Solubility and Reactivity of HNCO in Water: Insights into HNCO's Fate in the Atmosphere

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8 Abstract

9 A growing number of ambient measurements of isocyanic acid (HNCO) are being made, yet little is known about its fate in the atmosphere. To better understand HNCO's loss processes 10 11 and particularly its atmospheric partitioning behavior, we measure its effective Henry's Law coefficient $K_{\rm H}^{\rm eff}$ with a bubbler experiment using chemical ionization mass spectrometry as the 12 gas phase analytical technique. By conducting experiments at different pH values and 13 14 temperature, a Henry's Law coefficient $K_{\rm H}$ of 26 ± 2 M atm⁻¹ is obtained, with an enthalpy of dissolution of -34 ± 2 kJ mol⁻¹, which translates to a $K_{\rm H}^{\rm eff}$ of 31 M atm⁻¹ at 298 K and at pH 3. 15 Our approach also allows for the determination of HNCO's acid dissociation constant, which 16 we determine to be $K_a = 2.1 \pm 0.2 \times 10^{-4}$ M at 298 K. Furthermore, by using ion chromatography 17 18 to analyze aqueous solution composition, we revisit the hydrolysis kinetics of HNCO at different pH and temperature conditions. Three pH dependent hydrolysis mechanisms are in 19 play and we determine the Arrhenius expressions for each rate to be $k_1 = (4.4 \pm 0.2) \times 10^7 \exp(-10^7 \exp(-10^7$ 20 6000 ± 240 / T) M s⁻¹, $k_2 = (8.9 \pm 0.9) \times 10^6 \exp(-6770 \pm 450$ / T) s⁻¹ and $k_3 = (7.2 \pm 1.5) \times 10^8$ 21 $\exp(-10900 \pm 1400 / \text{T}) \text{ s}^{-1}$ where k_1 is for HNCO + H⁺ + H₂O \rightarrow NH₄⁺ + CO₂, k_2 is for HNCO 22 + H₂O \rightarrow NH₃ + CO₂ and k_3 is for NCO⁻ + 2 H₂O \rightarrow NH₃ + HCO₃⁻. HNCO's lifetime against 23 24 hydrolysis is therefore estimated to be 10 days to 28 years at pH values, liquid water contents, and temperatures relevant to tropospheric clouds, years in oceans and months in human blood. 25 26 In all, a better parameterized Henry's Law coefficient and hydrolysis rates of HNCO allow for 27 more accurate predictions of its concentration in the atmosphere and consequently help define 28 exposure of this toxic molecule.

1 1 Introduction

2 Until recently, the interest in studying HNCO was from a fundamental science perspective with research conducted on its structure, preparation and physical properties (Belson and Strachan 3 4 1982) and on its theoretical rovibrational spectra (Mladenović and Lewerenz 2008). Both 5 theoretical and experimental data indicate that HNCO is the most stable CHNO isomer with a near-linear π -bond system (Hocking et al. 1975, Jones et al. 1950, Poppinger et al. 1977). In 6 7 2010, Roberts et al. reported detection of HNCO using negative ion proton transfer chemical 8 ionization mass spectrometry (CIMS) from laboratory biomass burning and later determined its 9 emission factor to be 0.25 - 1.20 mmol per mol of CO for different types of biomass fuels (Veres et al. 2010). Shortly afterwards, the same authors reported the first ambient atmospheric 10 11 measurements of HNCO in Pasadena, California, reaching 120 pptv and raising concerns of 12 HNCO exposure due to its toxicity (Roberts et al. 2011). Indeed, HNCO has been observed to cause protein carbamylation leading to cardiovascular disease, rheumatoid arthritis and 13 cataracts (Beswick and Harding 1984, Lee and Manning 1973, Mydel et al. 2010, Wang et al. 14 15 2007).

16 Since Roberts et al.'s initial measurements, ambient HNCO has also been measured in Boulder and in Fort Collins, Colorado, (Roberts et al. 2014), in Toronto, Ontario (Wentzell et al. 2013) 17 18 and in Calgary, Alberta (Woodward-Massey et al. 2014). HNCO has also been detected 19 simultaneously in the gas phase and in cloud water in La Jolla, California (Zhao et al. 2014). 20 From these studies, typical urban concentrations range from below detection limits to 21 approximately 100 pptv, whereas concentrations as high as 1.2 ppbv, enough to be of health 22 concern, have been measured in air masses impacted by biomass burning in Boulder, Colorado (Roberts et al. 2011, Roberts et al. 2014, Woodward-Massey et al. 2014). 23

24 HNCO has a variety of anthropogenic and biogenic sources to the atmosphere. HNCO has been quantified from diesel engine exhaust (Kroecher et al. 2005, Wentzell et al. 2013) and light duty 25 26 vehicles (Brady et al. 2014) as well as from biogenic sources such as biomass burning (Roberts 27 et al. 2010, Roberts et al. 2011, Roberts et al. 2014, Veres et al. 2010). There also exist 28 secondary sources of HNCO to the atmosphere, including the gas phase oxidation of amines 29 and amides by OH radicals producing HNCO via H-abstraction mechanisms (Barnes et al. 30 2010, Borduas et al. 2013, Borduas et al. 2015). Evidence of secondary sources of HNCO has also been demonstrated in the field, with peak HNCO concentrations occurring during daytime 31 32 (Roberts et al. 2011, Roberts et al. 2014, Zhao et al. 2014)

The sinks of HNCO however remain poorly constrained. HNCO has a lifetime of decades 1 2 towards OH radicals in the atmosphere as estimated by extrapolating high temperature rate 3 coefficients to atmospheric temperatures (Tsang 1992, Mertens et al. 1992, Tully et al. 1989). 4 It is also not expected to photolyze in the actinic region since its first UV absorption band is 5 observed below 280 nm wavelengths (Brownsword et al. 1996, Dixon and Kirby 1968, Rabalais et al. 1969). Nonetheless, HNCO has served as a benchmark system in understanding 6 7 photodissociation decomposition pathways such as direct and indirect dissociation processes 8 and remains an area of active research (Yu et al. 2013) and references therein. HNCO is most 9 likely removed from the atmosphere by wet and/or dry deposition. HNCO's gas-to-liquid 10 partitioning is therefore an important thermodynamic property that can be used to predict its 11 atmospheric fate. Specifically, the Henry's Law coefficient $K_{\rm H}$ for the solubility of HNCO 12 represents the equilibrium ratio between its gas phase and aqueous phase concentrations at 13 infinite dilutions according to Eq. (1) (Sander 2015, Sander 1999). The Henry's Law coefficient for HNCO has only recently been measured by Roberts and coworkers but their experimental 14 set up was limited to a single pH measurement (Roberts et al. 2011). As HNCO is a weak acid 15 16 with a pK_a of 3.7, its Henry's Law coefficient is expected to have a large pH dependence as 17 described in Eq. (2). Furthermore, the enthalpy of dissolution for HNCO is currently unknown. 18 In lieu of measurements, modelling studies on HNCO have used formic acid's enthalpy of 19 dissolution to model the temperature dependence of HNCO's Henry's Law coefficient (Barth 20 et al. 2013, Young et al. 2012). In our present study, we measure the effective Henry's Law 21 coefficient of HNCO at a range of pH and temperatures to determine its enthalpy of dissolution 22 for the first time.

23

24

$$K_H = \frac{C_{HNCO}}{p_{HNCO}}$$
(1)

$$K_{\rm H}^{\rm eff} = K_{\rm H} \left(1 + \frac{K_a}{[H^+]} \right) \tag{2}$$

25 HNCO reacts irreversibly with water in the aqueous phase, an unusual property for an 26 atmospheric molecule. Once HNCO partitions to the aqueous phase, three mechanisms for its 27 hydrolysis are possible. The first (R1) is acid-catalysed and is therefore termolecular whereas 28 the second (R2) and third (R3) are bimolecular reactions involving either the protonated or 29 deprotonated form of HNCO (Scheme 1) (Amell 1956, Belson and Strachan 1982, Jensen 1958). In 1958, Jensen determined the hydrolysis rate of the three mechanisms through addition 30 of AgNO₃ to buffered solutions at different time points to precipitate unreacted isocyanate as 31 32 AgNCO, followed by back titration of excess AgNO₃ with NH₄SCN. Considering the

importance of these mechanisms in evaluating the fate of HNCO in the atmosphere, we follow 1 2 up on the study by Jensen with our own experiments using ion chromatography to determine the pH and temperature dependencies of the overall rate of hydrolysis of HNCO. Quantitative 3 4 knowledge of the ability of HNCO to partition to the aqueous phase and its subsequent reactions 5 with water allows for an accurate understanding of the chemical fate of HNCO in the atmosphere (Fig. 1). In this study, we therefore provide laboratory measurements of HNCO's 6 Henry's Law coefficient and enthalpy of dissolution as well as its three rates of hydrolysis and 7 8 their respective activation energies.

$$\begin{array}{c} H\\ N=C=O + H^{+} + H_{2}O & \xrightarrow{k_{1}} & NH_{3} + H^{+} + CO_{2} \\ H\\ N=C=O + H_{2}O & \xrightarrow{k_{2}} & NH_{3} + CO_{2} \end{array}$$
(R1)

$$9^{-}N=C=O + 2 H_2O \xrightarrow{k_3} NH_3 + HCO_3^{-}$$
 (R3)

10 Scheme 1: The three mechanisms involved in HNCO's hydrolysis.



11

Figure 1: The fate of HNCO in the atmosphere includes its partitioning between the gas and aqueous phases and its hydrolysis through three different mechanisms governed by k_1 , k_2 , and k_3 .

15 2 Experimental Methods

16 **2.1** Henry's Law coefficient experiments

17 To measure the effective Henry's Law coefficient $K_{\rm H}^{\rm eff}$ of HNCO, we use a bubbler column

18 experimental set up and detect HNCO through chemical ionization mass spectrometry.

1 2.1.1 Acetate reagent ion CIMS

2 The quadrupole chemical ionization mass spectrometer (CIMS) was built in house and is 3 described in detail elsewhere (Escorcia et al. 2010). We opted to use acetate as the reagent ion 4 which has been shown to be sensitive for the detection of acids (Roberts et al. 2010, Veres et 5 al. 2008). For this experimental set up, the reagent ion was generated by flowing 20 sccm of 6 nitrogen over a glass tube containing acetic anhydride (from Sigma-Aldrich and used as is) and 7 maintained at 30 °C. This flow was subsequently mixed with a nitrogen dilution flow of 2 L min⁻¹ and passed through a polonium-210 radioactive source to generate acetate ions. All flows 8 9 were controlled using mass flow controllers. The data acquisition was done under selected ion 10 mode where 10 m/z ratios were monitored with dwell times of 0.2 s each and each duty cycle 11 was 4 s. Ions measured included m/z 59 (AcO-), m/z 119 ((AcOH)AcO-), m/z 51 (black counts), 12 m/z 35 (Cl-), m/z 42 (NCO-), m/z 45 (HCOO-), m/z 46 (ONO-), m/z 96, m/z 102 and m/z 113. 13 The raw signals are then normalized to m/z 59 and reported as normalized counts per second 14 (ncps). For the exception of m/z 42, none of the ions were observed to change during the 15 experiments. The inlet flow of the CIMS is governed by a pin hole at 0.5 L min⁻¹, and a N_2 dilution flow of 0.4 L min⁻¹ into the inlet was used to avoid depletion of the acetate reagent ion 16 by high HNCO concentrations. Previous work suggests there is no significant role of water 17 18 vapour in HNCO's detection by acetate CIMS (Roberts et al. 2010). With the CIMS's inlet 19 dilution, the RH within the ion molecule region was < 20%.

20 2.1.2 Experimental set up for measurement of $K_{\rm H}$

To obtain the Henry's Law coefficient, $K_{\rm H}$, we monitored the decrease in gas phase HNCO 21 22 exiting a buffered aqueous solution for a range of volume flow rates. A bubbler column 23 experimental set up is used with online gas phase detection. This method is employed to 24 measure HNCO's partitioning and take into account the concurrent hydrolysis of HNCO in the 25 buffer solution at high time resolution. Our experimental setup is based on previous work 26 (Kames and Schurath 1995, Roberts 2005, Roberts et al. 2011) and our apparatus is comprised 27 of one fritted bubbler with an approximate volume of 70 mL which contained 15 mL of a citric 28 acid/Na₂HPO₄ buffer at varying pH. The 15 mL volume was chosen to reduce HNCO 29 equilibration times and to simultaneously ensure that the bubbler's frit was submerged. Experiments performed in 30 mL of buffer yielded identical results. The water lost to the gas 30 31 phase during the experiments (< 1 h) was at most 5% of the original buffer volume and so no 32 corrections to the latter were required. The bubbler was held in a temperature-controlled bath of approximately 1:1 mixture of deionized water and ethylene glycol. Upstream of the bubbler, where the RH was measured to be ~ 50%, was a valve and a tee connection where the dry HNCO flow could be connected and disconnected during the experiments. Downstream of the bubbler was another tee which connected to both the exhaust and the acetate reagent ion CIMS. Conveniently, the absolute concentration of gas-phase HNCO is not required in this approach since it relies on the decay of the signal, [HNCO]t/[HNCO]0 and not on the absolute gas phase and aqueous phase concentrations.

8 HNCO was produced using a permeation source which sublimes solid cyanuric acid at 250 °C 9 in a flow of dry nitrogen and is described in detail elsewhere(Borduas et al. 2015). This source 10 is based on HNCO sublimation techniques and on a similar source previously developed by 11 Roberts et al. (Belson and Strachan 1982, Roberts et al. 2010). The buffer solutions were made 12 with solid citric acid, disodium phosphate and deionized water with citric acid concentrations 13 ranging from 0.02 M to 0.0035 M to access a pH range of 2.5-4.0.

14 Each experiment began with gaseous HNCO flowing through a fresh buffer solution until a reasonably stable signal (> 0.01 ncps) was obtained by the CIMS (background counts ~ 5×10^{-10} 15 ⁴ ncps). The solution did not need to reach equilibrium for the experiment to proceed and so 16 lower temperatures and higher pHs (when the equilibration time is longest and may reach over 17 18 4-5 hours) were feasible. Once a normalized signal (i.e. relative to the reagent ion signal) of at 19 least 0.025 for HNCO was obtained, the flow of HNCO through the bubbler was turned off, 20 and only pure nitrogen continued to flow through. The HNCO signal then decayed exponentially as a function of time due to partitioning as well as hydrolysis. This decay was 21 22 monitored until it had decreased to less than one quarter of the original signal. This method also has the advantage of extracting an effective Henry's Law coefficient without needing to monitor 23 24 the aqueous phase HNCO concentration.

25 **2.2** Hydrolysis rate experiments

HNCO in the aqueous phase was measured using ion chromatography at different pH andtemperatures to determine its rates of hydrolysis.

28 2.2.1 Ion chromatography

The measurements for the hydrolysis of HNCO were made using a Dionex IC-2000 Ion Chromatography (IC) System. An IonPac (AS19) anion column consisting of a quaternary

ammonium ion stationary phase with diameter and length dimensions of 4 mm and 25 mm 1 2 respectively was employed. Sample runs used a concentration gradient of the eluent KOH ranging from 2 mM to 20 mM. An optimized elution program was written for each pH range 3 measured (between 25-60 minutes for each injection). Samples were injected using a Dionex 4 (AS40) automated sampler into a 25 µL loop for pre-injection. The use of a loop rather than a 5 6 concentrator was important and ensured that the total HNCO/NCO⁻ concentrations were being 7 measured. The IC was calibrated using matrix-matched standards of known HNCO/NCO-8 concentrations prepared from serial dilutions of KOCN (Sigma-Aldrich, 96% purity).

9 2.2.2 Hydrolysis kinetics experiments

10 The kinetics of the hydrolysis reactions in the pH range of 1-2 are very fast; complete decays occurred in a matter of minutes. The decay of HNCO at these low pH values is therefore too 11 12 quick for the 25 min IC method to capture. To circumvent this issue, we used a quenching 13 method. Specifically, we prepared an aqueous solution of 50 mL of sulphuric acid at the desired 14 pH. 5 mL of this acidic solution was subsequently added to a 0.02 M solution of KOCN in eight 15 different falcon tubes to initiate the rapid hydrolysis reaction. Each reaction was then quenched at different times by a 0.1 M aqueous solution of KOH. Increasing the pH to more than 10 16 17 slowed the hydrolysis kinetics by orders of magnitude and allowed for subsequent IC 18 measurements. Replacing sulphuric acid by nitric acid and/or KOH by NaOH yielded identical 19 hydrolysis rates and ensured the results were reproducible with different acids and bases.

20 Buffer solutions in the pH range of 3-5 were prepared by using appropriate molar ratios of citric 21 acid and disodium phosphate whereas buffer solutions in the pH range of 9-10 used sodium 22 carbonate and sodium bicarbonate. All buffer concentrations were < 0.002 M, and we assume 23 that the ionic strength of these solutions had minimal impact on the solubility of HNCO. For 24 the room temperature set of kinetic experiments, the experiment was initiated by the addition of 0.1 g of KOCN to 50 mL of the desired buffer solution. The solution was further diluted by 25 26 a factor of 500 and then split into 8 samples for analysis at succeeding intervals on the anion 27 IC.

Hydrolysis reactions were run at different temperatures to assess the activation energies of each
of the three hydrolysis mechanisms. Room temperature reactions were conducted inside the IC
autosampler AS40 (with a cover) and monitored by a temperature button (iButtons, Maxim
Integrated, San Jose, CA with 0.5 °C resolution)). Colder temperature reactions were done in a

water ice bath and monitored by a thermometer. Finally, warmer temperature reactions for high pH samples were run in a temperature-controlled water bath. These reactions took days to weeks to reach completion, and so 5 mL samples from the reaction mixtures were taken out of the water bath and measured on the IC at appropriate time intervals.

5 3 Results and Discussion

6 3.1 Henry's Law coefficient K_H

HNCO's effective Henry's Law solubility coefficient $K_{\rm H}^{\rm eff}$ expressed in M atm⁻¹ was determined based on the exponential decay of gaseous HNCO exiting a bubbler containing a buffered solution. The observed decay of HNCO is caused by its partitioning from the aqueous phase to the gas phase as well as its competing hydrolysis reaction. Equation (3) represents the rate law for the disappearance of HNCO during the experiment and Eq. (4) is the integrated rate law.

12
$$-\frac{d[HNCO]}{dt} = [HNCO]\frac{\varphi}{K_{\rm H}^{\rm eff}VRT} + [HNCO]k_{hyd}$$
(3)

13
$$ln \frac{[HNCO]_t}{[HNCO]_0} = -\left[\frac{\varphi}{K_{\rm H}^{\rm eff} VRT} + k_{hyd}\right] t \tag{4}$$

Where [HNCO]_t is the HNCO concentration at time t, [HNCO]₀ is the initial HNCO 14 concentration (at time t = 0), [HNCO]_t/[HNCO]₀ is the HNCO concentration in the gas phase 15 downstream of the bubbler measured by the CIMS, φ is the volumetric flow rate (cm³ s⁻¹), $K_{\rm H}^{\rm eff}$ is 16 the effective Henry's Law coefficient for solubility (mol L^{-1} atm⁻¹). V is the liquid volume of the 17 buffer (cm³), R is the ideal gas constant (8.21 \times 10⁻² L atm mol⁻¹ K⁻¹), T is the temperature (K), 18 k_{hyd} is HNCO's overall rate of hydrolysis (s⁻¹) and t is the time (s). To extract the value of $K_{\text{H}}^{\text{eff}}$ 19 from the experimental decay curves, we first plot the natural logarithm of change in HNCO 20 21 concentration versus time for different flow rates ranging from 175 to 800 sccm as shown in 22 Fig. 2A. The slope of each experiment is then plotted as function of the ratio of the flow rate and volume depicted in Fig. 2B. The slope of Fig. 2B leads to a value representing $(K_{\rm H}^{\rm eff} \rm RT)^{-1}$ 23 and so $K_{\rm H}^{\rm eff}$ can be calculated. 24



1

Figure 2: A) The concentration decay curves as a function of time according to Eq. (4) for each
flow rate shown; B) The slopes of each fit in Fig. 2A plotted as a function of the ratio of the
flow rate to the volume. The symbols in both figures represent the same flow rate shown.

5 These dynamic experiments were repeated with a range of buffer solutions ranging from pH 6 2.5-4.0 to determine the pH-independent Henry's Law coefficient, K_H , of HNCO. Experiments 7 at temperatures of 273-298 K were also conducted to determine HNCO's enthalpy of 8 dissolution, ΔH_{diss} .

9 3.1.1 pH dependence of $K_{\rm H}^{\rm eff}$

The pH dependence of the effective Henry's Law coefficient $K_{\rm H}^{\rm eff}$ of a weak acid like HNCO 10 11 depends on its pK_a as well as on the pH according to Eq. (2). Throughout our experiments, we measure the value of $K_{\rm H}^{\rm eff}$ and employ Eq. (2) to plot $K_{\rm H}^{\rm eff}$ as a function of the inverse of the 12 proton concentration, [H⁺], and thus to extract HNCO's Henry's Law coefficient for solubility, 13 $K_{\rm H}$. Figure 3A depicts this linear relationship and yields a value of 26 ± 2 M atm⁻¹ for $K_{\rm H}$. Our 14 K_H value compares well with the only other published value of 21 M atm⁻¹ determined solely at 15 pH 3 (Roberts et al. 2011). Figure 3B on the other hand shows experimentally determined $K_{\rm H}^{\rm eff}$ 16 17 at different pH values and at a constant temperature of 298.0 ± 0.2 K. Error bars in both Fig. 18 3A and 3B represent the percentage of the standard deviation of the slope as in Fig. 2B. The 19 slope in Fig. 3A also allows us to determine HNCO's acid dissociation constant, K_a , which at 298 K is 2.1 \pm 0.2 \times 10⁻⁴ M. Our K_a value also agrees well with previously reported K_a for 20 HNCO (Amell 1956, Belson and Strachan 1982). 21



1

Figure 3: A) The fit according to Eq. (2) of the experimental $K_{\rm H}^{\rm eff}$ values which allows for the determination of $K_{\rm H}$ and K_a at 298 K. B) The experimental $K_{\rm H}^{\rm eff}$ values as a function of pH at 298 K. The black line is the modelled dependence of $K_{\rm H}^{\rm eff}$ according to Eq. (2) based on the determined value of $K_{\rm H}$ and a value for K_a of 2.1×10^{-4} M. The inset shows the range of $K_{\rm H}^{\rm eff}$ across the full range of pH.

7 3.1.2 Temperature dependence

8 The temperature dependence of HNCO's solubility was established by running experiments at varying temperatures from 273 to 298 K. Since $K_{\rm H}^{\rm eff}$ is very sensitive to pH changes, all 9 10 experiments were conducted with a buffer solution from the same batch and same volumetric 11 flask within a few days. Plotting the natural logarithm of the effective Henry's Law coefficient 12 as a function of the inverse of temperature yields the ratio of the enthalpy of dissolution, ΔH_{diss} , to the gas constant, R (Fig. 4). We report a value of -34 ± 2 kJ mol⁻¹ for HNCO's enthalpy of 13 14 dissolution, where the uncertainty stems from the deviation from the slope depicted in Figure 15 4. This value compares to similar weak acids like HONO (- 40 kJ mol⁻¹) and HCN (- 42 kJ mol⁻¹), but differs from the value of formic acid $(-47 \text{ kJ mol}^{-1})$ which was the value assumed 16 for HNCO in the Young et al. and the Barth et al. modelling studies (Barth et al. 2013, Sander 17 18 2015, Young et al. 2012).





9

2 Figure 4: The temperature dependence of experimentally measured $K_{\rm H}^{\rm eff}$ at pH 3.08.

3 3.2 Rate of hydrolysis *k*_{hyd}

There are three mechanisms by which HNCO can react with water described in Scheme 1 (R1) to (R3) and depicted in Fig. 1. The disappearance of HNCO in the aqueous phase can therefore be described by the rate law shown as Eq. (5). The pH dependence of HNCO's hydrolysis manifests itself in the first term of Eq. (5) as the hydrogen ion concentration as well as in the concentration of the dissociated/non-dissociated acid in each term.

$$-\frac{d \,[HNCO]_t}{dt} = k_1 [HNCO] [H^+] + k_2 [HNCO] + k_3 [NCO^-]$$
(5)

10 To mathematically integrate this rate law, the concentration of HNCO needs to be expressed as the sum of undissociated HNCO and of isocyanate ion NCO⁻ in solution, which is denoted in 11 12 Eq. (6) as [HNCO]_{tot}. HNCO's acid dissociation constant K_a relates the concentration of HNCO 13 and NCO⁻ as shown in Eq. (6). The K_a -dependant expression of Eq. (6) is then substituted into 14 the rate law of Eq. (5), and subsequently integrated. The K_a value of HNCO has a slight 15 temperature dependence with a heat of dissociation previously measured to be 5.4 kJ mol⁻¹, 16 which for the temperature range of 273 to 298 K represents a 25% change (Amell 1956). We therefore use Amell's heat of dissociation value throughout our analysis to account for K_a 's 17 18 temperature dependence in the van't Hoff equation. Furthermore, Belson et al.'s evaluation of the K_a of HNCO literature recommends 2.0×10^{-4} M at 298 K (Belson and Strachan 1982). 19

1 Finally, our own work on the pH dependence of Henry's Law coefficient of HNCO, suggests a

2 K_a value of 2.1 ± 0.2 × 10⁻⁴ M at 298 K, consistent with the recommended value (Fig. 3A).

3
$$[HNCO] = [HNCO]_{tot} - [NCO^{-}] = \frac{[H^{+}][NCO^{-}]}{K_{a}} = \frac{[HNCO]_{tot}[H^{+}]}{K_{a} + [H^{+}]}$$
(6)

By integrating Eq. (5) with the appropriate substitutions, the resulting expression is Eq. (7), where k_{hyd} represents the observed first-order rate loss of hydrolysis of HNCO and depends on the individual reaction rates k_1 , k_2 and k_3 according to Eq. (8).

$$\frac{[HNCO]_t}{[HNCO]_0} = e^{-k_{hyd}t}$$
(7)

7

 $k_{hyd} = \frac{k_1 [H^+]^2 + k_2 [H^+] + k_3 K_a}{K_a + [H^+]}$ (8)

9 The aim of our hydrolysis experiments is to measure k_{hyd} at different pH values to subsequently solve for the values of the individual hydrolysis rate coefficients k_1 , k_2 and k_3 . To measure k_{hyd} , 10 11 we employ ion chromatography (IC) which allows for quantitative measurement of the total 12 isocyanic acid in solution as NCO⁻ using an anion chromatography column. The key to making 13 [HNCO]tot measurements was to use a loop injection port for the IC instead of a concentrator 14 column, since the latter retains only ions and would not measure any protonated HNCO in 15 solution. Appropriate buffer solutions were made to conduct experiments over a range of pH 16 values from 1.7 to 10.4. The decay of [HNCO]_{tot} was monitored by IC over time and plotting 17 the natural logarithm of the decay as a function of time as in Fig. 5 yields the k_{hvd} specific to 18 that temperature and pH. Hydrolysis experiments are listed in Table A1 in Appendix A.

19

20



Figure 5: Example of a hydrolysis experiment at pH 5.4 and at 25 °C where the [HNCO]_{tot} is measured by loop injections on the IC.

1 3.2.1 Determining k_1 and k_2

2 At a pH below 3, the third hydrolysis mechanism (Scheme 1 (R3)) will contribute minimally to 3 the overall k_{hyd} . Indeed, the third term in Eq. (8), $k_3K_a/(K_a+[H^+])$ will become very small because $[H^+] >> K_a$. Furthermore, very little of the HNCO is present as NCO⁻ at low pH. This 4 5 assumption (which we verify retroactively) simplifies the k_{hvd} expression to Eq. (9) with only 6 two unknowns, k_1 and k_2 . We can now solve for k_1 and k_2 from two k_{hyd} values derived from 7 experiments conducted at two different pH values but at the same temperature. For example, 8 solving for k_1 and k_2 at 295 K using the k_{hyd} in Table A1, we obtain a value of $(6.73 \pm 0.27) \times$ 10^{-2} M s⁻¹ for k_1 and of $(1.04 \pm 0.04) \times 10^{-3}$ s⁻¹ for k_2 . We do this calculation once per 9 10 temperature. The uncertainties associated with these measurements come from the slope of 11 decay of aqueous phase HNCO measured by IC.

12
$$k_{hyd@pH<2.7} = \frac{k_1[H^+]^2 + k_2[H^+]}{K_a + [H^+]}$$
(9)

13 3.2.2 Temperature dependence of k_1 and k_2

14 Hydrolysis experiments of HNCO at three different temperatures further enables us to solve for 15 the temperature dependence of k_1 and k_2 . We chose three temperatures relevant to tropospheric air masses: 270, 283 and 295 K. Figure 6 represents the slope of the natural logarithm of the 16 17 rate coefficient of hydrolysis as a function of the inverse of the temperature which according to the Arrhenius equation shown in Eq. (10) yields the activation energy specific to each 18 hydrolysis mechanism. We obtain activation energies of 50 ± 2 kJ mol⁻¹ and 56 ± 4 kJ mol⁻¹ for 19 k_1 and k_2 respectively. Furthermore, the y-intercept of these linear plots yields the value of $\ln(A)$ 20 21 in Eq. (10) and so the A factors of each hydrolysis mechanism can also be obtained, providing Arrhenius expressions of $k_1 = (4.4 \pm 0.2) \times 10^7 \exp(-6000 \pm 240 / \text{ T}) \text{ M s}^{-1}$ and $k_2 = (8.9 \pm 0.9)$ 22 $\times 10^{6} \exp(-6770 \pm 450 / T) \text{ s}^{-1}$. The uncertainties stem from the fit to the data points in Figure 6 23 (and their error bars comes from the slope of the decay of aqueous phase HNCO measured by 24 IC). 25

26

$$k = A e^{-E_a/RT} \tag{10}$$



1

Figure 6: The linear plots of the natural logarithm of each hydrolysis rate coefficient k_1 , k_2 and k_3 as a function of the inverse of temperature to yield the activation energies of each mechanism.

4 3.2.3 Determining k_3 and its temperature dependence

5 At high pH levels, the third hydrolysis mechanism (Scheme 1 (R3)) will dominate the observed k_{hyd} , however, the first two mechanisms may still have a non-negligible contribution to k_{hyd} and 6 7 can therefore not be disregarded. We can solve for k_3 , knowing k_1 and k_2 and their respective 8 temperature dependencies, using Eq. (8). The k_{hvd} values measured at pH above 9 and at 40 °C 9 are used (Table A1), and k_3 is determined for each pH. The average of our three measurements at 40 °C is $(5.77 \pm 0.35) \times 10^{-7}$ s⁻¹. The temperature dependence of k_3 is determined in an 10 analogous way to k_1 and k_2 and is also depicted in Fig. 6. We obtain a value of 91 ± 12 kJ mol⁻ 11 ¹ which translates to an Arrhenius expression of $k_3 = (7.2 \pm 1.5) \times 10^8 \exp(-10900 \pm 1400 / \text{ T})$ 12 s⁻¹. 13

Equipped with the values of k_1 , k_2 and k_3 and their temperature dependencies, a map of the expected total hydrolysis rate, k_{hyd} , as a function of temperature and pH can be generated using Eq. (8) and Eq. (10) and is plotted as Fig. 7. For reference, the colour scale of Fig. 7 also reads in hydrolysis lifetime of HNCO in hours. It is clear that HNCO's lifetime in the aqueous phase has a large temperature and pH dependence.

1 3.2.4 Comparing the rate of hydrolysis *k*_{hyd} through different methods

2 The individual rate coefficients of the three hydrolysis mechanisms (Scheme 1 (R1) to (R3)) 3 have only been evaluated one other time in the literature (Jensen 1958). Our IC experimental 4 method differs substantially from Jensen's back titration method, and yet we obtain similar 5 values for k_1 , k_2 and k_3 as well as for their respective activation energies. The values are 6 summarized in Table 2. Again, the colour scale of Fig. 7 is generated from Eq. (8) using our 7 obtained values for k_1 , k_2 and k_3 and for E_{a1} , E_{a2} and E_{a3} , and we superimpose all our k_{hvd} 8 measurements from Table A1 as circles. We further add Jensen's published raw data for 9 comparison (Jensen 1958) as triangles. The agreement is good and is consistently within the same order of magnitude (Fig. 7). 10

Physical parameter	Value	Energy	Reference
Henry's Law coefficient, <i>K</i> _H	$26 \pm 2 \text{ M atm}^{-1}$	$\Delta H_{diss} = -34 \pm 2 \text{ kJ mol}^{-1}$	This work
	21 M atm ⁻¹	_	Roberts et al. 2011
Acid dissociation constant, K_a^*	$2.1\pm0.2\times10^{-4}M$	_	This work
	$2.0 imes 10^{-4} \mathrm{M}$	$\Delta H_{diss} = -5.4 \text{ kJ mol}^{-1}$	Amell 1956
Hydrolysis rate coefficient, k_1^*	$7.6 \pm 0.3 imes 10^{-2} \text{ s}^{-1}$	$E_{a1} = +50 \pm 2 \ kJ \ mol^{1}$	This work
	$1.1 \times 10^{-1} \text{ s}^{-1}$	$E_{a1} = +63 \text{ kJ mol}^{-1}$	Jensen 1958
Hydrolysis rate coefficient, k_2^*	$1.4 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$	$E_{a2} = +56 \pm 4 \ kJ \ mol^{-1}$	This work
	$1.8 \times 10^{-3} \text{ s}^{-1}$	$E_{a2} = +83 \text{ kJ mol}^{-1}$	Jensen 1958
Hydrolysis rate coefficient, k_3^*	$8.1 \pm 1.7 \times 10^{-8} \text{ s}^{-1}$	$E_{a3} = +91 \pm 12 \text{ kJ mol}^{-1}$	This work
	$1.2 \times 10^{-8} \text{ s}^{-1}$	$E_{a3} = +100 \text{ kJ mol}^{-1}$	Jensen 1958

11 Table 2: HNCO's Henry's Law coefficient, acid dissociation constant and hydrolysis constants

12 * at 298 K

In addition, our Henry's Law coefficient experiment provides a complimentary way to determine k_{hyd} at different temperatures and pH values. Indeed, the intercept of the line which fit the data of dln(Ct/C₀)/dt versus φ /V yields k_{hyd} , representing the value for the loss process in the solution of the bubbler column experiment (an example is given in Fig. 2B). We show these values as squares in Fig. 7. Roberts et al. also determined k_{hyd} through this method at pH 3 and

at 25 °C and this value is appended to Fig. 7 (Roberts et al. 2011) as a diamond. The agreement 1 2 is good from all four cases. We can conclude that the lifetime of HNCO against hydrolysis in dilute aqueous solutions spans seconds to years depending on pH and temperature. The lifetime 3 4 of HNCO against hydrolysis in cloud water of pH 3-6 will be shorter and range from 10 hours 5 to ~20 days in the troposphere. On the other hand, HNCO's hydrolysis in ocean waters of pH 6 ~8.1 and temperatures below 30 °C will be very slow, translating to a lifetime of 1-2 years if 7 we assume no other reactive chemistry is taking place. Finally, in the context of exposure, if 8 HNCO is present in human blood at physiological pH and temperature, its lifetime to hydrolysis 9 will be as high as several months. On the other hand, if HNCO is present in the stomach, which 10 is more acidic, we would expect its lifetime to drop to minutes or hours.



11

Figure 7: k_{hyd} as function of temperature and pH generated from Eq. (8) using our obtained values for k_1 , k_2 and k_3 and for E_{a1} , E_{a2} and E_{a3} . All available k_{hyd} measurements for HNCO in the literature and from this work are superimposed and colour coded appropriately. As a guide, the colour scale also represents the lifetime in hours for HNCO in dilute aqueous solutions.

16 4 Atmospheric Implications

HNCO is a toxic molecule and can cause cardiovascular and cataract problems through protein
carbamylation (Beswick and Harding 1984, Mydel et al. 2010, Wang et al. 2007). Recently
reported ambient measurements of HNCO in North America raise concerns of exposure

particularly from biomass burning, diesel and gasoline exhaust and urban environments (Brady 1 2 et al. 2014, Roberts et al. 2011, Roberts et al. 2014, Wentzell et al. 2013, Woodward-Massey et al. 2014, Zhao et al. 2014). With the values for HNCO's Henry's Law coefficient and 3 4 hydrolysis rates reported here, a better understanding of HNCO's removal rate from the 5 atmosphere can be determined, and hence HNCO's atmospheric lifetime can be estimated. Note however that our HNCO lifetime estimates do not consider dry deposition and therefore 6 7 represent a higher limit, particularly since Young et al. found that dry deposition can be 8 significant for HNCO (Young et al. 2012).

Specifically, the lifetime of HNCO in the atmosphere will depend on its partitioning to the 9 aqueous phase $K_{\rm H}^{\rm eff}$, the temperature T, the pH and liquid water content (LWC) of the 10 11 aerosol/droplet and finally the hydrolysis of HNCO k_{hyd} once in solution. We can calculate 12 HNCO's lifetime against hydrolysis based on Eq. (11) where τ is the lifetime in seconds, L is 13 the fraction of air volume occupied by liquid water (dimensionless) and R is the gas constant. 14 Figures 8A and 8B depict outputs of Eq. (11) with different fixed variables. Figure 8A holds the LWC to 1 g m⁻³, a value representative of cloud water, highlighting the dependence of 15 16 HNCO's lifetime on temperature and pH (Ip et al. 2009). At atmospherically relevant pH of 2 17 to 6 and at temperatures below 30 °C, HNCO has a lifetime on the order of 10 days to hundreds 18 of years. Alternatively, Fig. 8B holds the pH at 4 and varies the LWC on the x-axis. Water concentrations relevant to wet aerosol $(1-100 \ \mu g \ m^{-3})$ are too small to act as a significant sink 19 for gas phase HNCO. However, Fig. 8B highlights the strong dependence of HNCO lifetime 20 21 on LWC in clouds, again ranging from days to hundreds of years. It therefore appears that if HNCO is incorporated into cloud water, it is more likely to be rained out or revolatilized than 22 23 to hydrolyse given typical times in clouds of minutes to hours. There is also the possibility that HNCO has other currently unknown sinks in cloud water that may be competitive with its 24 hydrolysis and further work on HNCO's aqueous phase chemistry with nucleophiles such as 25 26 amines and alcohols is currently underway in our laboratories. Finally, HNCO will partition 27 readily in oceans at pH ~8, but will take years to hydrolyze.

$$\tau = 1/K_{\rm H}^{\rm eff} RTLk_{hyd} \tag{11}$$



1

Figure 8: A) The lifetime of HNCO in days as a function of temperature and pH at 1 g m⁻³ of
LWC and B) the lifetime of HNCO in days as a function of temperature and LWC at pH 4

Zhao et al. (2014) observed higher concentrations of HNCO in the cloud water in La Jolla, 4 5 California than predicted by its Henry's Law coefficient at 298 K(Zhao et al. 2014)(Zhao et al. 6 2014)(Zhao et al. 2014). This observation remains puzzling but may point towards sources of 7 HNCO within cloud water other than simple partitioning chemistry. The Barth et al. 2013 8 modeling study concluded that fog, low-level stratus clouds or stratocumulus clouds were the 9 most efficient cloud conditions at removing HNCO from the gas phase, particularly in polluted 10 scenarios where the cloud water was more acidic. The authors highlighted the high dependence 11 of HNCO's fate on liquid water pH and temperature, consistent with our findings (Barth et al. 12 2013). The Young et al. 2012 study, which modelled global HNCO budgets, assumed the 13 aqueous loss of the weak acid occurred only when the cloud liquid water content was greater than 1 mg m⁻³. Based on Fig. 8B, 1 mg m⁻³ is low for HNCO to significantly partition into the 14 15 aqueous phase and rather requires water mass concentrations 1000 times greater for HNCO's 16 lifetime to drop to days. The model may have overestimated the ability for LWC to act as a sink for HNCO. HNCO may be a longer lived species than previously thought and exposure of this 17 18 toxic molecule may pose a threat to regions with HNCO point sources like biomass burning 19 and engine exhaust, as pointed out by Young et al. in 2012 and Barth et al. in 2013.

1 5 Conclusions

In summary, we provide laboratory measurements of HNCO's important thermochemical
properties related to its behavior in water. We measured its Henry's Law coefficient using a

- 4 bubbler column experiment to be 26 ± 2 M atm⁻¹ with an enthalpy of dissolution of 34 ± 2 kJ
- 5 mol⁻¹. Using ion chromatography, we determined the Arrhenius expression of HNCO's three
- 6 hydrolysis mechanims: $k_1 = (4.4 \pm 0.2) \times 10^7 \exp(-6000 \pm 240 / \text{ T}) \text{ M s}^{-1}$, $k_2 = (8.9 \pm 0.9) \times 10^6$
- 7 exp(-6770 ± 450 / T) s⁻¹ and $k_3 = (7.2 \pm 1.5) \times 10^8 \exp(-10900 \pm 1400 / T) s^{-1}$. These values will
- 8 provide better constrains on the sinks and thus lifetime of HNCO in the atmosphere with the
- 9 aim of minimizing exposure of this toxic molecule.

10 Appendix A:

рН	Т (К)	k _{hyd} (S⁻¹)	
1.75	270	$(8.30 \pm 0.64) \times 10^{-4}$	
1.75	295	$(2.22 \pm 0.06) \times 10^{-3}$	
1.81	283	$(1.17 \pm 0.06) \times 10^{-3}$	
2.23	270	$(1.92 \pm 0.16) \times 10^{-4}$	
2.23	295	$(1.39 \pm 0.02) \times 10^{-3}$	
2.26	283	$(5.13 \pm 0.28) \times 10^{-4}$	
2.30	295	$(1.09 \pm 0.04) \times 10^{-3}$	
3.40	297	$(9.90 \pm 0.25) \times 10^{-4}$	
3.91	296	$(3.74 \pm 0.03) \times 10^{-4}$	
4.27	296	$(2.99 \pm 0.02) \times 10^{-4}$	
5.00	296	$(6.55 \pm 0.21) \times 10^{-5}$	
5.40	298	$(2.10 \pm 0.05) \times 10^{-5}$	
9.26	313	$(5.39 \pm 0.26) \times 10^{-7}$	
9.46	313	$(6.07 \pm 0.28) \times 10^{-7}$	
10.20	313	$(6.03 \pm 0.33) \times 10^{-7}$	
10.36	333	(4.84 ± 0.09) × 10 ⁻⁶	
10.37	325	$(1.70 \pm 0.09) \times 10^{-6}$	

11 Table A1: Compilation of k_{hyd} experiments at different pH and temperatures

1 Author contribution

- 2 N.B. designed the experimental approach with critical input from J. P. D. A. and J. G. M. on
- 3 the mass spectrometry method and from J. G. M. and G. R. W. on the ion chromatography
- 4 method. N. B. undertook the Henry's Law experiments and B. P. conducted the HNCO
- 5 hydrolysis experiments. N. B. analysed the data from both sets of experiments and N. B. wrote
- 6 the manuscript with feedback from all co-authors.

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