and orientation of reactant molecules. For a diffusion-limited case, the pre-reaction barrier is 770 ± 110 K with a pre-exponential factor of $\sim7.6 \times 10^{−3}$ s$^{−1}$. Acid-base chemistry of common ice constituents is thus a potential cold pathway to generating ions in interstellar ices.

**Key words:** astrochemistry – ISM: molecules – methods: laboratory: solid state – molecular processes

1. INTRODUCTION

Complex organic molecules (COMs) have been detected toward a wide range of interstellar environments (Herbst & van Dishoeck 2009) and are thought to be the precursors to prebiotic molecules (e.g., Jørgensen et al. 2012; Belloche et al. 2013). It is of particular interest to understand how they are formed and inherited through different stages of evolution in star-forming regions that may ultimately develop into solar systems capable of sustaining life. Current models of COM formation involve electron- or photon-induced dissociation of molecules in the icy mantles coating interstellar grain surfaces, producing radical species which diffuse and recombine to form larger molecules. This formation pathway requires temperatures exceeding ∼30 K (Garrod & Herbst 2006; Herbst & van Dishoeck 2009). COMs were first detected in the cores of high-mass protostars (e.g., Blake & Sutton 1987; Helmich & van Dishoeck 1997), which undergo heating as they collapse and therefore experience temperatures above 30 K; thus, these early detections are readily explained by the radical diffusion mechanism.

Recently, COM detections in cold pre-stellar environments (e.g., Öberg et al. 2010; Bachmann et al. 2012; Cernicharo et al. 2012; Vastel et al. 2014) have challenged the established need for lukewarm ice chemistry, as there must be efficient cold channels to chemical complexity in order to produce COMs in these regions. Several mechanisms, both gas-phase and grain-surface, have been suggested to explain COM production at low temperatures. Based on observations of the B1-b core and the pre-stellar core L1544, respectively, Cernicharo et al. (2012) and Vastel et al. (2014) propose grain-surface formation of methanol and other smaller species, followed by non-thermal desorption and gas-phase reaction to form more complex molecules. Balucani et al. (2015) have developed a gas-grain model to account for such a mechanism. This model relies on efficient non-thermal desorption of methanol, followed by gas-phase radical-neutral and radical–radical reactions, and fairly well reproduces the observations of dimethyl ether and methyl formate toward L1544. Ice chemistry alone could also be a viable pathway, provided that non-thermal diffusion is efficient, since it is the diffusion step that limits surface reactivity in low-temperature regimes. For example, experiments involving UV photoprocessing of CH$_2$OH-rich ices have demonstrated efficient production of COMs at temperatures as low as 20 K (Öberg et al. 2009), and Öberg et al. (2010) suggest this mechanism to explain COM detections in the B1-b core. Bachmann et al. (2012) similarly rely on non-thermal ice processing to explain the observed abundances toward the pre-stellar core L1698B: since it is well shielded from UV radiation, they suggest that chemistry is likely induced by cosmic ray bombardment, secondary UV radiation from cosmic ray interactions with H$_2$, or energy from exothermic chemical reactions.

Radical–radical reactions are not the only reactions without barriers, and reactions between ions and neutral molecules offer an alternative cold route to chemical complexity. However, the importance of this channel is unknown since most previous work on COM formation has focused on radical reactions. In the gas phase, ion-neutral reactions are responsible for many of the observed molecules in cold interstellar regions, and there may be an analogous grain-surface pathway. Notably, recent theoretical work by Woon (2011) demonstrates several such surface reactions to be barrierless. Furthermore, compared to radical chemistry, ion chemistry does not rely on access to dissociative radiation. While diffusion is still an obstacle for both ion chemistry and radical chemistry, it is important to understand their relative contributions to complex molecule formation.

Ions have been observed in ice mantles in a range of different interstellar environments, particularly OCN$^−$, and potentially also HCOO$^−$ and NH$_3^+$ (see, e.g., Grim & Greenberg 1987; Grim et al. 1989; Schutte et al. 1998, 1999; Keane et al. 2001; Knez et al. 2005; Bisschop et al. 2007; Öberg et al. 2011). Acid-base reactions are one potential source of ion generation in ice mantles. This study will focus on the
grain-surface reaction between NH$_3$ and HCOOH, which are among the most common constituents of ices in star-forming regions; observations indicate abundances with respect to water of 1%–5% for HCOOH (Bisschop et al. 2007; Boogert et al. 2008, 2014) and 3%–8% for NH$_3$ (Boogert et al. 2008, 2014; Bottinelli et al. 2010; Öberg et al. 2011).

Similar acid-base systems have been studied experimentally in the past. There have been several qualitative studies on the reaction of HNPC with NH$_3$, motivated by the identification of solid OCN$^-$ toward many different astrophysical objects. Raunier et al. (2003) observe the proton transfer at 10 K when HNCO is co-deposited with an excess of NH$_3$ (1:10); however, HNCO deposited on top of NH$_3$ does not react until warmed to 90 K. To explain this, the authors perform quantum calculations and determine that the proton transfer is only spontaneous when the HNCO–NH$_3$ pair is stabilized by three or more solvating NH$_3$ molecules. van Broekhuizen et al. (2004) deposit mixed H$_2$O/NH$_3$/HNCO gases with varying H$_2$O concentrations and confirm that thermal processing is a robust mechanism for OCN$^-$ production. They suggest that the reaction they observe at 10–15 K may be due to kinetic energy brought by molecules when they freeze onto the surface, in addition to the solvation-induced reaction described in Raunier et al. (2003). Subsequent reaction during warm up is attributed to increasing NH$_3$ mobility.

In a quantitative study on the reaction between HCN and NH$_3$, Noble et al. (2013) co-deposit both species with an excess of NH$_3$. The reaction is found to be thermally active, with some reaction occurring during deposition at 10 K and further growth during warm up. They model isothermal growth curves as pseudo-first-order with respect to HCN concentration and determine an activation energy of 324 K. In another quantitative proton transfer study, Mispelaer et al. (2012) characterize and model the kinetics of the reaction between NH$_3$ and HNCO. Fitting isothermal growth curves with rate equations, they find that it follows a two-step process: an initial slow orientation step, followed by a fast reaction step, with an activation energy of 48 K for the reaction. They also perform fitting using a gamma-distribution of reaction constants to account for the fact that there will be a distribution of energy barriers to the orientation process, depending on the original position of different molecules. Using this second method, they determine an activation energy of 73 K.

There has been no quantitative study of the NH$_3$–HCOOH reaction at cryogenic temperatures; however, there have been several studies demonstrating that this reaction can occur at temperatures as low as 10 K. Early work by Schutte et al. (1998) was focused on spectroscopic assignments for the NH$_3^+$HCOO$^-$ ion pair, which was extended in Schutte et al. (1999) to demonstrate that in-situ proton transfer occurs after deposition of an H$_2$O/NH$_3$/HCOOH mixture and the conversion increases during sample warm up. The kinetics are not quantified, but the authors note that the reaction seems to have a very small reaction barrier and that growth is limited by diffusion of reactant molecules. Later theoretical work by Park & Woon (2006) suggests that the proton transfer is barrierless as long as at least three water molecules are present per reacting pair to stabilize the system. More recently, experimental work by Gálvez et al. (2010) confirms a thermally induced in-situ reaction of co-deposited NH$_3$ and HCOOH, with a small fraction (15%) of reaction occurring upon deposition at 14 K, and continuing as temperature is increased.

The objective of this paper is to elucidate the kinetics and mechanisms of this process, and thus its feasibility and importance for the evolution of interstellar ices. Experimental details are described in Section 2, followed by the data analysis and modeling procedures in Section 3. The experimental results are presented in Section 4, including the kinetic parameters extracted from the experiments as well as mechanistic inferences. In Section 5 we compare our results with previous cryogenic acid/base studies and discuss the implications for surface channels to chemical complexity.

2. EXPERIMENTAL DETAILS

2.1. Experimental Setup

The experimental setup used for this experiment has been described previously by Lauck et al. (2015). Briefly, it consists of a CsI substrate window capable of being cooled to 11 K by a closed-cycle He cryostat, with temperature monitored by a temperature controller (LakeShore 335) with an estimated accuracy of 2 K and a relative uncertainty of 0.1 K. The substrate is suspended inside an ultra-high vacuum chamber with a base pressure of $\sim5 \times 10^{-10}$ Torr. Ices are grown by introduction of gas vapors at a normal incidence through 4.8 mm diameter pipes 0.7 inches from the substrate, unless otherwise noted.

A Fourier transform infrared spectrometer (Bruker Vertex 70v) in transmission mode was used to measure the amount of each infrared-active species in the ice. Gas-phase species present in the chamber were continuously monitored by a quadrupole mass spectrometer (Pfeiffer QMG 220M1). The experiments were performed using NH$_3$ gas (≥99.99% purity, Sigma), HCOOH (98%, Sigma), and deionized water (Sigma). The HCOOH and water were purified using three freeze-thaw cycles with liquid nitrogen.

2.2. Experimental Procedures

Table 1 summarizes all experiments presented in this paper. HCOOH and NH$_3$ were either co-deposited from separate pipes to form a mixed ice or sequentially deposited to form a layered structure. All dosing took place at 14 K. Apart from the TPD experiments, the ices were heated at 5 K minute$^{-1}$ to a target temperature and maintained there for one to four hours while monitoring the ice composition, and finally the ices were heated to desorption. IR scans taken at intervals of 10 minutes or less throughout the duration of each experiment.

Temperature programmed desorption (TPD) experiments (1–3) were performed for pure NH$_3$, pure HCOOH, and a layered NH$_3$/HCOOH ice. By monitoring the masses of desorbing molecules and the temperatures at which they desorb, TPDs show chemical conversions that have occurred over the course of warm up. These experiments were performed by depositing $\sim10$ monolayers (ML) of each species and ramping the temperature at 5 K/minute until desorption (see Section 3.1 for how thickness is determined).

For the co-deposition experiments (4–6), NH$_3$ and HCOOH were simultaneously deposited from two separate dosers at a distance of $\sim1.2$ inches and at an angle normal to the substrate. The temperature was ramped at 5 K/minute to a specified temperature, held for 4 hours, and then ramped again at 5 K/minute to 240 K. The co-deposition at normal incidence resulted in a high degree of ice mixing, as evidenced by the large amount of salt growth. A quantitative analysis of these
experiments, NH$_3$ was deposited and layered experimental setups. For all layered during dosing. Figure 1
homogeneity, which is beyond the scope of this study.

Most experiments (7–23) were performed using a layered ice configuration to reduce the amount of reaction that occurs during dosing. Figure 1 (top) shows a comparison of the co-deposited and layered experimental setups. For all layered experiments, NH$_3$ was deposited first, followed by HCOOH. The sample was heated at 5 K minute$^{-1}$ to a target temperature and held for a given amount of time, and then heated to 240 K.

We perform two types of layered experiments: “step” and “single-temperature,” shown schematically in Figure 1 (bottom). Step experiments are each held for 1 hr at several increasing temperatures within an experiment; thus, each step experiment yields several short isothermal growth curves at different temperatures. Single-temperature experiments are each held for 4 hr at a single temperature per experiment, yielding a single long isothermal growth curve. Experiments 7–9 are step experiments of different thicknesses: 1 ML, 3 ML, and 8 ML. Experiments 10–13 are single-temperature experiments of thin ices (1 ML NH$_3$: 1 ML HCOOH), and experiments 14–23 are single-temperature experiments of thick ices (9 ML NH$_3$: 7 ML HCOOH). Experiment 24 is a single-temperature experiment of a thick ice, with an 8 hr isothermal hold instead of 4 hours in order to verify that the growth curve is sufficiently sampled within a 4 hr timescale. By varying the conditions of thickness and time, we can assess the salt growth kinetics under different experimental conditions and thereby better constrain the mechanism of reaction.

### Notes

- $^a$ 20% uncertainty due to band strength uncertainty (Bouilloud et al. 2015).
- $^b$ ~4 hr isothermal hold unless otherwise noted.
- $^c$ Continuous heating, 5 K/minute.
- $^d$ Multiple 1 hr holds at 10–20 K intervals within range.
- $^e$ Duplicates for reproducibility.
- $^f$ 8 hr hold.

### Table 1

| Expt. | NH$_3$ (ML)$^a$ | HCOOH (ML)$^a$ | Set Temp (K)$^f$ |
|-------|----------------|----------------|-----------------|
| TPD experiments$^a$ | 1 | 10.0 | … | N/A |
| | 2 | … | 13.2 | N/A |
| | 3 | 9.2 | 6.3 | N/A |
| Co-deposition experiments | 4 | 17.6 | 6.9 | 20 |
| | 5 | 18.5 | 7.5 | 65 |
| | 6 | 18.4 | 7.4 | 85 |
| Layered step experiments | 7 | 1.3 | 1.3 | 75–125$^d$ |
| | 8 | 3.7 | 2.9 | 40–140$^d$ |
| | 9 | 8.6 | 7.5 | 40–140$^d$ |
| Layered single-temperature experiments (1 ML) | 10 | 1.5 | 1.0 | 75 |
| | 11 | 1.5 | 1.1 | 85 |
| | 12 | 1.8 | 1.2 | 95 |
| | 13 | 1.8 | 0.9 | 105 |
| Layered single-temperature experiments (8 ML) | 14 | 9.2 | 6.3 | 40 |
| | 15 | 9.3 | 7.9 | 85 |
| | 16 | 9.2 | 6.8 | 95 |
| | 17$^c$ | 9.1 | 7.3 | 95 |
| | 18 | 9.1 | 7.3 | 105 |
| | 19 | 9.7 | 6.7 | 115 |
| | 20$^c$ | 8.2 | 6.1 | 115 |
| | 21 | 8.3 | 7.5 | 125 |
| | 22 | 8.4 | 6.8 | 130 |
| | 23 | 9.0 | 6.9 | 140 |
| | 24 | 9.5 | 6.4 | 115$^f$ |

#### 3. ANALYSIS AND MODELING

#### 3.1. IR Spectra

Concentrations of ice species of interest were determined from baseline-subtracted infrared spectra. Each spectrum is averaged over 128 interferograms and takes approximately 2 minutes to complete. Ice thickness was calculated from the formula

$$N_i = \frac{2.3 \int \tau_i(\nu)d\nu}{A_i},$$

where $N_i$ is column density (molecule cm$^{-2}$), $\int \tau_i(\nu)d\nu$ is the integrated area of the IR band (absorbance units), and $A_i$ is the band strength in optical depth units. The standard monolayer coverage of 10$^{15}$ molecules cm$^{-2}$ was assumed.

The band positions and strengths used to determine the thickness of NH$_3$ and HCOOH are taken from Bouilloud et al. (2015) and were chosen to be the strongest features that do not overlap with the growing salt features (Table 2). Band strength uncertainties of 20% will result in the same uncertainty for the measured ice thicknesses listed in Table 1.

IR scans are taken throughout the course of an experiment, enabling in situ monitoring of the concentrations of ice species. These ice concentrations are plotted as a function of time over the course of an experiment to yield growth curves.
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3.2. Growth Curve Fitting

In order to extract kinetic parameters, isothermal growth curves are fit according to rate equations. To measure the reaction rate ideally, growth would depend only on the barrier to proton transfer; in reality, however, it is likely that an ensemble of diffusion and re-orientation processes ("pre-reaction" steps) will inhibit growth. Because it is not clear which of these will contribute under different experimental conditions, we have used several different models to see which provides the best fit to the experimental growth curves. We first give a brief overview of the kinetic modeling, and then describe the four models used in this work.

The general formalism for reaction kinetics is

\[
\frac{dX}{dt} = k(T) f(X),
\]

where \(X\) is the reaction fraction, \(k\) is the rate constant, \(T\) is temperature (K), and \(f(X)\) is the reaction model. The reaction fraction is determined by normalizing each growth curve to the final amount of salt at the completion of the reaction (i.e., just prior to desorption). The rate constant can in turn be expanded to

\[
k(T) = A e^{-E_a/kT},
\]

where \(A\) is the Arrhenius pre-factor and \(E_a\) is the activation energy. For solid-state reactions, the choice of reaction model \(f(X)\) is not obvious since local inhomogeneities and diffusion effects preclude the kinetics from being described by concentration-dependent rate laws used for homogeneous fluid systems. However, order-based methods are still useful as empirical models that allow kinetic parameters to be extracted from experiments (Vyazovkin & Wight 1997; Khawam & Flanagan 2006). Recently, order methods have been successfully applied to a number of thermal reactions of astrochemical relevance (Bossa et al. 2009a, 2009b; Theule et al. 2011; Mispelaer et al. 2012; Noble et al. 2013). For the reaction studied here,

\[
\text{NH}_3 + \text{HCOOH} \rightarrow \text{NH}_4^+ + \text{HCOO}^-, \tag{4}
\]

we define the change in reaction fraction

\[
\frac{dX}{dt} = \frac{d(\text{HCOO}^-)}{dt} = \frac{d(\text{NH}_4^+)}{dt} = -\frac{d(\text{HCOOH})}{dt}, \tag{5}
\]

where parentheses denote the fraction of each individual species relative to its maximum value in the course of the experiment. The fractional changes in concentration of HCOO\(^-\), NH\(_4^+\), and HCOOH can be equated since each have a maximum value equal to the initial value of HCOOH, the limiting reactant. The reaction order model is then

\[
\frac{dX}{dt} = k(T)(\text{NH}_3)^\alpha(\text{HCOOH})^\beta.
\]

In this work, growth curves were fit with different variations of this general model in order to evaluate different mechanisms by which the reaction may take place.

**Pseudo-first-order:** because NH\(_3\) is in excess of HCOOH for the majority of experiments, the simplest kinetic model would be pseudo-first-order with respect to HCOOH:

\[
\frac{dX}{dt} = k(T)(\text{HCOOH}). \tag{7}
\]

**Second order:** the next step in complexity is if the reaction is first-order with respect to both HCOOH and NH\(_3\), for a total order of two:

\[
\frac{dX}{dt} = k(T)(\text{NH}_3)(\text{HCOOH}). \tag{8}
\]

Modeling the reaction as second-order with respect to either reactant did not improve the fit, and no higher-order processes were considered.

Both (7) and (8) are single-step processes that consider only the reaction rate. We also tested a single-step model that assumes diffusion-regulated kinetics, and a more complex model that accounts for both mobility and reaction kinetics potentially at play in the solid-state environment.

**Diffusion model:** a Fickian diffusion model was adapted (see Lauck et al. 2015 for details) to describe the layered system of NH\(_3\) beneath HCOOH. In this model, the NH\(_3\) is assumed to be the mobile diffusant into a matrix of inmobile HCOOH. The mixed fraction is described by:

\[
N_{\text{max}}(t) = \frac{N_i(h - d)}{h} - \sum_{n=1}^{\infty} \frac{2N_i h}{n^2 \pi^2 d} \sin^2 \left( \frac{n \pi d}{h} \right) \times \exp \left[ -\frac{n^2 \pi^2}{h^2} D(t + t_0) \right], \tag{9}
\]

where \(h\) and \(d\) are, respectively, the total ice height and the height to the interface (both in nm), \(D\) is the diffusion constant (cm\(^2\) s\(^{-1}\)), \(N_i\) accounts for thickness uncertainties, and \(t_0\) is a time offset. This model assumes that the kinetics are determined entirely by diffusion, and that reaction occurs immediately; in other words, the rate of mixing entirely determines the rate of salt growth.

**Two-step model:** the final model used was a two-step model involving a slow pre-reaction step followed by a fast reaction step. A similar treatment was used by Mispelaer et al. (2012) in fitting the reaction of NH\(_3\) with HNCO. Several mechanistic possibilities exist for the pre-reaction step; as we discuss in more detail in the following section, it likely consists of both orientation and diffusion, with different processes dominating.

| Molecule | IR mode | Position (cm\(^{-1}\)) | Band Strength \(A_i\) (cm molec\(^{-1}\)) | Literature | Derived- 15 K |
|----------|---------|---------------------|-----------------------------------|-----------|--------------|
| HCOOH    | \(v_6\) CO str | 1216 | 2.9 \times 10^{-17} \(a\) | ... | ... |
| NH\(_3\) | \(v_1\) s-str | 3375 | 3.0 \times 10^{-17} \(a\) | ... | ... |
| HCOO\(^-\) | \(v_2\) CO a-str | 1573 | 1.3 \times 10^{-16} \(b\) | 1.1 \times 10^{-16} | ... |
| \(v_3\) CH bend | 1377 | ... | 1.3 \times 10^{-17} | ... | ... |
| \(v_4\) CO s-str | 1346 | ... | 2.1 \times 10^{-17} | ... | ... |
| NH\(_4^+\) | \(v_4\) bend | 1476\(d\) | 4.4 \times 10^{-17} \(c\) | 4.8 \times 10^{-17} | ... |

Notes.
\(a\) Bouilloud et al. (2015).
\(b\) Gálvez et al. (2010).
\(c\) Schutte & Khanna (2002).
\(d\) Indicates broadband.
the pre-reaction kinetics under different conditions. Because of this mixed nature, the pre-reaction step may depend on the temperature, ice structure, and elapsed time of a given experiment. The two-step model allows us to absorb the pre-reaction processes into the first step and therefore isolate the actual reaction step.

Here, we express the slow pre-reaction step as a unimolecular conversion of HCOOH from an inactive form to an active form. We write this step as

$$\text{HCOOH}^\circ \rightarrow \text{HCOOH}^*, \quad (10)$$

with a rate $k_p$, where $\circ$ and $^*$ represent the inactive and active form, respectively. The fast reaction step that follows is then

$$\text{NH}_3 + \text{HCOOH}^* \rightarrow \text{NH}_2^+\text{HCOO}^- \text{,} \quad (11)$$

with a rate $k_r$. We can express the kinetics of the total process in terms of the fractional conversion of HCOOH:

$$\frac{d(\text{HCOOH}^\circ)}{dt} = -k_p(\text{HCOOH}^\circ) \quad (12)$$

$$\frac{d(\text{HCOOH}^*)}{dt} = k_p(\text{HCOOH}^\circ) - k_r(\text{HCOOH}^*). \quad (13)$$

This system of equations is solved for the concentrations of both HCOOH$^\circ$ and HCOOH$^*$ as a function of time; since the two are indistinguishable by IR spectroscopy, our observable quantity (the total rate of consumption of HCOOH) is the sum of these two contributions. Recalling Equation (5), we derive an expression for the reaction fraction $\alpha$ as a function of time:

$$X(t) = \frac{e^{-t(k_p+k_r)}[e^{k_p}t(k_p-k_r)c - e^{k_r}t(1-c)]}{k_p-k_r}, \quad (14)$$

where $c$ is the initial fraction of HCOOH in the active form, or (HCOOH$^*$)$_{h=0}$.

Because kinetic fits are performed with respect to the reaction fraction, any uncertainties in the absolute band strength of the salt will not impact the kinetic parameters derived from the growth curves, as we are fitting a ratio. However, because the final amount of salt is measured at a different temperature than the growth curves, uncertainties in the temperature dependence of the band strength may introduce error into the fitting (see Section 3.3 and the Appendix).

All modeling is done only for isothermal growth curves. We do not attempt to model salt growth that occurs during deposition, as this may be governed by a different mechanism. For instance, it is possible that a "hot molecule" mechanism by which energy dissipated by gas-phase molecules is in part responsible for the initial salt formation that occurs during deposition.

3.3. Uncertainty Analysis

We consider five sources of error: spectral line fit errors, band strength uncertainties, kinetic fit uncertainties, dispersion between identical experiments, and absolute temperature calibration errors. The spectral line fit uncertainty consists of both Gaussian fit uncertainty and uncertainty due to baseline selection. The former is very small, with errors generally at least 4 orders of magnitude smaller than the values of the peak areas. The latter is thickness-dependent and results in uncertainties of 0.5%–1% in the peak areas of measured salt features. This source of uncertainty dominates the error bars for individual measurements of IR peak area.

Uncertainties in the IR band strength of the measured salt feature will not contribute to the uncertainty for an individual fit of a growth curve, as we fit the reaction fraction rather than the total number of monolayers of salt. Thus, any uncertainty in the absolute value of the band strength will cancel out. However, the band strength likely varies with temperature and this must be considered when comparing salt growth in experiments run at different temperatures. We assume a 5% uncertainty in the magnitude of growth curves due to this temperature dependence (see the Appendix for a detailed explanation of band strength uncertainty). This is the most important contribution to the error bars on rate constants for individual experiments.

Statistical errors from fitting the kinetic growth curves are very small and do not contribute significantly to the rate constants uncertainties (less than 1%).

Dispersion measurements are determined using identical experiments to incorporate variations in chamber and ice morphology that cannot be directly controlled for. This is the main source of uncertainty when comparing multiple experiments, with a 15% uncertainty for reaction rate constants and 17% uncertainty for pre-reaction rate constants which are propagated into fitting for the reaction barriers and pre-exponential factors.

The error from calibration of the absolute temperature reading will contribute only to the derived energy barriers and pre-exponential factors. However, this uncertainty is very small compared to the dispersion error.

4. RESULTS

The experimental results are presented in the following order: IR spectra in Section 4.1, TPDs in Section 4.2, co-deposited experiments in Section 4.3, qualitative analysis of layered experiments in Section 4.4, growth curve fitting in Section 4.5, reaction barrier determination in Section 4.6, and pre-reaction barrier determination in Section 4.7. It should be noted that the ultimate aim is to determine the reaction barrier of the proton transfer, which is necessarily tangled with other processes due to the limits of experimental constructs. We attempt to constrain pre-reaction steps as well as possible in order to isolate the reaction barrier, but the kinetic parameters derived for the pre-reaction are not necessarily relevant to astrophysical conditions since our system consists of simple, well controlled ice structures rather than a more complicated and water-dominated mixture.

4.1. IR Spectra

Figure 2(a) shows the IR spectra for pure NH$_3$, pure HCOOH, and a layered NH$_3$/HCOOH mixture at increasing temperatures. Salt features, identified as those that grow over the course of the reaction, are consistent with those reported by Gálvez et al. (2010) and are listed in Table 2. Small salt features are apparent at 15 K, with slow growth until 80 K and rapid growth beyond this. Desorption is complete by ~220 K.

The four most prominent peaks associated with salt growth occur within the spectral window of 1300–1600 cm$^{-1}$; while there is some overlap of especially the inner two peaks, a Gaussian fitting of the four peaks produces an excellent fit to the overall shape of the spectrum, as shown in Figure 2(b).
The fitting procedure uses the spectral window from $\sim 1320$–$1600 \text{ cm}^{-1}$, excluding the tail from 1600–1750 cm$^{-1}$ which is due to the pure HCOOH feature at 1710 cm$^{-1}$ and the pure NH$_3$ feature at 1625 cm$^{-1}$. Regions outside of this window are assigned a value of zero to allow the model to return to the baseline. The growth curves derived from the areas of the two outermost peaks at 1346 and 1573 cm$^{-1}$ are in very good agreement with one another, providing confirmation that these peaks are indeed originating from the growth of the same species. The inner two peaks follow less consistent growth curves, possibly due to their greater degree of overlap. In addition, the NH$_4^+$ $\nu_3$ band is very broad and it is difficult to distinguish an exact peak position. The HCOO$^-$ $\nu_5$ band at 1377 cm$^{-1}$ may also have a contaminating component from the pure HCOOH band at 1380 cm$^{-1}$, although this is weaker by an order of magnitude (Bouilloud et al. 2015). The $\nu_2$ formate band at 1573 cm$^{-1}$ is used for all growth-curve fitting since it is the most consistent and prominent salt feature. Band strengths for the salt IR modes were derived for each of the four peaks and are listed in Table 2. Details of their derivation are given in the Appendix, along with an analysis of structure and temperature dependencies.

4.2. TPDs

Temperature programmed desorption experiments were performed for pure NH$_3$, pure HCOOH, and a layered experiment of NH$_3$ under HCOOH. The ices were heated at 5 K/minute until desorption while continuously monitoring gas-phase concentrations with the QMS. Figure 3 shows the resulting QMS traces for these experiments. Mass 29 traces the dominant HCOOH fragment, and mass 17 traces NH$_3$. The mixture of NH$_3$ and HCOOH desorbs at higher temperatures than either pure ice, indicating a chemical conversion has indeed occurred (peak desorption temperatures for NH$_3$, HCOOH, and the salt are 96 K, 144 K, and 203 K, respectively). Furthermore, some NH$_3$ desorbs prior to salt desorption, but HCOOH desorbs only as the salt; this indicates that the HCOOH has undergone complete conversion, and in experiments with excess NH$_3$, the total salt formation will be determined by the initial dose of HCOOH.

We note that mass 17 also traces a fragment of H$_2$O in addition to the major NH$_3$ channel. We expect that water will be a minor contribution to the total QMS signal since the samples are formed from high purity gases maintained under ultra-high vacuum. However, there may be background deposition of water onto the sample throughout the experiment and thus some degree of this signal could be due to water. Based on an analysis of the dominant water channel at mass 18, around the water desorption temperature of 160 K, water contamination contributes up to 20% of the total mass 17 signal; at all other temperatures, the water contamination contributes 10% or less to the measured mass 17 signal.

4.3. Salt Formation in Co-deposited Ices

Growth curves for co-deposited experiments are shown in Figure 4. For all co-deposited experiments, considerable salt growth occurs immediately following dosing at 14 K ($\sim$30% of the total salt conversion), with further growth during subsequent warm up from 14 K to the target temperature. For the target temperature of 85 K, growth during the isothermal...
hold is evident; however, no isothermal growth was seen for the co-deposited experiments with 20 and 65 K target temperatures. After the isothermal holds, the temperature was increased until desorption, and growth continued once again during this final warm up. The rapid growth during the initial warm up followed by a lack of growth at target temperatures below 85 K suggests that the kinetics of salt formation under these conditions are complex: growth is evidently accessible at low temperatures as long as the sample is being warmed, but during isothermal periods the growth is arrested unless the temperature is sufficiently high.

4.4. Qualitative Analysis of Salt Growth in Layered Ices

A comparison of layered and co-deposited experiments, both with 85 K target temperatures, is shown in Figure 5. Following deposition, both experiments exhibit similar patterns of salt growth over the course of the experiment. However, a layered setup offers the advantage of greatly reducing the amount of salt formation that occurs during dosing (≈0.5 ML, compared to ≈1.8 ML in co-deposited ices). This enables a better estimation of the amount of available reactants compared to the co-deposited case. Additionally, it minimizes the amount of salt that has formed during the warm up to the targeted temperature, enabling a better evaluation of the early kinetics of the reaction. Because of this, we performed our analysis using a layered ice setup, rather than co-deposition, as is used by many previous kinetic studies (e.g., Mispelaer et al. 2012; Noble et al. 2013).

We note that, while the layered experiments exhibit a lower absolute growth, it is in fact a higher reactivity per molecule in contact: ≈50% salt conversion occurs in the 1 ML HCOOH in contact for the layered experiment compared to ≈25% salt conversion for the 7 ML HCOOH in contact in the co-deposited experiment. It is possible that the salt formation during deposition may be occurring by different mechanisms in the co-deposited and layered experiments. For instance, a hot molecule mechanism might contribute to growth preferentially in the layered experiment.

We first look qualitatively at the amount of salt that has formed at the end of each isothermal hold for the different categories of experiments described in Section 2.2. Figure 6(a) shows the growth differences between step experiments of ices with different thicknesses. Above 80 K, the 3 ML and 8 ML experiments produce more salt than the 1 ML experiment. In this regime, diffusion must occur since non-interface molecules contribute to salt growth in the multilayer ices. Furthermore, the 3 ML and 8 ML experiments grow identically until about 120 K, at which point the 8 ML ice growth continues faster than the 3 ML growth. This can be attributed once again to diffusion: while short-range diffusion appears to contribute above 80 K, long-range diffusion is important only above 120 K.

In Figures 6(b)–(c), the 8 ML and 1 ML step experiments are compared to the single-temperature experiments with the same thicknesses. Regardless of the fact that prior reaction has occurred in the step experiments, roughly the same amount of salt is produced by a given temperature as for the single-temperature, long-hold experiments. This has several implications, notably that most salt growth occurs in the first hour at a given temperature, and that at each temperature the salt formation kinetics does not depend on how pre-existing salt has formed. We discuss this observation in more detail in Section 5.

4.5. Growth Curves and Model Fitting

In fitting the kinetics of salt formation, we do not attempt to model growth that occurs during deposition or temperature ramps. Our modeling of isothermal growth takes into account previous salt formation, however, and so this warm up growth should not be problematic to our kinetic derivations. Previous works (Mispelaer et al. 2012; Noble et al. 2013) offset the reaction fraction to equal zero at time zero, which models salt growth as if there is no salt present in the ice at the start of the isothermal period. Instead, we fit for a time offset that encompasses any salt growth prior to time zero of the isothermal hold. This allows us to account for prior salt growth regardless of its origin, i.e., whether it formed during deposition, warm up, or isothermal growth. All resulting reaction constants ($k_r$) and pre-reaction constants ($k_p$) are summarized in Table 3.
experiments (isothermal growth period. \(\sim\) Figure 6. Salt growth (monolayers) that has occurred by the end of each isothermal growth period. (a): different thicknesses of the step experiments (1 hr isothermal hold), (b)-(c): step experiments (short holds) and separate experiments (long holds) for thick and thin ices.

Thin short experiments: the layered step experiment of \(\sim1\) ML NH\(_3\) under 1 ML HCOOH is shown in Figure 7. The salt grows rapidly during warm up periods, and isothermal periods exhibit slower growth. Isothermal holds at 85 K, 95 K, and 105 K produce the most salt growth; the kinetics are likely quite slow at 75 K, and above 105 K the reactants are mostly consumed and of limited availability, thus slowing growth. The growth curves are well fit by the pseudo-first-order model, and more complex models do not improve the fit. Indeed, the diffusion model does not converge on a solution at all, which is not surprising given that diffusion should not contribute much to growth in single-ML ice layers. The two-step model produced negative values for \(k_r\), indicating that in the case of short reaction timescales and thin ices, salt growth is determined by only the reaction barrier. In other words, under these conditions the energy barrier of the proton transfer dominates the kinetics, and dynamical processes do not play an important role.

Thin long experiments: the growth curves for single-temperature experiments of 1 ML ices are shown in Figure 8. Early reaction times were fit with the single-step model as was done for the step experiments of 1 ML ices. We expect that if a single kinetic process contributes to growth, then the same

| Series        | Expt. | Set Temp (K) | \(k_r\) (s\(^{-1}\)) | \(k_p\) (s\(^{-1}\)) |
|---------------|-------|--------------|-----------------------|-----------------------|
| Steps (1 ML)  | 7     | 75           | \(3.7 \times 10^{-4}\) | ...                   |
|               | 85    | ...          | \(4.4 \times 10^{-4}\) | ...                   |
|               | 95    | ...          | \(8.0 \times 10^{-4}\) | ...                   |
|               | 105   | ...          | \(5.5 \times 10^{-4}\) | ...                   |
|               | 115   | ...          | \(3.3 \times 10^{-3}\) | ...                   |
|               | 125   | ...          | \(6.6 \times 10^{-4}\) | ...                   |
| Steps (3 ML)  | 8     | 40           | ...                   | ...                   |
|               | 60    | ...          | ...                   | ...                   |
|               | 80    | \(4.0 \times 10^{-3}\) | \(1.3 \times 10^{-5}\) | ...                   |
|               | 100   | ...          | ...                   | ...                   |
|               | 120   | ...          | ...                   | ...                   |
|               | 140   | ...          | ...                   | ...                   |
| Steps (8 ML)  | 9     | 40           | ...                   | ...                   |
|               | 85    | ...          | ...                   | ...                   |
|               | 105   | \(1.9 \times 10^{-3}\) | \(1.6 \times 10^{-6}\) | ...                   |
|               | 125   | ...          | ...                   | ...                   |
|               | 140   | \(4.2 \times 10^{-3}\) | \(7.1 \times 10^{-5}\) | ...                   |
| Single-temp (1 ML) | 10   | 75           | \(6.3 \times 10^{-4}\) | \(7.4 \times 10^{-6}\) |
|               | 11    | 85           | \(6.4 \times 10^{-4}\) | \(1.4 \times 10^{-5}\) |
|               | 12    | 95           | \(5.7 \times 10^{-4}\) | \(2.3 \times 10^{-5}\) |
|               | 13    | 105          | \(8.1 \times 10^{-4}\) | \(3.3 \times 10^{-5}\) |
| Single-temp (8 ML) | 12   | 40           | ...                   | ...                   |
|               | 15    | 85           | \(5.5 \times 10^{-4}\) | \(2.1 \times 10^{-6}\) |
|               | 16    | 95           | \(9.1 \times 10^{-4}\) | \(2.4 \times 10^{-6}\) |
|               | 17    | 95           | \(7.1 \times 10^{-4}\) | \(2.1 \times 10^{-6}\) |
|               | 18    | 105          | \(5.9 \times 10^{-4}\) | \(4.2 \times 10^{-6}\) |
|               | 19    | 115          | \(1.0 \times 10^{-3}\) | \(1.3 \times 10^{-5}\) |
|               | 20    | 115          | \(7.0 \times 10^{-4}\) | \(7.6 \times 10^{-6}\) |
|               | 21    | 125          | \(7.7 \times 10^{-4}\) | \(1.8 \times 10^{-5}\) |
|               | 22    | 130          | \(9.1 \times 10^{-4}\) | \(2.7 \times 10^{-5}\) |
|               | 23    | 140          | \(1.4 \times 10^{-3}\) | \(5.9 \times 10^{-5}\) |
|               | 24\* | 115          | \(7.9 \times 10^{-4}\) | \(7.1 \times 10^{-6}\) |

Note.
* 8 hr isothermal hold.
model should work at early and late timescales. However, it is clear that different kinetics contribute at early and late times, and a model of early growth cannot reproduce late growth. In the limit of longer experiments, salt growth is instead best modeled by two-step kinetics, dependent on both the reaction barrier and a pre-reaction barrier. This suggests that while the growth seen in the shorter experiments is dominated by reaction between molecules already in an active state, in the limit of longer time when these active molecules are fully consumed, the contribution of the slow pre-reaction step becomes evident. Because each ice layer is \( \sim 1 \) ML thick, it is unlikely that diffusion is the important pre-reaction step in this case. Instead, we propose a re-orientation of reactant molecules into a favorable reaction configuration, similar to that described in Mispelaer et al. (2012).

**Thick long experiments:** The 8 ML step and single-temperature experiments were initially fit with all four kinetic models; an example growth curve is shown in Figure 9. Again, the two-step model produces an excellent fit, while the other models do not capture the shape of the growth curve. In this case, the pre-reaction step is likely a combination between diffusion and orientation since, as discussed previously, diffusion is seen to contribute to salt growth in multilayer ices.

The pre-reaction barrier becomes an important contribution to growth on long timescales; thus, to verify that it is being sufficiently sampled on 4 hr timescales, we performed an experiment with an 8 hr isothermal hold. Comparing experiment 24 with the 4 hr experiments 19 and 20 in Table 3, we find that both the reaction and pre-reaction barrier for the 8 hr experiment are consistent with the values extracted from the 4 hr experiments. The 4 hr growth curves are therefore sufficient for use in fitting, as the inferred kinetics do not change on longer timescales. The two-step model predicts that the growth curve should approach a stable value equal to a reaction fraction of 1 on the timescale of tens of hours.

**4.6. Reaction Barrier Determination**

The reaction rate constants derived from the growth curve fitting were used to generate an Arrhenius plot (Figure 10(a)). Fitting all data points simultaneously, we derive a reaction energy barrier \( E_a = 70 \pm 30 \) K and pre-exponential factor \( A = 1.4 \pm 0.4 \times 10^{-3} \text{ s}^{-1} \). Note that rate constants from below 70 K and above 130 K are excluded in this fitting, as the reaction is too slow to fit growth at low temperatures and most of the reactants have already been consumed by high temperatures. The error bars for thin ices are much larger than for the thick ices, as it is more difficult to constrain the fit when the magnitude of growth is smaller, and especially so when the timescale is short as for the step experiments.

![Figure 8](image)

**Figure 8.** Isothermal salt growth from single monolayer experiments held at 85 K (exp 11) and 95 K (exp 12) are shown as black circles. As for Figure 7, the first hour of reaction is fit with the single-step model (pink dotted lines). Blue lines show the two-step model fitting.

![Figure 9](image)

**Figure 9.** Growth curve for a thick long-hold experiment at 115 K (experiment 19), fit by four different reaction models.

![Figure 10](image)

**Figure 10.** Arrhenius plot for the reaction barrier (a) and pre-reaction barrier (b), along with fits to each experimental category. Barriers for the 1 ML short experiments (pink circles, panel (a)) were derived using a single-step reaction model; all other barriers are derived using a two-step model. Of the 8 ML long experiments, experiments with 4 hr isothermal holds (14–23) are shown with black x’s, while the experiment with an 8 hr hold (24) is shown with green x’s.
The reaction rate constants for the thin short, thin long, and thick long experiments at the same temperature are in very good agreement, and fall within each others error bars as seen in Figure 10(a). Likewise, when each category is fit individually, the derived values for $E_a$ and $A$ are all consistent within the combined uncertainties (Table 4). Thus, despite differences in thickness and timescale, we still find consistent values for the reaction barrier using the two-step model, indicating that we are in fact isolating the reaction step from the pre-reaction processes.

### 4.7. Pre-reaction Barrier Determination

A similar treatment can be performed on the pre-reaction constants as is described above. Unlike for the reaction barrier, each category of experiments is likely to have a different pre-reaction barrier depending on the experimental conditions; in other words, orientation and diffusion are expected to contribute to growth to different extents between setups.

Fitting the thick long (single-temperature) experiments results in a pre-reaction activation barrier of 950 K with a pre-factor of order 0.04; however, the uncertainties on these numbers are very large. To better constrain the pre-reaction barrier, we have re-fit all experiments with a fixed reaction constant $k_f(T)$ based on the combined $E_a$ and $A$ values in Table 4. This is especially important for experiments with thin ices or short timescales since these fits are more uncertain. The resulting fits to growth curves using the fixed parameter method are in excellent agreement with the data. The pre-reaction rate constants from the fixed fitting reaction kinetics are shown in Figure 10(b), and the resulting kinetic parameters are listed in Table 4.

The pre-reaction rates from thick experiments with short and long isothermal holds appear reasonably consistent, and Arrhenius fitting results in a much steeper slope than for the thin experiments, corresponding to a higher energy barrier. We expect the pre-reaction process to be dominated by diffusion for the thick ices and by orientation for the thin ices, and it is not surprising that orientation would have a lower energy barrier than diffusion. Additionally, the pre-reaction barrier for the thick ices appears to have a tail at the 85 K and 95 K temperature points. Based on the qualitative analysis of Figure 6(a), diffusion appears to contribute to multilayer growth above 80 K; it is likely that the shallower slope of the Arrhenius plot at lower temperatures corresponds to an orientation-dominated, pre-reaction step, and the steeper slope at higher temperatures represents a diffusion-dominated, pre-reaction step.

### Table 4

| Category            | $E_a$ (K) | $A$ (s$^{-1}$) |
|---------------------|-----------|---------------|
| **Reaction**        |           |               |
| Combined$^a$        | 70 (30)   | 1.4 (0.4) $\times 10^{-3}$ |
| Thick ice, long hold | 86       | 1.6 $\times 10^{-3}$ |
| Thin ice, long hold | 40       | 9.8 $\times 10^{-4}$ |
| Thin ice, short hold | 95     | 1.7 $\times 10^{-3}$ |
| **Pre-reaction**    |           |               |
| Diffusion-limited   | 770 (110) | 7.6 (7.6) $\times 10^{-3}$ |
| Orientation-limited | 400 (10) | 1.5 (0.2) $\times 10^{-3}$ |

**Note.** Uncertainties listed in parentheses where applicable.

$^a$ Recommended value.

Figure 11. Arrhenius plots for energy barrier distributions. Rate constants are calculated for a single energy barrier across all temperatures (blue dotted line, all panels) and compared to those calculated using an energy barrier that varies with temperature (circles; best-fits shown as black dotted lines).

### 5. DISCUSSION

#### 5.1. NH$_3$ + HCOOH Reaction

We extract an energy barrier of 70 K for the proton transfer between NH$_3$ and HCOOH using the isothermal rate constants from different experiments (Figure 10). This barrier is consistent for different experimental conditions, demonstrating that it is indeed isolated from the pre-reaction processes that depend on the experimental construct.

The salt growth observed in this work is consistent with the qualitative description by Schutte et al. (1999), who observed some reaction upon deposition at 10 K and further growth during warm up. The authors speculated that the reaction would have a low barrier and be limited by the diffusion of reactants, both of which we have demonstrated here. Indeed, we find that not only diffusion but also an orientation of reactant molecules contribute to the overall growth rate of the salt.

Comparing our results with previous quantitative proton transfer studies, the reaction barriers are quite similar, despite differences in fitting methodologies: Noble et al. (2013) derive the reaction barrier for NH$_3$ + HCN to be 324 K, Mispleaer et al. (2012) find the barrier for HNCO + NH$_3$ to be 48 K, and we find the barrier for NH$_3$ + HCOOH to be 70 K. The HCN barrier perhaps appears high in comparison, but HCN is also a far weaker acid than HCOOH in the aqueous phase.

We note three differences with these existing studies that may impact the derived kinetic parameters. First, Mispleaer et al. (2012) use a two-step model as in this work, but Noble et al. (2013) use a single-step, pseudo-first-order model; if the reaction indeed follows two-step kinetics, a single-step fit would likely result in too high of a reaction barrier since the slow pre-reaction step is also being incorporated into the fit.
This may contribute to the relatively high barrier found for the HCN + NH$_3$ reaction. Second, both previous studies analyzed reaction in co-deposited ices, whereas our ice is layered. This introduces diffusion as an important pre-reaction process in our salt growth, whereas orientation may be the most important pre-reaction step in previous works. Finally, the previous works perform fitting on growth curves that are normalized such that at time zero the pure ice has a fraction of unity and the product has a fraction of zero. This method assumes that any reaction that has already occurred during the warm up phase of the experiment does not influence the kinetics during the isothermal period. In this work, we do not offset our growth curves to begin at a reaction fraction of zero because prior reaction could inhibit further reaction and should therefore be taken into account in the isothermal modeling.

5.2. Pre-reaction Processes

Unlike the reaction barrier, the derived pre-reaction barriers differ between experimental setups, reflecting the different dynamical processes at play under different experimental conditions. Re-orientation of reactant molecules into favorable reaction configurations should occur in all ices; this process contributes to growth once molecules that are already oriented to react are consumed. Diffusion of reactant molecules occurs only in thick ices, with molecules not originally at the interface replenishing the reactive stock. We find diffusion-limited (thick) ices to have much higher pre-reaction barriers than orientation-limited (thin) ices, which is consistent with the degree of mobility required for each process.

The pre-reaction mechanism will depend on the position and orientation of the molecules in the ice. This may differ from other experimental setups if a hot molecule mechanism is at play during deposition. As mentioned in Section 4.4, it is possible that molecules could be preferentially oriented to react due to energy dissipation following condensation. If molecules were deposited cold instead of at room temperature, it may result in a smaller fraction of activated reactants. However, since the two-step model fits for the initial active fraction of reactants, this will not impact our derived reaction barrier. A hot molecule mechanism may impact whether or not a pre-reaction step is required, but the barrier should not be impacted since pre-reaction kinetics depend only on molecules that are in the inactive state.

Comparing with previous studies, the pre-reaction step in the case of Mispelaer et al. (2012) is likely only an orientation process, as diffusion is not expected to play a role under their experimental conditions of co-deposition with a great excess of NH$_3$. We cannot make a comparison to their pre-reaction barrier, however, since they do not observe a temperature dependence for their pre-reaction step, and instead claim that the amount of salt that can form at a given temperature would be controlled by the fraction of pre-reaction barriers that are thermally accessible at that temperature.

Physically, a distribution of energies for the pre-reaction step would not be surprising given that it represents both orientation and diffusion. These two processes will contribute to a different extent to growth depending on ice thickness, temperature, and reaction progress. In particular, the barrier for each process may change over the course of an experiment; for instance, diffusion later in the course of an experiment is likely more difficult as more salt will have built up in between the pure ice layers.

However, it is not obvious why we would observe an Arrhenius-like relationship between pre-reaction rates and temperature in the case of a temperature-dependent distribution of energy barriers. While we see a tail end to the Arrhenius plot at low temperatures in Figure 10, the experiments above ~90 K appear linear and thus consistent with Arrhenius behavior. We performed a toy calculation to evaluate whether a distribution of energy barriers could produce a log-linear relationship between measured rates and temperatures (Figure 11). We assume that the measured energy barrier increases as a function of temperature since the lower barriers would be overcome at lower temperatures. Rate constants are calculated using the Arrhenius Equation (3) with a fixed value of A and with $E_a$ varying according to three different distributions: a symmetric equally spaced distribution from 80% to 120%; a symmetric Gaussian distribution from 80% to 120%; and an asymmetric equally spaced distribution from 90% to 130%.

For both linear distributions we see that the rate constants are still linear on the Arrhenius plot despite being derived from different energy barriers. The Gaussian distribution can appear linear or deviate substantially from linear depending on the choice of standard deviation; we show the results using a moderate value, which could certainly be possible within the scatter of the rate constants we derive for the pre-reaction barrier. In all three models, the derived barrier would be lower than the median barrier, and thus the reported pre-reaction barriers should be considered lower limits.

These plots demonstrate that it is possible under a number of conditions to reproduce linear Arrhenius behavior despite each rate constant being defined by a different energy barrier. Given the nature of the pre-reaction step, such a distribution is likely to be at play in this system. It should be noted that, by contrast, the reaction barrier appears to be a single value, independent of temperature and ice environment, as discussed in Section 5.1.
5.3. Astrophysical Implications

We next extend our laboratory results to assess the temperature at which the NH$_3^+$/HCOO$^-$ salt formation reaction should be efficient under interstellar conditions. Because this is an ice process, it should not be impacted by the lower pressure of the interstellar medium compared to the ultra-high vacuum setup. However, the timescales of astrophysical processes are many orders of magnitude longer than laboratory timescales. Following Pontoppidan et al. (2008), we relate the critical temperature $T_{\text{crit}}$ of the reaction under interstellar conditions to that under laboratory conditions:

$$\frac{\tau_{\text{astro}}}{\tau_{\text{lab}}} = \exp \left[ \frac{E_a}{T_{\text{astro}}(1/T_{\text{astro}} - 1/T_{\text{lab}})} \right],$$

where $\tau_{\text{astro}}$ and $\tau_{\text{lab}}$ are the e-folding timescales (i.e., a single exponential lifetime) for the reaction in the interstellar medium and the laboratory, respectively, and $T_{\text{astro}}$ and $T_{\text{lab}}$ correspond to the critical temperatures for each environment. For $T_{\text{astro}}$ we assume a typical star formation timescale of $10^6$ years for a cold cloud, and for $E_a$ we use the reaction barrier of 70 K derived in this work. Since our reaction model is first-order, $\tau_{\text{lab}}$ is simply the inverse of the rate constant (i.e., $1/s^{-1}$) measured at a given temperature $T_{\text{lab}}$. Using the rate constants measured in this work, we find a critical temperature $T_{\text{astro}}$ of 3 K. Such low critical temperature implies that, in the case where reactants are in the appropriate configuration, we expect reaction to proceed under cloud core conditions of <10 K. Note that this treatment assumes HCOOH and NH$_3$ are already in the proper position and orientation, i.e., we do not consider pre-reaction steps. The availability of reactants may therefore limit the degree to which this reaction occurs.

The impact of pre-reaction barriers on growth kinetics is of particular importance to astrochemical modeling. Most Monte Carlo models of grain-surface chemistry already account for diffusion using a "hopping" barrier; however, we have demonstrated that other mobility-related barriers may be equally important to ice chemistry. Orientation has a lower barrier than diffusion, but is not currently incorporated in models and needs to be considered to create a full picture of the chemistry. The matrix-dependent nature of mobility barriers means that the values of pre-reaction barriers derived in this work are likely not suitable for use in astrochemical models; further work is required to derive appropriate pre-reaction barriers for modeling use.

Additionally, more work is required to assess the role of ions as initiators of surface chemical pathways. As discussed by Woon (2011), surface reactions involving ions offer a promising low-energy pathway to chemical complexity, without the destructive effects of energetic processing. Woon presents theoretical calculations of several protonated species undergoing barrierless reactions with neutral water molecules; analogous to the gas-phase ion-neutral reactions that are responsible for many gas-phase processes in low-energy interstellar environments, these surface ion-neutral reactions are spontaneous and offer an energetic advantage over neutral-neutral reactions mediated by barriers. Woon's calculations consider ions as depositing onto water ices, but an in situ method of ion formation such as that considered in this paper could equally drive these ion-neutral reaction pathways. As NH$_3$ and HCOOH are fairly abundant components of ice mantles, the reaction described in this work has the potential to be a robust source of ion generation, and could increase chemical complexity via low-barrier, ion-neutral reactions.

6. CONCLUSION

The kinetics and mechanisms of the reaction between NH$_3$ and HCOOH were examined by continuously monitoring product formation in layered ices held at constant temperatures. Based on our results we conclude the following:

1. Under laboratory conditions, the reaction between NH$_3$ and HCOOH is accessible as low as 14 K and proceeds to completion upon warm up.
2. The proton transfer to form the salt has a barrier of 70 K if the molecules are positioned to react.
3. A two-step process (a slow pre-reaction step followed by a rapid reaction step) best describes the mechanism of salt growth. The pre-reaction step is likely a combination between orientation and diffusion of reactant molecules.
4. Multilayer ices exhibit a pre-reaction barrier of ~770 K while that of single layer ices is only ~400 K. The former includes both diffusion and orientation barriers, while the latter is only orientation.
5. The pre-reaction barrier may actually be a distribution of barriers. Pre-reaction barriers at the higher end of the energy distribution are sampled at higher temperatures. As a result, the values of the pre-reaction barriers listed here are likely upper limits to the actual median barriers.
6. NH$_3^+$/HCOO$^-$ salt formation in the interstellar medium is potentially possible below 10 K provided that the reactants are correctly positioned at neighboring sites.

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APPENDIX

Band strengths were derived as follows. A layered ice with NH$_3$ beneath HCOOH was heated at 5 K/minute to 165 K. At this point, the HCOOH band at 1216 cm$^{-1}$ has disappeared, but HCOOH has not begun to desorb (as monitored by QMS). This indicates that the reactant has been fully converted, and none is lost to desorption. Also at this point the salt has not yet crystallized (as seen by IR spectra) or desorbed. The final peak area for the salt upon reaching 165 K is then equated to the initial amount of formic acid. This method assumes that the salt features do not change as a result of the temperature or the structure of the ice. This is likely not entirely accurate, and we have assessed the dependencies of each. Figure 12 shows the experiment used to do so.

A structure dependence would arise from the fact that the salt forming at low temperatures may not be configured in the same way as salt at higher temperatures. Salt crystallization occurs above the range of temperatures we are interested in for this study, but more minor bulk rearrangements may occur at lower temperatures. We explore the magnitude of this effect by comparing the consumption of HCOOH with the formation of salt during warm up of a layered HCOOH/NH$_3$ ice from 14 K to 150 K (Figure 12, left of vertical dotted line). We then
assume that there is a one-to-one conversion from HCOOH to HCOO$^-$ and assign a temperature-dependent band strength such that the sum of HCOOH and HCOO$^-$ remains constant throughout the conversion. When there are low abundances of either species the uncertainties of the derived band strengths are large, but we focus on the range 60–130 K in which most experiments are performed. Here, the determined band strength varies by less than 5%.

We next assess the temperature dependence of the salt band strength for an ice with a constant structure by comparing the strength of the salt feature at 165 K with the strength of the same feature after the salt has been cooled down (Figure 12, right of vertical dotted line). After reaching 165 K, the salt was cooled back to 11 K at 5 K/minute and then heated once again at 5 K/minute until fully desorbed. The band strength does change by ~5% over this temperature range, and the change in band strength is fully reversible.

We do not attempt to correct for these dependencies in performing our fitting, as this would introduce many more uncertainties but not ultimately change the values substantially. Instead, these uncertainties are incorporated into the error analysis.

Figure 12. Band strength determination. Salt growth and HCOOH consumption are overplotted with the temperature profile. The sample is heated to 165 K (vertical dotted line), at which point HCOOH consumption is complete. The sample is cooled to 14 K and re-heated to desorption. Horizontal dotted lines represent 0 ML and the sum total of HCOOH and HCOO$^-$. 

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