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Solubility and Solution-phase Chemistry of Isocyanic Acid, Methyl Isocyanate, and Cyanogen Halides

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Abstract

Condensed phase uptake and reaction are important atmospheric removal processes for reduced nitrogen species, isocyanic acid (HNCO), methyl isocyanate (CH_3NCO) and cyanogen halides (XCN, X =Cl, Br, I), yet many of the fundamental quantities that govern this chemistry have not been measured or are understudied. Solubilities and first-order reaction rates of these species were measured for a variety of solutions using a bubble flow reactor method with total reactive nitrogen (N_r) detection. The aqueous solubility of HNCO was measured as a function of pH, and exhibited the classic behavior of a weak acid, with an intrinsic Henry's law solubility of 20 (±2) M/atm, and a K_a of 2.0 (±0.28) $\times 10^{-4}$ M (which corresponds to pK_a = 3.7 ±0.06) at 298K. The temperature dependence of HNCO solubility was very similar to other small nitrogen-containing compounds and the dependence on salt concentration exhibited the "salting out" phenomenon that was also similar to small polar molecules. The rate constant of reaction of HNCO with 0.45 M NH_4^+ was measured at pH=3, and found to be 1.2 (±0.1) $\times 10^{-3}$ $M^{-1}sec^{-1}$, which is much faster than the rate that would be estimated from rate measurements at much higher pHs, and the assumption that the mechanism is solely by reaction of the un-dissociated acid with NH_3. The solubilities of HNCO in the non-polar solvents n-octanol (n-$C_8H_{17}OH$) and tridecane ($C_{13}H_{28}$) were found to be higher than aqueous solution for n-octanol (87 ±9 M/atm at 298K) and much lower than aqueous solution for tridecane (1.7 ±0.17 M/atm at 298K), but the first-order loss rate of HNCO in n-octanol was determined to be relatively slow 5.7 (±1.4) $\times 10^{-5} sec^{-1}$. The aqueous solubility of CH_3NCO was measured at several pHs and found to be 1.3 (±0.13) M/atm independent of pH, and CH_3NCO solubility in n-octanol was also determined at several temperatures and ranged from 4.0 (±0.5) to 2.8 (±0.3) M/atm. The aqueous hydrolysis of CH_3NCO was observed to be slightly acid-catalyzed, in agreement with literature values, and reactions with n-octanol ranged from 2.5 (±0.5) to 5.3 (±0.7) $\times 10^{-3}$ sec^{-1} from 298 to 310K. The aqueous solubilities of XCN, determined at room temperature and neutral pH, were found to increase with halogen atom polarizability from 1.4 (±0.2) M/atm for ClCN, 8.2 (±0.8) M/atm for BrCN, to 270 (±54) M/atm for ICN. Hydrolysis rates, where measurable, were in agreement with literature values. The atmospheric loss rates of HNCO, CH_3NCO, and XCN due to heterogeneous processes are estimated from solubilities and reaction rates. Lifetimes of HNCO range from about 1 day against deposition to neutral pH surfaces in the boundary layer, but otherwise can be as long as several months in the mid troposphere. The loss of CH_3NCO due to aqueous phase processes is estimated to be slower than, or comparable to, the lifetime against OH reaction (3 months). The loss of XCNs due to aqueous uptake are estimated to range from quite slow, lifetime of 2-6 months or more for ClCN, 1 week to 6 months for BrCN, to 1 to 10 days for ICN. These characteristic times are shorter than photolysis lifetimes for ClCN, and BrCN, implying that heterogeneous chemistry will be the controlling factor in their atmospheric removal. In contrast, the photolysis of ICN is estimated to be faster than heterogeneous loss for average mid-latitude conditions.

I. Introduction

The earth's atmosphere is a highly oxidizing environment in which chemical compounds are typically destroyed through radical pathways. The reduced nitrogen species, isocyanic acid (HNCO) and hydrogen cyanide (HCN), are an exception to this, as they have slow reactions with atmospheric radicals and have primarily condensed-phase sources and sinks. Cyanogen halides (XCN, where X = Cl, Br, I) are compounds that are present in the environment, and whose atmospheric chemistry is of emerging interest. XCN compounds likewise have very slow reaction rates with radical species and, with the exception of ICN, very slow photolysis rates in the troposphere. These general classes of reduced nitrogen species, isocyanates (R-NCO), cyanides (RCN), and cyanogen halides (XCN) have potential health impacts that are related to their condensed phase chemistry. Therefore, information on solubility and reaction rates are needed to understand the atmospheric fate of such compounds and define their impact on human and ecosystem health. Five reduced nitrogen species will be focused on here: isocyanic acid, HNCO, methyl isocyanate, CH_3NCO, cyanogen chloride, ClCN, cyanogen bromide, BrCN, and cyanogen iodide, ICN.

The isocyanate compounds are products of the pyrolysis or combustion of N-containing materials (biomass, polyurethanes) (Blomqvist et al., 2003; Koss et al., 2018) and the two simplest ones, HNCO and CH_3NCO, have also been observed in interstellar and cometary media (Goesmann et al., 2015; Halfen et al., 2015). The atmospheric chemistry of HNCO has received considerable attention in the past few years as it has become clear that it is present in ambient air, and could be related to health impacts through specific biochemical pathways (Roberts et al., 2011) involving the reaction of cyanate ion with proteins. There are relatively few observations of HNCO in ambient air, and those show that there are "background" mixing ratios that range from 10pptv to over several ppbv depending on the nature of regional sources, and that peak mixing ratios approaching a few ppbv are observed in areas impacted by local biomass burning (Chandra and Sinha, 2016; Kumar et al., 2018; Mattila et al., 2018; Roberts et al., 2014; Sarkar et al., 2016; Wentzell et al., 2013; Woodward-Massey et al., 2014; Zhao et al., 2014). The aqueous phase solubility of HNCO was examined by Roberts et al., (Roberts et al., 2011) and Borduas et al., (2016), wherein it was found that HNCO is only slightly soluble at pHs characteristic of atmospheric aerosol (pH= 2-4) and as a weak acid (pKa=3.9), it is quite soluble at physiologic conditions (pH=7.4). Attempts to model the global distribution of HNCO (Young et al., 2012) and the cloud water uptake of HNCO (Barth et al., 2013) used the limited solubility and hydrolysis data available at that time, (Jensen, 1958; Roberts et al., 2011). Several aspects of HNCO solubility remain unknown, such salt effects on aqueous solubility, and solubility in non-aqueous solvents, a property important for predicting HNCO behavior in biological systems. The pH dependent hydrolysis of HNCO had been studied some time ago (Jensen, 1958), the mechanism for this process involves three separate reactions;

$$HNCO + H_3O^+ \Rightarrow NH_4^+ + CO_2 \qquad (R1)$$

$$HNCO + H_2O \Rightarrow NH_3 + CO_2 \qquad (R2)$$

$$NCO^- + 2H_2O \Rightarrow NH_3 + HCO_3^- \qquad (R3)$$

and Borduas et al. (2016), recently re-measured these rates under a wider range of conditions and found their measurements to be essentially consistent with the previous work at pHs of interest in the atmosphere. Rates of reaction of HNCO with other compounds in aqueous solution are not as well studied, especially under atmospheric conditions, e.g. low pH, relatively high ionic strength. Rates of reaction of HNCO/NCO^- with nitrogen bases have been measured but only at the pK_as of the BH^+, which are typically pH 9-10 (Jensen, 1959; Williams and Jencks, 1974a, b).

Methyl isocyanate is most notable for its part in the one of the largest industrial disasters in history, when a large quantity of CH_3NCO was released from a chemical plant and fumigated the city of Bhopal, India. There are other, more common sources of CH_3NCO to the atmosphere including combustion of biomass (Koss et al., 2018) and N-containing polymers such as polyurethanes and isocyanate foams (Bengtstrom et al., 2016; Garrido et al., 2017), and cooking (Reyes-Villegas et al., 2018). Recent measurements of CH_3NCO in laboratory wildfire studies have observed mixing ratios up to 10 ppbv or so in fuels characteristic of western North America (Koss et al., 2018). CH_3NCO is also produced in photochemical reactions of methylisothiocyanate (CH_3NCS), which is the main degradation product of the agricultural fungicide metam-sodium (CH_3NHCS_2Na) (Geddes et al., 1995). In addition, CH_3NCO has been observed in studies of the photooxidation of amides (Barnes et al., 2010; Borduas et al., 2015; Bunkan et al., 2015) and by extension will be formed in dimethyl amine oxidation. To our knowledge there is only one reported set of ambient measurements of CH_3NCO, conducted near a field where metam-sodium was being used as a soil fumigant (Woodrow et al., 2014), and the resulting CH_3NCO mixing ratios were as high as 1.7 ppbv. The California Office of Environmental Health Hazard Assessment has placed an inhalation reference exposure level of 0.5 ppbv (1 $\mu g/m^3$) on CH_3NCO due to its propensity to cause respiratory health effects (State of California, 2008).

There have been only a few studies of the gas phase loss rates of CH_3NCO including reaction with OH radical (Lu et al., 2014), which appears to be slow based on the mostly recent measurements (Papanastasiou et al., in preparation, 2018), reaction with chlorine atoms (Cl) which might be as much as 20% of OH under some atmospheric conditions (Papanastasiou et al., in preparation, 2018), and UV photolysis which has a negligible contribution to atmospheric loss (Papanastasiou et al., in preparation, 2018). Thus, heterogeneous uptake might compete with these gas phase loss processes. The solubility of CH_3NCO has not been previously determined experimentally, but is probably low, <2 M/atm, by analogy to CH_3NCS (3.7 M/atm) (Geddes et al., 1995). In addition, there are no data on the solubility of CH_3NCO in non-aqueous solvents. The hydrolysis of CH_3NCO is acid catalyzed;

$$CH_3NCO + H_2O + H^+ \Rightarrow CH_3NH_3^+ + CO_2 \quad \text{(R4)}$$

$$CH_3NCO + H_2O \Rightarrow CH_3NH_2 + CO_2 \quad \text{(R5)}$$

producing methyl amine and carbon dioxide. The rate constants for these reactions are fairly well established (Al-Rawi and Williams, 1977; Castro et al., 1985).

Cyanogen halides are less well studied as atmospheric species, but have potentially important environmental sources. Cyanogen chloride was once produced as a chemical warfare agent, however its importance to the atmosphere is more related to its possible formation in the reaction of active chlorine species (HOCl/OCl^-, chloramines) with N-containing substrates such as amino acids and humic substances (Na and Olson, 2006; Shang et al., 2000; Yang and Shang, 2004). These reactions are known to be important in systems where chlorination is used for disinfection such as swimming pools and water treatment (see for example (Afifi and Blatchley III, 2015), and perhaps indoor surfaces (J. Abbatt, personal communication). We are not aware of any measurements of ClCN in ambient air. Cyanogen bromide can likewise be formed through reactions of HOBr/OBr- with reduced nitrogen species, and there are observations of BrCN in bromide-containing waters that have been received chlorine treatment (see for example (Heller-Grossman et al., 1999). The formation results from the facile reaction of HOCl/OCl- with bromide to make HOBr/OBr-, which then reacts with nitrogen species in the water. In addition, there is a natural source of BrCN from at least one strain of marine algae (Vanelslander et al., 2012) that is thought to be related to allelopathic activity, i.e. secreted to control the growth of competing organisms. This marine algae source may be responsible for BrCN levels observed in remote atmospheres (J.A. Neuman and P.R. Veres, personal communication). Cyanogen iodide can also potentially be formed from the chlorination of water or wastewater because iodide is easily oxidized by $HOCl/OCl^-$, however iodide is usually quite small in concentration, so the several studies that report total cyanogen halides report ClCN and BrCN but not ICN (Diehl et al., 2000; Yang and Shang, 2004). There are also biochemical pathways for ICN formation involving several enzymes that are part of the immune defense system (see for example (Schlorke et al., 2016)), but the extent to which ICN might be volatilized from those systems is not clear. There are some observations of ICN in the remote marine troposphere (J.A. Neuman and P.R. Veres, personal communication), but their origin is currently unclear.

The possible gas phase loss processes of cyanogen halides include reaction with radicals or ozone, and photolysis. Radical reaction rates (OH, Cl) have not been measured at room temperatures, but are likely to be slow due the electronegativity of each group (X-CN). The UV-visible absorption spectra of all three of these compounds have been measured (Barts and Halpern, 1989; Felps et al., 1991; Hess and Leone, 1987; Russell et al., 1987), and indicate a range of photolysis behavior ranging from no tropospheric photolysis of ClCN, to slight photolysis of BrCN, and faster photolysis of ICN. The rates of photolysis need to be balanced against condensed phase losses of XCN compounds to obtain a full picture of their atmospheric losses.

The aqueous phase solution chemistry of cyanogen halides is not as well studied as the isocyanates. The aqueous solubilities of XCN compounds are not known with the exception of ClCN whose solubility is thought to be fairly low, 0.6 – 0.52 M/atm at 293-298K (Weng et al., 2011; Yaws and Yang, 1992) as reported by (Hilal et al., 2008). The hydrolysis of XCN compounds are known to be base-catalyzed and so involve the following reactions;

$$XCN + 2H_2O \Rightarrow HOCN + H_3O^+ + X^- \quad \text{(R6)}$$

$$XCN + H_2O + OH^- \Rightarrow HOCN + X^- + H_2O \quad \text{(R7)}$$

with R6 being fairly slow at medium to low pH (Bailey and Bishop, 1973; Gerritsen et al., 1993). The product, cyanic acid, HOCN, is unstable with respect to HNCO in aqueous solution (Belson and Strachan, 1982);

$$HOCN + H^+ \Rightarrow HNCO + H^+ \quad \text{(R8)}$$

Thus, XCN compounds represent potential intermediates in the condensed-phase formation of HNCO, for which there is some observational evidence (Zhao et al., 2014). So, in addition to being active halogen species, XCN

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compounds represent potential condensed phase source of HNCO in systems where there is halogen activation and there are reduced nitrogen species present, e.g. wildfire plumes, bio-aerosols and indoor surfaces.

Measurements of solubility and reaction rates will be presented here for HNCO, CH_3NCO, and the XCN species: ClCN, BrCN, and ICN. The aqueous solubility of HNCO was measured as a function of pH, temperature and salt concentration. The rate of reaction of HNCO with NH_4^+ was measured at pH3, to examine the importance of this reaction to atmospheric uptake of HNCO. The solubilities of HNCO in the non-polar solvents n-octanol and tridecane were also measured as a function of temperature, and the first-order loss rate of HNCO in n-octanol was also determined. The aqueous solubility of CH_3NCO was measured at several at several pHs, and the solubility in n-octanol was also determined at several temperatures. Finally, the aqueous solubility of ClCN, BrCN, and ICN were determined at room temperature, and at 273.15 K (ClCN, BrCN) and neutral pH, and the solubility and first loss of these compounds in n-octanol was also determined. These data will be used to estimate atmospheric lifetimes against aqueous uptake and to assess the relative bioavailability of these compounds.

II. Methods

Most of the techniques used for the work presented here have largely been presented elsewhere (Borduas et al., 2016; Kames and Schurath, 1995; Kish et al., 2013; Roberts, 2005) and will only be briefly summarized here. The basic principle is that the compound of interest is equilibrated with solution in a bubble flow reactor, and then removed from the gas-phase and the exponential decay of the signal due to loss of the compound is measured with a sensitive and selective method. The dependence of decay rates on flow rate-to-liquid volume ratio can then be related to solubility and first-order loss rate due to reaction in solution. This technique relies on being able to produce a consistent gas stream of the compound of interest, and being able to selectively detect the compound exiting the reactor. This method has limitations in that the solubility must be within a certain range, and the first-order loss rate slow enough that there are measurable amounts of compound exiting the reactor.

A. Preparation of Gas-Phase Standards

The general system used for preparation of gas phase streams of HNCO, CH_3NCO, BrCN, and ICN was the capillary diffusion system described by (Williams et al., 2000) and (Roberts et al., 2010). Isocyanic acid was produced in a steady stream by heating the trimer, cyanuric acid (Sigma-Aldrich, USA) to 250°C under N_2 and establishing a constant diffusion rate through a short length of capillary tubing (1mm ID x 5cm length). Care was taken to condition the system for several days before use, by keeping the system under flow and at a minimum of 125°C even when not in active use, to prevent the build-up of unwanted impurities, particularly NH_3. Standards in the range of several ppmv in 40 SCCM could easily be prepared in this way.

The same capillary diffusion cells were used for CH_3NCO preparation, starting with a sample of the pure liquid (Alinda Chemicals, UK). FTIR analysis of samples of this material were found to contain small amounts (3%) of siloxanes, which probably came from a chloro-silane added as a stabilizer, but no measurable presence of any other nitrogen compounds. The high volatility of CH_3NCO (BP 38 °C) required that low concentration solution (1%

vol/vol) of CH_3NCO in n-tridecane ($C_{13}H_{28}$) solvent at a temperature of 0°C be used in the diffusion cell. Under these conditions a 40 SCCM stream resulted in a mixing ratio of 10ppmv. The output of the source was stable for long periods of time (days) and could be used for the solubility study and calibration of other instruments. The source was also analyzed by an H_3O^+ chemical ionization mass spectrometric system, which showed that it had no impurities detectable above the 1% level.

The preparation of a gas phase standard of ClCN is described by Stockwell et al., (2018) and is based on chemical conversion of an HCN calibration mixture. It has been known for some time that HCN reacts readily with active chlorine compounds to yield ClCN (Epstein, 1947), for example:

$$HCN + HOCl \Rightarrow ClCN + H_2O \quad \text{(R9)}$$

In fact, this reaction has been used as the basis for measuring HCN in the gas phase by conversion to ClCN with detection by gas chromatography with electron capture (Valentour et al., 1974). In those systems, Chloramine-T (Sigma-Aldrich), a non-volatile sulfonyl N-chloro compound, has proven useful. The method used in this work consisted of passing a small stream (5-10 SCCM) of a 10ppmv gas-phase standard of HCN in N_2, combined with humidified Zero Air (ZA, 80% RH, 30-50 SCCM) over a bed packed with glass beads coated with a solution of Chloramine-T. The glass beads were prepared by coating glass 3 mm OD beads with a 2 g/100mL solution and packing ~20cc of them in a 12.7mm OD PFA tube and flowing ZA over them until they appeared dry. The reaction was shown to be essentially 100% (±10%) when conducted in a humidified atmosphere (RH ≥60%), PTR-MS, and FTIR analysis of the gas stream before and after passing through the chlorination bed. The ClCN source was also checked by measuring the total nitrogen content of the gas stream before and after the chlorination step, and the resulting signal was found to be 98±1% of the original HCN standard. This means that the combination of the chlorination reaction and N_r conversion (see below) were at least 98% efficient.

Preparation of BrCN and ICN gas streams was accomplished with the diffusion cell apparatus using commercially available samples of BrCN (98% purity, Sigma-Aldrich) and ICN (97% purity ACROS Organics), that were used without further purification. BrCN is a volatile solid, so was kept in a diffusion cell at 0°C while in use. ICN is a relatively non-volatile solid and so was placed in a diffusion cell and heated to 80°C while in use. These resulted in sample streams that had mixing ratios on the order of 250-350 ppbv in 1 SLPM. Analysis by iodide ion chemical ionization mass spectrometry indicated traces of the molecular halogen species (Br_2, I_2), but no other significant N-containing species.

B. Detection of Nitrogen Compounds

The method for detection of the compounds studied in this work relies on high temperature conversion of any N-containing species, except for N_2 or N_2O, to nitric oxide (NO) and detection of the resulting NO by O_3 chemiluminescence (Williams et al., 1998). This technique, which we will refer to as Total Reactive Nitrogen, N_r, has been shown to measure a wide range of reduced nitrogen species as well as the more familiar oxides of nitrogen (Hardy and Knarr, 1982; Saylor et al., 2010; Stockwell et al., 2018), provided care is taken to convert any nitrogen dioxide that is formed in the Pt converter back to NO prior to detection (Schwab et al., 2007). In this work, this was accomplished with a solid molybdenum tube operated at between 350 and 450 °C, with the addition of a small amount of pure H_2 resulting in a 0.8% mixing ratio in the catalyst flow. The detection system was routinely calibrated with a NO standard (Scott-Marrin, Riverside, CA) and the conversion efficiency was confirmed with a low concentration (10ppmv) HCN standard (GASCO, Oldsmar, FL). The high conversion efficiencies (≥98%) for HNCO and ClCN were confirmed by other methods as described by Stockwell et al. (2018). The conversion efficiencies for BrCN, and ICN are assumed to be equally high due to the fact the X-CN bond strengths of these compounds are lower than for H-CN and Cl-CN (Davis and Okabe, 1968) and the CH_3-NCO bond is weaker than the H-NCO bond (Woo and Liu, 1935). Although readily measured here, a solubility measurement of this kind does not require the determination of the absolute concentration of the analytes, it only requires that the measurement be linear (i.e. constant sensitivity) throughout the range of signals measured. The NO instrument is linear from the low pptv into the low ppmv range, the chief limitation being the ability to count photon rates above 5MHz. The magnitude of the gas phase sources used and the flow rate of the instrument (1 SLPM) insured that instrument signals did not reach the non-linear range.

The requirement for the detection method to be selective could be an issue with a general method such as N_r. In practice, the reactions of the nitrogen species studied here form products that are not volatile under the conditions used in this work, and so do not interfere with the measurement. In aqueous-phase reactions, HNCO produces NH_3/NH_4^+, CH_3NCO produces $CH_3NH_2/CH_3NH_3^+$, and XCN compounds produce HOCN/NCO^- all of which are non-volatile in the pH ranges at which those experiments were conducted. The products of the organic-phase reactions are not as well known: tridecane should not react with HNCO, n-octanol will form carbamyl or methyl carbamyl groups with n-octyl substituents which should be non-volatile. Possible reactions of XCN compounds with n-octanol are less well known, particularly in the absence of water in the solution, so those experiments will need to be interpreted with care.

The bubble flow reactor has been described in a number of publications (Borduas et al., 2016; Kames and Schurath, 1995; Kish et al., 2013; Roberts, 2005), so will be only briefly summarized here. The reactor used for the most of the experiments is a modification of the one described by Roberts (2005), the main modification being a reduction in volume to 125 mL. Liquid volumes used in the experiments ranged from 20 to 50 mL, and the volumetric flow rates used ranged from 170 to 1070 ambient mL/min. Temperatures were measured using a calibrated mercury thermometer, and in temperatures different than room temperatures were controlled using a water bath with either ice/water, or a temperature control system. The uncertainties in the temperatures were ±0.5 °C.

The bubble flow reactor method relies on the rapid equilibration of a gas stream that contains the analyte of interest, with solution by means of the creation of small, finely divided bubbles. In the system used here, these bubbles are created by passing the gas stream through a fine glass frit, situated at the bottom of the glass vessel. The main sample flow is passed through the bubbler and into the detector stream to establish a baseline. A small flow of the analyte is added upstream of the reactor by means of a PFA solenoid valve to start the measurement and the effluent is monitored until the measured concentration attains equilibrium. At this point, the analyte entering the reactor is switch off, and the concentration exiting the reactor begins to decay. This decay is due to a combination of loss of the analyte as it re-equilibrates with the gas stream, and first-order loss in the solution due to reaction. Under conditions of rapid equilibration, this decay takes the form of a single exponential equation, dependent on the ratio of flow rate (ϕ, cm^3/sec) to liquid volume (V, cm^3), the Henry's Law solubility (M/atm), and the first-order loss rate (k):

$$ln(C_0/C_t) = [\phi/(HRTV) + k]t \qquad \text{Eq. (1)}$$

Measurements performed at a series of ϕ/V should be linear with a slope of the decay rate (d $ln(C_0/C_t)$/dt) vs phi/V of 1/HRT, where R is the ideal gas constant, and T the temperature (K), and an x-intercept of k, the first-order loss rate (sec^{-1}). In practice, the linearity of this relationship and the performance of the measurement at different liquid volumes and flow rates that result in the same ϕ/V provide a check on the assumption of rapid equilibration within the reactor.

Attempts to measure the solubility of ICN with the glass bubbler system described above were unsuccessful, because ICN did not equilibrate at the levels and timescales typical of the other compounds measured in this work, and the decay profiles were not reproducible nor exponential. The possibility that this was due to higher solubility, faster reaction, or decomposition of ICN on glass surfaces was explored by using a smaller reactor fabricated from 12.7 mm O.D. PFA tubing and PFA compression fittings (see supplemental Figure S1). In these experiments, liquid volumes of between 1.0 and 2.0 mL and flow rates of 100 to 600 ambient cc/min were used. This resulted in equilibration and decay profiles more similar to the other experiments, when the solubility of ICN in water was measured at room temperature.

Solution for the aqueous solubility/reaction experiments were prepared from reagent-grade materials. The pH 2-4 buffer solutions were commercial preparations, made from citric acid monohydrate with differing amounts of hydrochloric acid, sodium chloride, and sodium hydroxide (Fixanal, Fluka Analytical), having anion concentrations ranging from 0.08 to approximately 0.2 M. The manufacturer specifications (Fluka, Sigma-Aldrich) of the pH=3 buffer showed a slight temperature dependence, with the pH ranging from 3.03 at 0 °C to 2.97 at 90 °C. An ammonium chloride solution of 0.45 M was prepared through addition of a measured amount of the solid to the pH=3 buffer. Sodium chloride solutions ranging up to 2.5 M were prepared gravimetrically in the pH buffer solution. The pHs of NH_4Cl and NaCl were measured at room temperature with a pH meter and found to be within 0.1 pH unit of the nominal buffer pH value.

III. Results and Discussion

A typical experiment consisted of a series of exposures of the solution of interest to the analyte in a gas stream at a series of known flow rates. The analyte was introduced by switching the small flow from the source into the bubbler gas stream using an all-Teflon PFA 3-way valve (Roberts, 2005). The total reactive nitrogen content of the gas exiting the bubbler was measured continuously and approached a plateau as the analyte equilibrated with the solution. At this point, the analyte was switched out of the bubbler stream, using the 3-way valve so as not to otherwise perturb the flow through the system. The N_r concentration exiting the bubbler decayed exponentially due to a combination of re-equilibration and first-order reactive loss of dissolved analyte (due to hydrolysis for example). An example of the data generated by these experiments is shown in Figures 1 and 2, which show the exponential decays for a series of gas flow rates (Figure 1) and the correlation of the decay rates versus the ratio of volumetric flow rate to solution volume (Figure 2). The uncertainties in the Henry's coefficients are derived from a combination of the reproducibility of the decay rates, the agreement between decay rates at the same ϕ/V (but different flows and liquid volumes) and the fits to the slope of relationships like those shown in Figure 2, and were generally ±10% or better. The uncertainties in first-order lass rate are the corresponding uncertainties in the intercepts. The results of the experiments with HNCO, CH_3NCO, ClCN, BrCN, and ICN with the variety of solvents and conditions employed are summarized in Table 1 and described below.

A. Results for Aqueous Solution

1. Solubility and Reactions of HNCO

Here we report results for pHs between 2 and 4, and for the temperature range 279.5 to 310.0 K at pH=3. In addition, we report data for the effect of salt concentrations on the solubility at pH=3, and the effect of ammonium concentrations on solubility and apparent first-order loss rate in solution. The dependence of aqueous solubility of HNCO on pH is expected given it is a weak acid;

$HNCO_g \Leftrightarrow HNCO_{aq}$ $\quad H_{HNCO}$ $\quad$ Eq. (2)

$HNCO_{aq} + H_2O_{aq} \Leftrightarrow H_3O^+ + NCO^-$ $\quad K_a$ $\quad$ Eq. (3)

so that the effective Henry's coefficient has a term that accounts for the acid-base equilibrium and that equilibrium constant:

$$H_{eff} = H_{HNCO}(1 + K_a/[H_+]) \quad \text{Eq. (4)}$$

The plot of H_{eff} vs $1/[H+]$ is shown in Figure 3, the slope of which is $H_{HNCO}*K_a$ and the intercept is the intrinsic Henry's Law constant, H_{HNCO}. The resulting fit ($R^2 = 0.99$) gave a $H_{HNCO} = 20$ (±2) M/atm, and a K_a of 2.0 (±0.28) $\times 10^{-4}$ M (which corresponds to $pK_a = 3.7 \pm 0.06$). The uncertainties in these numbers were derived from the standard deviations of the fitted parameters, where the value for K_a is the propagated uncertainty in both H and the slope. Figure 4 shows the comparison of the H measurements from this work with those of Borduas et al., (2016) plotted according to Eq. 4 equation. There are approximately 20% differences in the two data sets, which is just at the limits of the quoted uncertainties, when both the uncertainties in the intrinsic H and pKa are taken into account.

The temperature dependence of the solubility measured at pH=3, obeys the simple Van't Hoff relationship;

$$d\ln H_{eff}/d(1/T) = -\Delta H_{soln}/R \quad \text{Eq. (5)}$$

shown in Figure 5 as a linear relationship of log H vs. 1/T. These data were not corrected for the slight dependence of the buffer pH on temperature (3.02-2.99 pH units over this range). The slope of the correlation yields a ΔH_{soln} of -37.2 ±3 kJ/mole, calculated using dimensionless Henry's coefficients ($H_{eff}RT$), (Sander, 2015). This enthalpy of solution agrees with that measured by Borduas et al., (2016) (-34 ±2 kJ/mole) within the stated uncertainties. Moreover, this enthalpy is similar to those of other small N-containing molecules: HCN (-36.6 kJ/mole), CH_3CN (-

34.1 kJ/mole), and nitromethane (-33.3 kJ/mole) (Sander, 2015), but different than that of formic acid (-47.4 kJ/mole) which was used by the cloud uptake modeling study (Barth et al., 2013).

Often the Henry's Law solubility can depend on salt concentration of the solution, usually resulting in a lower solubility (salting out), but occasionally resulting in a higher solubility (salting in), with higher salt concentrations. These effects are most applicable to aerosol chemistry, where ionic strengths can be quite high. This effect on HNCO solubility was measured at pH=3 and 298 K for NaCl solutions between 0 and 2.5 M concentration. The results, shown in Figure 6, exhibit the classic "salting out" effect where HNCO was only about 60% as soluble at 2.5 M compared to the standard pH=3 buffer. The Setschenow constant, k_s, can be determined by the relationship:

$$-\mathrm{Log}(H/H_0) = k_s \times [I] \qquad \text{Eq. (6)}$$

where H is the Henry's coefficient at a given ionic strength, I, and H_0 is the Henry's coefficient in pure water. For a salt with two singly charged ions, I is equal to the salt concentration. In this experiment, k_s was found to be 0.097 ± 0.011 M^{-1}. The magnitude of the salting out effect on HNCO is similar or slightly smaller than those found for other small organic compounds in NaCl (Clever, 1983; Schumpe, 1993).

The net hydrolysis reaction rates observed in this study are listed in Table 1, and range from 0.22 to 4.15 $\times 10^{-3}$ s^{-1} and are both pH and temperature dependent. The main reactions of HNCO/NCO^- in aqueous solution are hydrolysis reactions that involve the acid or its conjugate anion, as detailed in Reactions 1-3 noted above. The expression for the net hydrolysis reaction is;

$$k_{hydr} = \frac{k_1[H^+]^2 + k_2[H^+] + k_3K_a}{K_a + [H^+]} \qquad \text{Eq. (7)}$$

as derived by Borduas et al., 2016. The rates of these reactions that were determined in several previous studies (Borduas et al., 2016; Jensen, 1958) and are in reasonable agreement except for Reaction 3, which is not atmospherically relevant. Equation 7 was used to calculate the values from those two studies that would correspond to the rates at pH=3 measured in our work, and are also listed in Table 1. The rate constants reported in this work agree within the range observed in the two previous studies, except for one temperature, and the relative standard deviations of mean values calculated from all three observations ranged from 5 to 30%.

The above hydrolysis reactions represent a lower limit on the condensed phase loss of HNCO, so reaction with other species present in the condensed phase might result in faster loss, and produce unique chemical species. HNCO/NCO^- are known to react with a variety of organic compounds having an "active hydrogen" (Belson and Strachan, 1982) through simple addition across the N=C bond. For example, alcohols react to yield carbamates, i.e. esters of carbamic acid:

$$HNCO + ROH \Rightarrow H_2NC(O)OR \qquad \text{(R10)}$$

In the same fashion, HNCO/NCO^- can react with ammonia in solution to yield urea

$$HNCO + NH_3 \Leftrightarrow H_2NC(O)NH_2 \qquad \text{(R11)}$$

And in a more general sense, react with amines to yield substituted ureas:

$$HNCO + RNH_2 \Leftrightarrow H_2NC(O)NHR \qquad \text{(R12)}$$

Reaction 11 is known to be an equilibrium that lies far to the product side under all conditions pertinent to this work (Hagel et al., 1971). While the forward reaction rate for R11 has been measured under neutral to slightly basic conditions (Jensen, 1959; Williams and Jencks, 1974b), it has not been measured at pHs applicable to atmospheric aerosol or cloud droplets, i.e. pH=2-4. These previous studies have assumed that the mechanism involves the reaction of the un-ionized species, e.g. NH_3 and HNCO, although there is some evidence that Reaction 12 for some amines (RNH_2) has a more complicated reaction mechanism (Williams and Jencks, 1974a). As a consequence of this assumption, the previous studies reported their reaction rates corrected for the acid-base equilibria of each species. The solubility/reaction experiment in this work was performed at pH=3 and [NH_4^+] of 0.45 M, so a substantial correction of the literature values for the acid-base equilibria in the case of NH_4^+ and a minor correction for the dissociation of HNCO was required in order to compare with our result. The results of our study (Table 1) show that the solubility of HNCO in NH_4Cl solution at 292 K is essentially the same as that of the pH=3 buffer alone (31.5 ±3 vs 32.6 ±3 M/atm). This implies that R11 does not impact the aqueous solubility. However, the measured first-order loss rate, 1.2 (±0.03) $\times10^{-3}$ sec^{-1} is faster than the hydrolysis at pH3, 0.66 (±0.06) $\times10^{-3}$ sec^{-1}. The reaction can be expressed as the sum of hydrolysis and reactions of HNCO and NCO^- with NH_4^+ (the predominant form at pH3).

$$\frac{d[HNCO+NCO]}{[HNCO+NCO]} = -(k_{hydr} + k_{11}[NH_4{}^+])dt \qquad \text{Eq. 8}$$

We calculate a value of 1.2 (±0.1) $\times10^{-3}$ $M^{-1}sec^{-1}$ for k_{11} from our measurements which is much faster than the rate constants reported by previous studies, 5 $\times10^{-6}$ $M^{-1}sec^{-1}$ (Jensen, 1959) and 1.5 $\times10^{-5}$ $M^{-1}sec^{-1}$ (Williams and Jencks, 1974b), when corrected for acid-base equilibria.

2. Solubility and Reactions of CH_3NCO

The solubility and first-order loss rate of CH_3NCO were measured at pH=2 and pH=7 at 298 K, and the results are listed in Table 1. The Henry's coefficients, 1.3 (±0.13) and 1.4 (±0.14) M/atm, were lower than those measured for HNCO, and independent of pH, within the uncertainties of the measurements. This is consistent with CH_3NCO being a less polar compound, with no dissociation reactions that might be pH dependent. In addition, these results imply that solution complexation due to the presence of anions does not affect CH_3NCO solubility, at least at the concentrations and anions present in the pH=2 buffer solution, 0.2 M for the sum of citrate and chloride.

The first-order loss rates of CH_3NCO, presumably due to hydrolysis, did show a pH dependence that implies acid catalysis. These hydrolysis rates were faster than the rates for HNCO at the same temperatures and pHs. Solution-based studies of CH_3NCO hydrolysis in the presence of strong acid anions (Al-Rawi and Williams, 1977; Castro et al., 1985) have shown that a complex mechanism takes place, involving a reversible complexation, (shown here for HSO_4^-):

$$CH_3NCO + HSO_4^- \Longleftrightarrow CH_3NH\text{-}C(O)\text{-}OSO_3^- \qquad \text{(R13)}$$

happening in parallel with catalyzed and un-catalyzed hydrolysis:

$$CH_3NCO + H_3O^+ \Rightarrow CH_3NH_3^+ + CO_2 \qquad \text{(R4)}$$

$$CH_3NCO + H_2O \Rightarrow CH_3NH_2 + CO_2 \qquad \text{(R5)}$$

Rate constants for reactions R4 and R5 were reported by Castro et al., (1985) but the precision of these were somewhat compromised by the presence of the R13 equilibrium. In this study, the Henry's coefficient results imply a negligible role for complexation, so the following simplified expression for the pH dependence is used:

$$k_{MIC} = k_5 + k_4[H_3O^+] \qquad \text{(Eq9)}$$

to derive the following values for k_5 =1.9 (±0.6) ×10^{-3} sec^{-1}, and k_4 = 0.13 (±0.07) $M^{-1}sec^{-1}$. These values are in reasonable agreement with the value for k_5 given by Al-Rawi and Williams, (1977), 1.47 x10^{-3} sec^{-1} considering those measurements were at 1M KCl, and the value for k_4 = 0.16 $M^{-1}sec^{-1}$ given by Castro et al., (1985) for reaction with HCl in the absence of a buffer.

3. Solubility and Reactions of XCN Compounds.

The solubilities and first-order loss rates of XCN compounds were measured at room temperature and neutral pH in pure DI water, and at ice/water temperature for ClCN and BrCN. The resulting Henry's coefficients are listed in Table 1. The ClCN solubility was essentially the same as that measured for CH_3NCO at room temperature, and is in reasonable agreement with the value of 0.52 M/atm at 298 K based on a model estimate (Hilal et al., 2008), and one reported measurement, 0.6 M/atm at 293 K (Weng et al., 2011). In contrast, BrCN was more soluble than ClCN, 8.2 ±0.8 M/atm at 296°K, but fairly insoluble in an absolute sense. The temperature dependences of H_{ClCN} and H_{BrCN} were as expected, showing higher solubility at lower temperatures, however, they had very different heats of solution, -27.8 kJ/mole for ClCN, and -38.3 kJ/ mole for BrCN, although there are only two data points for each compound. Both the higher solubilities and larger ΔH_{soln}, could be a result of the higher dipole moment and polarizability of BrCN relative to ClCN (Maroulis and Pouchan, 1997).

The solubility of ICN was measured a room temperature using a combination of different flow rates (208 – 760 amb cm^3/min) and liquid volumes (1.95 and 0.95mL). A plot of the decay rates versus ϕ/V for those runs is shown in Figure 7. Where those data sets overlap there is agreement to within about 15%, implying that the equilibration could be fast enough to meet the criteria for these types of flow experiments. The resulting Henry's coefficient, 270 (±54) M/atm. Is significantly larger than the other two XCN compounds, but is consist with the trend of increasing solubility with dipole moment and polarizability. Attempts to use the small reactor to measure the solubility of ICN at ice/water temperatures was not successful, e.g. did not yield simple single exponential decays with time, under the same range of flow conditions as used in the room temperature experiment.

The hydrolysis of XCN compounds is known to be base-catalyzed, and can be susceptible to anion complexation (Bailey and Bishop, 1973; Gerritsen et al., 1993) in a manner similar to CH_3NCO:

$$XCN + A^- <=> [XCN\bullet A]^- \qquad \text{(R14)}$$
$$XCN + 2H_2O => HOCN + H_3O^+ + X^- \qquad \text{(R6)}$$
$$XCN + OH^- + H_2O => HOCN + X^- + H_2O \qquad \text{(R7)}$$

This complexation can be ignored in our study for ClCN and BrCN since the experiment was performed in DI water. Accordingly, the expression for the ClCN and BrCN hydrolysis rate constant is;

$$k_{XCN} = k_w + k_{OH}[OH^-] \qquad \text{(Eq10)}$$

Bailey and Bishop (1973) found $k_w = 2.58 \times 10^{-6}$ sec^{-1} and $k_{OH} = 4.53$ M^{-1}sec^{-1} at 299.7 K, for ClCN, which corresponds to 3.03 x10^{-6} at pH7. This is consistent with the results of this study which found that the first-order loss rate was zero, within the error of the linear fit (±4.2 ×10^{-4} sec^{-1}). The study of BrCN hydrolysis of Gerritsen et al., 1993 did not derive k_w nor did it present sufficient data for k_w to be estimated. However, there are two other studies that presented data from which k_w can be estimated, and those range from 1.9 – 9.2 ×10^{-5} sec^{-1}, (Heller-Grossman et al., 1999; Vanelslander et al., 2012).

The hydrolysis of ICN is slightly more complicated since there is some evidence that ICN might complex with iodide (Gerritsen et al., 1993). The room temperature hydrolysis rate observed in our experiment was not significantly different than zero, 4.4 (±7.6) ×10^{-5} sec^{-1}, but is in the same range of the rate constant estimated from the data given by Gerritsen, et al., (1993), by extrapolating their rate constant vs. [OH^-] data to zero [OH^-], assuming no complexation reactions.

B. Non-aqueous Solution

Solubility in non-aqueous solvents is a standard indicator of how compounds will be distributed between different compartments in the environment, i.e. lipids in the body, organic aerosols in the atmosphere. In addition, the ratio of organic to aqueous solubility (K_{ow}) is used to estimate membrane transport of a chemical species, a key factor in estimating physiologic effects of a pollutant. Several non-aqueous solvents were used in this study, tridecane to represent a completely non-polar solvent and n-octanol, which is used as a standard material for such studies.

1. Solubility and Reactions of HNCO

The experiments performed on HNCO were conducted with tridecane, 10% (V/V) n-octanol/tridecane, and pure n-octanol, and the results are summarized in Table 1. HNCO is the least soluble in tridecane, 1.7 (±0.17) M/atm and increasingly soluble as the proportion of n-octanol is increased, to pure n-octanol, 87 (±9) M/atm at 298 K. Experiments at two other temperatures were performed to confirm that these solubilities follow the expected temperature dependence, and to obtain the solubility in pure n-octanol at body temperature (310 K) to match data for the aqueous solubility. The lower solubility of HNCO in tridecane is expected since tridecane is completely non-polar and has no tendency to hydrogen bond or interact with the polarizable end of the HNCO molecule. In contrast, the increase in solubility of HNCO with increasing proportion of n-octanol is due to the polar –OH group at the end of the molecule.

The rate of reactions of HNCO with the non-aqueous solvents were below the limit of detection by this method for all combinations except for pure n-octanol at 310 K. Even still, the measured rate was quite a bit lower than the corresponding hydrolysis rate in aqueous solution at pH=3. The manner in which these two factors (solubility and reaction) affect the net uptake and loss of HNCO will be discussed below.

2. Solubility and Reactions of CH_3NCO

The solubility of CH_3NCO in n-octanol was measured at several temperatures, as summarized in Table 1. The value for 298 K is approximately 3 times higher than that of aqueous solubility, and has the expected temperature dependence. In addition, the first-order reaction rates for CH_3NCO in n-octanol were in the same range or slightly higher than the aqueous reactions. The reaction with n-octanol is expected to go via the carbamylation reaction (R9), although there is some evidence that this reaction has as more complex mechanism possibly involving multiple alcohol molecules (Raspoet et al., 1998). These rates are much faster than the corresponding rates for HNCO, and may provide some guidance concerning the loss rates of CH_3NCO to heterogeneous processes.

3. ClCN and BrCN

The solubilities of ClCN and BrCN in n-octanol were measured at room temperature. Cyanogen chloride has an only a slightly higher Henry's coefficient in n-octanol than in water, in contrast to BrCN, which is relatively more soluble in n-octanol. The first-order loss rates of ClCN and BrCN could be determined from the flow reactor experiments and were 1.3 (±0.4) $\times 10^{-3}$ sec^{-1} and 9 (±2) $\times 10^{-5}$ sec^{-1}, respectively. Reactions of ClCN with alcohols are known (see for example (Fuks and Hartemink, 1973)), and form carbamates, in a mechanism that appears to be second-order in the alcohol, and acid catalyzed, but rate constants for ClCN-alcohol reactions have not been reported to our knowledge. There are studies of rates of reactions of ClCN with nucleophiles, e.g. nitrogen bases, and those reactions appear to result in –CN substitution and formation of a Cl^- ion (Edwards et al., 1986). In addition, BrCN has been used by protein chemists to selectively cleave disulfide bonds and has been used for some time by synthetic chemists to selectively convert tertiary amines to secondary amines (Siddiqui and Siddiqui, 1980; von Braun and Schwarz, 1902) and can carbamylate amino acids (Schreiber and Witkop, 1964). The importance of these reactions to the atmospheric fate of XCN compounds remains an open question, but it is important to note that they constitute losses of active halogen, i.e. conversion of the halogen to a halide ion.

4. Octanol/Water Partition Coefficients

The ratio of solubilities between a non-polar solvent and water is a fundamental quantity that is useful in predicting the fate of a compound in the environment and biological systems (Leo et al., 1971). This parameter is used to predict lipid solubility, membrane transport, and the potential of uptake of a particular compound by organic aerosol. n-Octanol is a standard non-polar solvent that is commonly for this purpose, as it has an overall non-polar character with a substituent that is capable of hydrogen bonding. The data from this study can be used to calculate the octanol/water partition coefficients for HNCO, CH_3NCO, ClCN, and BrCN as the ratio of the respective Henry's coefficients;

$$K_{ow} = H_{oct}/H_{H2O} \qquad \text{(Eq.11)}$$

The results are listed in Table 3 along with K_{ow}s for some related small molecules. Both CH_3NCO, and BrCN are fundamentally more soluble in n-octanol than in water, while ClCN has nearly the same solubility in both materials. The weak acid equilibrium of HNCO makes it more soluble in n-octanol at pH 3, but much more soluble in water at neutral pH. Formic acid is a similarly weak acid (pKa = 3.77) and so is a good point of comparison to HNCO. The n-octanol partition coefficient of HNCO is a factor of 15 larger than that of formic acid. Similarly, the n-octanol partition coefficient of CH_3NCO is 6.8 times larger than that of acetonitrile. The two cyanogen halides measured here had differing behavior, with ClCN showing almost no difference in solubility, and BrCN having about the same increase in solubility in n-octanol as HNCO and CH_3NCO.

IV. Atmospheric and Environmental Chemistry Implications

The atmospheric loss of the compounds studied here are either: solely or predominantly through heterogeneous uptake and reaction for HNCO, CH_3NCO, ClCN, BrCN, or in the case of ICN due to both heterogeneous chemistry and photolysis. The aqueous solubility and reaction data from this study allow some prediction of uptake parameters and loss rates in some important systems, e.g. cloud water and natural water surfaces like oceans. In addition, some indications can be gained about the uptake of HNCO, CH_3NCO, ClCN, and BrCN to organic aerosol, using n-octanol as a model. Finally, the n-octanol/water partition coefficient is often used as a key parameter in modeling cross-membrane transport, and the data from this study can be used to predict the behavior of these reduced-N compounds relative to other well-studied compounds.

The reactive uptake of HNCO, CH_3NCO and XCN on environmental surfaces, small particles and aqueous droplets can be parameterized using the uptake coefficient, γ, defined as the fraction of collisions of a molecule with a surface that lead to incorporation of that molecule in the condensed phase. If solubility and reaction are the limiting processes, a good assumption for the species in this work, then γ_{rxn} can be estimated from the following equation (Kolb et al., 1995):

$$\gamma_{rxn} = \frac{4HRT\sqrt{kD_a}}{<c>} \qquad \text{(Eq.12)}$$

where H and k are the Henry's coefficient and first-order loss rate in solution measured in this work, R is the gas constant, T is temperature, D_a is the diffusion coefficient in aqueous solution (assumed here to be 1.9×10^{-5} cm^2sec^{-1} for HNCO and 1.6 $x10^{-5}$ cm^2sec^{-1} for CH_3NCO and ClCN, 1.2 $x10^{-5}$ cm^2sec^{-1} for BrCN, and 1.0 $x10^{-5}$ cm^2sec^{-1} for ICN at 298 K), and <c> is the mean molecular velocity. The results of these calculations are shown in Figure 8 for the H measurements reported here, k_{hydr} for HNCO reported by Borduas et al., (2016), k_{hdyr} or CH_3NCO from this work and k_{hydr} for ClCN from Bailey and Bishop (1973).

Deposition of a compound to the surface can be parameterized as essentially two processes taking place in series, physical transport within the planetary boundary layer to the surface and then chemical uptake on the surface (see for example (Cano-Ruiz et al., 1993)). In this formulation, the deposition velocity, v_d (the inverse of the total resistance) is expressed as follows:

$$v_d = \frac{1}{\frac{1}{v_t} + \frac{1}{\gamma\frac{<c>}{4}}} \qquad \text{(Eq.13)}$$

where $1/v_t$ is the resistance due to transport, and $\frac{1}{\gamma\frac{<c>}{4}}$ is the resistance due to chemical uptake. For a species for which uptake is rapid, e.g. a highly soluble acid, the chemical resistance becomes small and $v_d \cong v_t$. This is the case for HNCO deposition to land or natural water surfaces (pHs ~7-8). Typical v_ts are on the order of 0.5 to 1 cm/sec for a reasonably mixed boundary layer (Wesely and Hicks, 2000). For compounds for which γ is quite small, the chemical term predominates.

$$v_d \cong \gamma\frac{<c>}{4} \qquad \text{(Eq. 14)}$$

The lifetime of a species within the PBL then can be estimated as h/v_d, where h is the boundary layer height. The lifetime estimates for HNCO, CH_3NCO, and XCN compounds are given in Table 2, and range from the short lifetime noted for HNCO, to quite long lifetimes for the least soluble species, for example ClCN.

The loss rates due to uptake of species to atmospheric aerosol particles can be estimated from the pH dependent uptake coefficients in Figure 8, using parameterizations described in the literature (Davidovits et al., 2006; Sander, 1999). In the limited case of surface-controlled uptake, i.e. neglecting gas phase diffusion, the loss of a species is;

$$k = \frac{A\gamma<c>}{4} \qquad \text{(Eq. 15)}$$

where A is the aerosol surface area. If we take the γs from Figure 8, and assume highly polluted conditions, A = 1000 $\mu m^2/cm^3$ and pHs between 1 and 2, then the lifetimes listed in Table 2 are arrived at. The values for HNCO and CH_3NCO show a range because the uptake is pH dependent, and it should be noted that the values for CH_3NCO, ClCN, and BrCN are over estimated by this method, as their chemistry is slow enough that a volume-based estimate may be more appropriate. The more important effect here is that the γ values are based on hydrolysis losses, which are undoubtedly much slower than many of the solution-phase reactions that these species can undergo, hence the lifetimes against aerosol deposition are upper limits.

The loss of HNCO to cloudwater is the subject of extensive work discussed by Barth et al, 2013, and no attempt will be made here to update that analysis. The fastest loss rates for HNCO were observed in warm dense clouds into which SO_2 was also dissolving and adding considerable acidity, so that value for HNCO was included in Table 2. For the other compounds we use a simple parameterization of cloudwater reaction to estimate the in-cloud loss rates for CH_3NCO and the XCN compounds. In the estimate of reaction rate:

$$k = k_l L_c HRT \qquad \text{(Eq. 16)}$$

k_l is the liquid phase rate constant, L_c is the cloud liquid water content, and H is the Henry's coefficient. If we assume a L_c of 2 x10^{-6}, and T ≅298 K, and we use the H and k values measured in this work (the exception is that the literature value for CH_3NCO at pH=2 was used), then the values for lifetimes of CH_3NCO, and XCN compounds listed in Table 2 were obtained. Below we discuss the characteristic times obtained for each compound in the context of what else is known about their sources and atmospheric chemistry.

A. HNCO

The loss of HNCO via heterogeneous processes occurs in two separate regimes: in aerosols and cloud droplets at relatively low pH, and in surface waters and on terrestrial surfaces that are neutral or slightly basic in pH. In the former case, HNCO solubility is relatively low but hydrolysis is acid catalyzed. In the latter case, solubility is high enough that uptake will be limited by the transport of HNCO to the surface, much like other strong acids such as HNO_3. Ambient measurements of HNCO at surface sites are consistent with deposition of HNCO to the ground, exhibiting diurnal profiles similar to those of O_3 or HNO_3 (Kumar et al., 2018; Roberts et al., 2014; Mattila et al., 2018; Zhao et al., 2014).

Several aspects of the aqueous solubility and hydrolysis, and heterogeneous removal of HNCO have been examined in modeling studies. A global modeling study by Young et al. (2012) was a first attempt to model global HNCO by scaling the source to fire emissions of HCN. Loss of HNCO was assumed to be due to wet and dry deposition with efficiencies similar to HNO_3 and HC(O)OH, and that HNCO was lost once it was taken up by clouds. Young et al., concluded that HNCO had an average lifetime of about 37 days. Barth et al., (2013) addressed part of this analysis by modeling the cloud removal of HNCO using actual solubility and reaction data in a cloud parcel model, albeit, the hydrolysis rates used were from Jensen, (1957) which were approximately 50% higher than the Borduas results, and the temperature dependence of H was assumed equal to that of formic acid, and resulted in higher solubilities at low temperature. This cloud model showed that cloud water uptake was reversible in that most cases hydrolysis was slow enough that some HNCO returned to the gas phase after cloud evaporation. The Barth et al., study estimated HNCO lifetimes as short as 1 hour in warm polluted clouds (i.e. high SO_2 => H_2SO_4 formation). The results of our study and those of Borduas et al., (2016) add to these analyses in that now the measured temperature dependence of H can be used, and the hydrolysis rate constants can be updated.

The results in this paper allow for further refinement of HNCO loss estimates. For example, the salting-out effect may be important for aerosol with high inorganic content, and high ammonium concentrations will result in reactive loss rates that are faster than hydrolysis. The solubility of HNCO in aerosol particles with substantial organic character can be higher or low depending on the nature of substituent groups, e.g. degree of -OH functionalization.

In studies of the condensed phase oxidation of dissolved N species, as well as biological processes produce cyanate ion, there is a growing recognition that cyanate is part of the natural N cycle in the ocean (see (Widner et al., 2013) and references there-in). Observed near-surface cyanate levels often reached a few 10s of nM in near shore productive areas. The observations of cloud/aerosol source of HNCO presented in (Zhao et al., 2014) on the coast of California might be explained by a combination of this NCO^- seawater source and aerosol/cloud water acidification by local sources of strong acids, particularly HNO_3. In specific, acidification of sea spray containing about 10 nM NCO^- to pH=4 or so, would correspond to H_{eff} of around 50 M/atm, and result in an equilibrium HNCO concentration of several hundred pptv. Such a source would most likely be limited by the concentration of sea salt-derived aerosol, but could easily account for the source implied by the measurements of (Zhao et al., 2014).

B. CH_3NCO

The atmospheric chemistry of CH_3NCO is less well studied than HNCO. There is a single reported measurement of the reaction rate of CH_3NCO with OH by relative rates which gave k = 3.6 $\times 10^{-12}$ molec cm^{-3} sec^{-1} (Lu et al., 2014). The uptake coefficients estimated for CH_3NCO in Figure 8 are relatively low with only a slight increase at the lowest pHs in atmospheric media. As a consequence, atmospheric lifetimes of CH_3NCO towards surface deposition are estimated to be quite long, 6 months or more if hydrolysis is the sole loss process. The loss due to aerosol of cloudwater uptake is estimated to be slightly faster, due primarily to the slight acid-catalysis of the CH_3NCO hydrolysis rate. The lifetime estimates should be considered upper limits since there are number of condensed-phase reactions that might be faster than hydrolysis, and would need to be the subject of further research.

C. ClCN, BrCN, and ICN

To date, we know of no observations of ClCN in the ambient atmosphere, but its formation in the chlorination of water, waste water, and swimming pools (Afifi and Blatchley III, 2015; Daiber et al., 2016; Lee et al., 2006) indicates that there could be sources from human activities, including the use of chlorine bleach for cleaning indoor surfaces. In addition, there might also be a source from aerosol systems were chlorine is being activated, i.e. oxidized from Cl^- to $ClNO_2$, Cl_2, or HOCl (see for example (Roberts et al., 2008)) in the presence of reduced nitrogen. The results of our solubility measurements indicate that ClCN will volatilize from the condensed phase fairly readily, so its atmospheric removal should be considered. BrCN has been observed in systems where bromide-containing water or wastewater were treated with halogens (Heller-Grossman et al., 1999), and there are biological mechanisms that make BrCN and ICN as well (Schlorke et al., 2016; Vanelslander et al., 2012). The potential for remote atmospheric sources of these compounds is currently being investigated, but BrCN could be the result of the same bromine activation chemistry that depletes ground level ozone in that environment (Simpson et al., 2007).

Gas phase radical reactions of XCN compounds have not been studied under atmospheric conditions. A few studies at higher temperatures and the studies of HCN and CH_3CN can be used to roughly predict how fast the relevant reactions are. For example, the reactions of ClCN and BrCN with O atoms at 518-635 K are very slow (<3 $\times 10^{-15}$ molec cm^{-3} sec^{-1},(Davies and Thrush, 1968)) and the reaction of Cl atom with ClCN at high temperature is also quite slow (<1.0 $\times 10^{-14}$ molec cm^{-3} sec^{-1}, (Schofield et al., 1965)). However, these observations do not preclude the presence of another reaction channel at low temperature, e.g. a mechanism involving addition to the CN group. The reactions of HCN and CH_3CN with OH, Cl atom and O atom at atmospherically relevant temperatures are all quite slow, implying such addition channels are not likely to be substantially faster for these XCN compounds. We conclude that rate constants for the reactions of OH or Cl with X-CN compounds are likely quite low (<2 $\times 10^{-14}$

molec cm^{-3} sec^{-1}), making the lifetimes of these compounds against these reactions on the order of a year or longer. The UV-visible absorption spectra of all three of these compounds have been measured (Barts and Halpern, 1989; Felps et al., 1991; Hess and Leone, 1987; Russell et al., 1987), have maxima that range from <200nm for ClCN, 202nm for BrCN, and 250nm for ICN, with absorption that tails into near-UV and visible wavelengths, (see Figure S2 in the Supplemental Material). Extrapolation of the spectra, combined with photo fluxes estimated from the NCAR TUV model for mid-summer 40° North at the surface, result in a range of photolysis behavior ranging from no tropospheric photolysis of ClCN, to slight photolysis of BrCN ($\tau \cong 135$ days), and faster photolysis of ICN ($\tau \cong 9$ hours). The above gas phase processes provide the context in which to assess the importance of condensed phase loss processes of ClCN, BrCN, and ICN. Rates of loss of XCN compounds due to surface deposition, cloudwater or aerosol uptake would need to be faster than the gas phase processes to be important in the atmosphere. In addition, condensed phase reactions convert XCN to halide ions either by hydrolysis to cyanate, or creation of a carbamyl functionalities. Only photolysis reforms the halogen atom, and therefore maintains active halogen reaction chain. Estimated atmospheric lifetimes of XCN compounds against loss due to condensed phase reactions listed in Table 2 shows a general trend. The lifetimes become shorter as the halogen atom goes from Cl to Br to I, primarily due to higher solubilities. The actual condensed phase losses are likely much shorter than those estimated here because of faster condensed phase reactions that are not taken into account by the brief analysis presented here.

D. Solubility in non-polar media, uptake to organic aerosol, and membrane transport.

The solubilities of HNCO, CH_3NCO, and BrCN in n-octanol were roughly a factor 4 larger than water, while that of ClCN was virtually the same. Reaction rates with n-octanol were the same or slower than for aqueous solutions, except for ClCN which was faster than hydrolysis at pH=7. As a result, loss due to uptake to organic aerosol will be only slightly faster for all of these species. Membrane transport is a key process in determining the extent to which a chemical species will impact biological systems. Simple membrane transport models parameterize this process as diffusion through a lipid bi-layer according to a partition coefficient, K_p, which the ratio of solubilities in lipid versus aqueous media (Missner and Pohl, 2009), and K_{ow} is often used for this partition coefficient. The results of our work indicate that both HNCO and CH_3NCO are more soluble in n-octanol than water, in contrast to other similar small organic acids and N–containing compounds (Table 3). These features will need to be accounted for in assessing the connection by between environmental exposure to HNCO, CH_3NCO, ClCN and BrCN and resulting biochemical effects.

V. Data availability. The data are available on request.

VI. Author contributions. YL and JR performed the laboratory experiments and JR and YL wrote the paper.

VII. Competing interests. The author declare no competing interests.

VIII. Disclaimer. Any mention of commercial products or brands were solely for identifying purposes and should not be construed as an endorsement.

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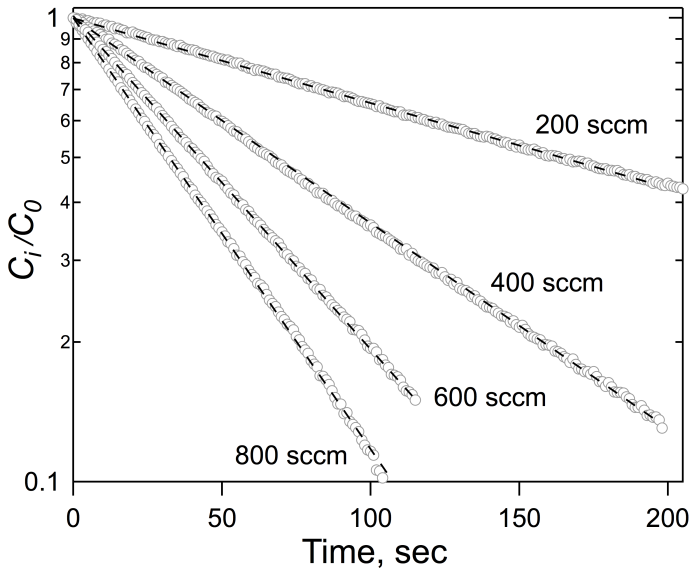

Figure 1. Plots of the ratio of HNCO concentration at time t, C_i, to the initial concentration, C_o, versus time for a series of flow rates. The solvent was tridecane ($C_{13}H_{28}$) and 299 K.

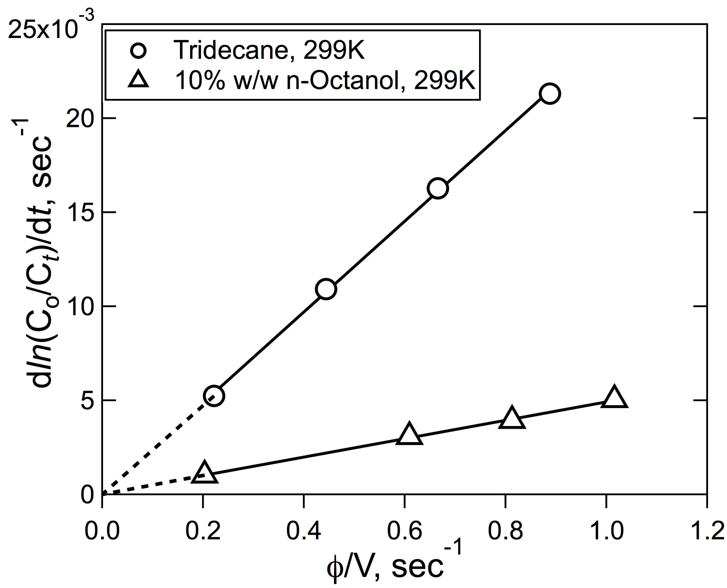

Figure 2. Plots of HNCO loss rate versus the ratio of volumetric flow rate, ϕ, to solution volume, V, for the experiment shown in Figure 1, (circles), and the experiment with 10% w/w n-octanol in tridecane at 299 K (triangles).

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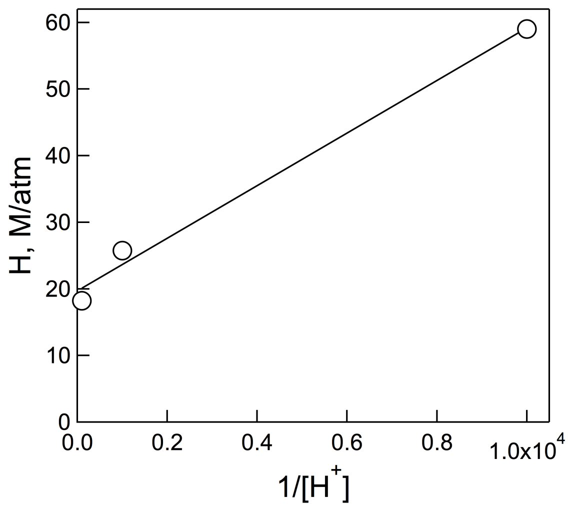

Figure 3. Plot of effective Henry's coefficient of HNCO vs 1/[H+] for the measurements at pH=1, pH=2 and pH=3, and 298 K.

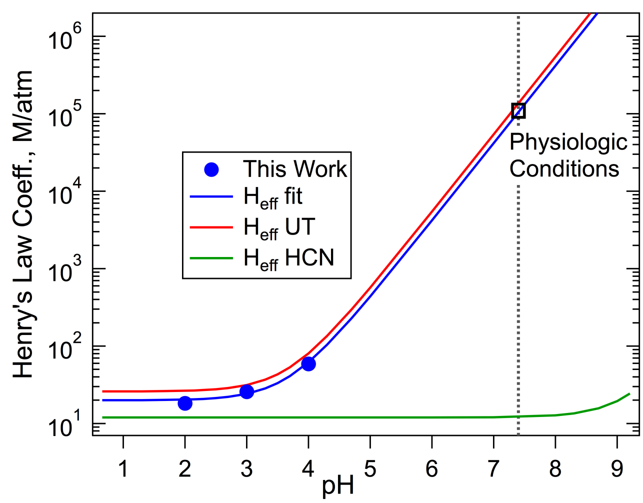

Figure 4. Comparison of effective Henry's coefficients of HNCO measured in this work (blue) with those reported by Borduas et al., 2016, plotted versus pH, according to Equation 4.

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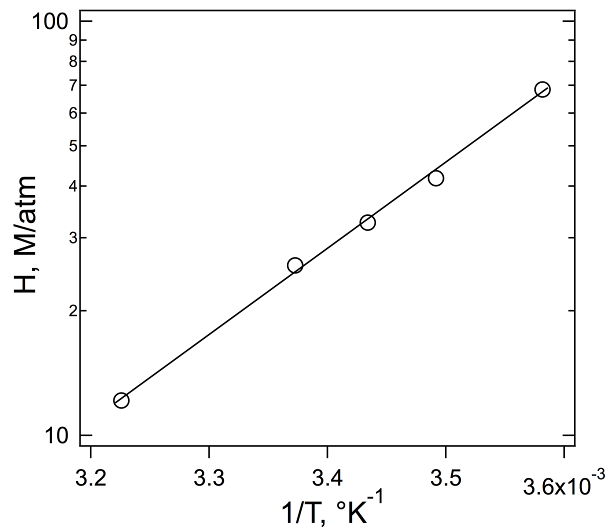

Figure 5. The plot of ln H_{eff} vs 1/T for the experiments performed with HNCO at pH=3. R^2=0.997

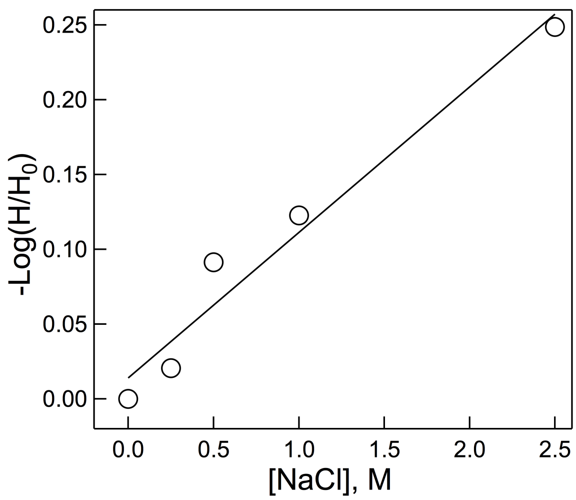

Figure 6. Dependence of the Henry's coefficient (H) at a given salt concentration, relative to that with no added salt (H_0) versus NaCl molarity. R^2 = 0.960

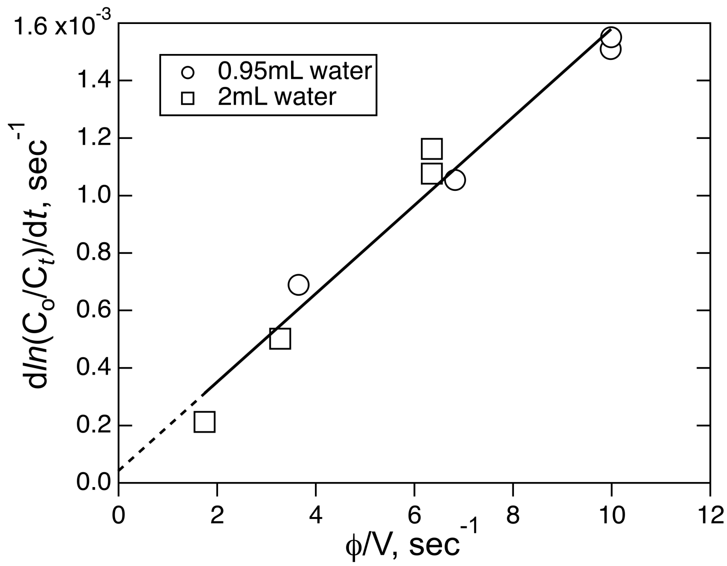

Figure 7., The Plot of ICN loss rate versus the ratio of volumetric flow rate, ϕ, to solution volume, V, for the experiment involving the solubility of ICN in water with the small reactor. The line is the least-square fit to the data (R^2 = 0.968)

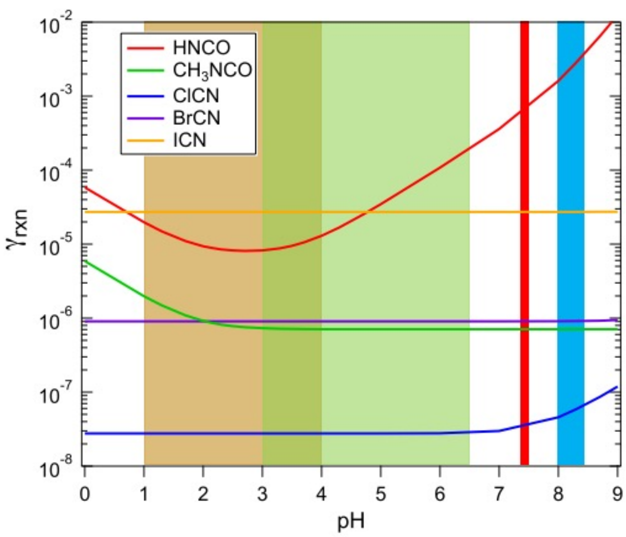

Figure 8. The uptake coefficients of HNCO, CH_3NCO, ClCN, BrCN, and ICN as a function of pH for aqueous solution at approximately 298 K. The shaded areas show the range of pHs characteristic of: aerosols (light brown), cloud/fog water (green), human physiology (red), and ocean surface water (light blue).