Response to Reviewers Comments

We thank the reviewers for their thorough and considered comments. In the following, the authors' responses are shown in *italics* and any added text is shown in red and the location noted by line number in the revised text.

Anonymous Referee #1

General comments: The manuscript presents necessary thermodynamic data for relevant atmospheric compounds including HNCO, CH_3NCO, ClCN, BrCN and ICN. Specifically, values for solubility in water, octonol and tridecane and values for hydrolysis rates were determined with some pH and temperature dependence. In addition, the information on HNCO's solubility and hydrolysis are extended here to salt effect and organic solvent partitioning, useful parameters for fate modeling. The authors use established methods previously described by themselves and others. The HNCO data is well compared with existing literature. The output of this measured thermodynamic data is then used to estimate the lifetimes of HNCO, CH_3NCO, ClCN, BrCN and ICN in the atmosphere against deposition, particle uptake and in cloud reactions/hydrolysis.

These values are important for the atmospheric chemistry modelling community and thus this manuscript is certainly appropriate for publication in ACP. Finally, the study also opens the door for further work on XCN in general and its presence in our atmosphere. I suspect the community will be prompted by this study to go and measure these compounds in ambient air.

We thank the review for these kind introductory comments.

The authors make a great point on line 196-197 that XCN could be a precursor to HNCO. I think this point links the species together very well and should be better emphasized. This important connection can be mentioned in the abstract as well as in the introduction. It is of importance to others studying the atmospheric fate of HNCO. For instance, the authors are encouraged to comment on this pathway being relevant to coastal HNCO measurements such as were made by (Zhao et al., 2014).

We now mention this connection in the abstract with addition of the clause:
… like the XCN species, have the potential to be a significant condensed-phase source of NCO^- and therefore HNCO. (*Lines 58-59).*

As the authors note, we have mentioned this aspect of XCN chemistry in the Introduction, and have now added a sentence at the end of Section IV.C: Depending on the mechanism of condensed phase XCN reactions, this chemistry could be a condensed phase source of NCO^- and therefore HNCO similar that observed by Zhao et al. (2014) in coastal clouds. (Lines 794-796). *We do not go any further on this point as there are no XCN measurements at mid-latitude with which to work.*

To further improve this manuscript, additional attention to detail is required along with presenting all experimental data, whether it is in the text or in the supplementary information.

Unfortunately, only the data for HNCO partitioning is depicted, and the rest of the data is simply missing. It is necessary to include all data acquired and used to determine the experimental values listed in Table 1.

This request is contrary to accepted practice in the presentation of laboratory (or field) results, as the presentation of all the data would make this paper unnecessarily long and difficult to read. However, we are sensitive to this reviewer's desire to see more of the data that underlie the quantities presented in the paper. As a compromise, we have included more plots of the kind shown in Figures 1 and 2 in the original paper. Those are now Figures S2-S12, and represent a reasonable sampling of results for each of the compounds studied here, and include the liquid volumes and flow rates used. In addition, the raw and processed data are available on request as was made clear in the original submission.

Furthermore, the organization and flow of ideas could be streamlined to be more precise and concise. Rather than organize the discussion based on compound, the discussion could be organized based on thermodynamic value. This flow would improve the readability of the manuscript, the organization of the ideas as well as the comparability between thermodynamic data among the compounds studied.

We have carefully considered the reviewer's suggestion for reorganizing the paper and feel strongly that it would be best to leave it organized the way it is. Organizing by thermodynamic quantity, and then discussing each compound in turn, would be very cumbersome, since many of the thermodynamic quantities were only measured for HNCO.

Moreover, when comparing results, a hypothesis can be presented to offer an explanation as to why for example ClCN and BrCN have different solubilities in octonol (lines 548-549).

We have reconsidered our statement on lines 548-549 (original MS) because the relative differences between water and n-octanol solubilities of ClCN and BrCN are both about a factor of 4. This aspect is now commented on and we include a hypothesis for the different n-octanol solubilities of ClCN and BrCN. We now add the sentence: Cyanogen chloride and BrCN have about the same relative differences in solubility in n-octanol (a factor of 3-4) as they did H_2O. The higher solubility of BrCN relative to ClCN could again be due to its higher dipole moment and polarizability (Maroulis and Pouchan, 1997), Lines (596-599)

Finally, a lack of attention to formatting and quantitative detail makes this manuscript somewhat a little harder to read and follow than it should be. For instance, Table 1 is difficult to navigate, Table 2 has inconsistent units and extraneous periods, and Table 3 is missing units. IS units should be used for seconds (s rather than sec).

We now have divided up Table 1 into two tables, one for HNCO and CH_3NCO, and one for the XCN compounds. We hope this will make these easier to read. We have eliminated extraneous periods in what is now Table 3, but wish to keep the units the *way they are since hours, days, weeks and years are easier to conceptualize than if we made each quantity one unit, for example how does one convert 'years' into another unit that is easy to understand? The Table that has K_{ow} data is now Table 4, perhaps the reviewer did not understand that K_{ow} and therefore LogK_{ow} is a unitless quantity. The time units have now been changed to the SI unit 's'*

Principle criteria: -Scientific significance: good -Scientific quality: good/fair – can be easily improved by adding the missing data -Presentation quality: good/fair – can be improved by giving context for studying these specific compounds, streamlining the discussion, being attentive to details and adding clarity to Figures and Tables.
Reviewer recommendation: accept with revisions

Specific comments:
Abstract: In general, the abstract can be edited for conciseness: present (1) solubility rates (2) pH (3) organic solvents.
We have studied the abstract with an eye towards making it more concise, and have done so chiefly by eliminating extraneous explanation (see crossed out words and phrases). We are not sure what a "solubility rate" is, but once again we feel strongly that it is best to summarize the results by compound, and not as the reviewer has suggested. The chief reason being that there were more features of HNCO studied than the other compounds, so arranging by quantity measured, i.e. solubility, reaction rate, pH effects, organic solvents, etc. makes the presentation much more awkward and less concise.

State rational for studying those specific 5 compounds. Some have previously been studied and others have not. It would be interesting to understand why these chemicals were selected.
We have now added a sentence in the abstract explaining the reasons (Lines 56-59):
These nitrogen species are of emerging interest in the atmosphere as they have either biomass burning sources, i.e. HNCO and CH_3NCO, or like the XCN species, have the potential to be a significant condensed-phase source of NCO^- and therefore HNCO.

Line 57: specify reaction rates with water
This suggestion is not appropriate as this clause was meant to encompass the entire study and several other solvents were studied, i.e. n-octanol and tridecane.

Line 61: specify which "other small nitrogen-containing compounds"
We have added the phrase (Line 64); such as HCN, acetonitrile (CH_3CN), and nitromethane

Justify the use of octonol and tridecane (although octonol is evident for Kow values, but tridecane, I am less familiar with and would like to see a brief justification and relevance to the atmosphere). Missing concluding statement
In the interest of concision, we have included a justification for these two solvents in the main text: Tridecane was used because it is the heaviest n-alkane that is still a liquid at

273.15K, and it has purely non-polar character, i.e. no functional groups, so is a slightly different model for non-polar matrices. (Lines 565-566).
We have added the concluding phrase (Lines70-71): features that have implications for multi-phase and membrane transport of HNCO.
This subject is elaborated on in the main text (Lines 625-628).

Introduction:
First paragraph is missing references and context. What is already known about (1) the presence of these compounds in the atmosphere (2) their toxicity/ecosystem impact (3) current and gaps in knowledge relating to their atmospheric fate.
The first paragraph of the introduction was meant to set the stage for the rest of the introduction, which covers almost all of the points that the reviewer feels are missing, in extensive detail. We have added references to the first paragraph to provide context for some of the statements made, and have modified the last sentence of the paragraph, which now reads: "which are biomass burning products, and cyanogen chloride, ClCN, cyanogen bromide, BrCN, and cyanogen iodide, ICN, which could be condensed-phase sources of cyanate ion (NCO^-) and therefore HNCO." (Lines 103-104).

Line 177: unclear statement about electronegativity. Clarify the link between slow OH/Cl reaction rates and electronegativity
We have changed this part of the paper as the phenomenon is much better explained by the fact that the X-CN bond is quite stable, and we have now added a reference to that effect: Radical reaction rates (OH, Cl) have not been measured at room temperatures, but are likely to be slow due to the strength of X-CN bonds (Davis and Okabe, 1968). (Lines 183-184).

Line 205: specify range of pH and temperatures (in general try to be more quantitative)
We have added the following text: in the range pH 2-4, temperature in the range 279-310K, and salt concentration up to 2.5M NaCl. 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, in the range 298-310K, 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 pH 2 and7, and the solubility in n-octanol was also determined at several temperatures, 298 and 310K (Lines 207-213).

Methods: The method is reliable and well explained. The technique does not require calibration since the authors observe a signal decay relative to a starting concentration. However, the authors give concentration ranges of their prepared standards and thus need to explain how these values were calibrated. This information could be included in the supplementary information but needs to be explained.
We point the reviewer to lines 272 – 274 of the original paper, where we explain that we determined the concentrations in the sample stream by comparison to a nitric oxide standard. In addition, we routinely confirm our conversion efficiency using a 10ppmv HCN standard mixture. We also reference Stockwell et al., 2018 where we explain how we determined conversion efficiencies. We feel no additional explanation is needed.

Examples include line 231 (3% of siloxane – 3% of signal intensity? By mass?);
The siloxane impurity was 3% by mole, that is now noted on line(240).

line 238 (1% level impurity);
This was determined on a N basis, and we now reference two papers on the instrument that was used for that determination, so the sentence now reads: The source was also analyzed by an H_3O^+ chemical ionization mass spectrometric system (H_3O^+ CIMS) (Koss et al., 2018; Yuan et al., 2016), which showed that it had no impurities detectable above the 1% (as N) level. (Lines 245-246).

line 235 (how was 10 ppmv mixing ratio quantified?);
This was a commercially prepared gas standard, the clause now reads: … a commercially-prepared 10ppmv gas-phase standard of HCN in N_2 (GASCO, Oldsmar, FL),… (Lines 254-255).

line 259 and so on.
We assume the reviewer is asking how we determined the mixing ratio? This was done using the NO standard as noted above.

Line 277-278: incorrect statement because a C-H bond (413 kJ/mol) is stronger than a N-H bond (391 kJ/mol). It is also not clear what point is being made. This discussion could benefit from being revisited.
The point being made is this. We do not have an independent measure of the conversion efficiency of CH_3NCO, so we are arguing that the thermochemistry measured by Woo and Liu indicates that CH_3NCO should be more easily converted than HNCO. We base this on the bond energies of the weakest bonds in the molecule, which are the ones shown. The C-H bond is not the weakest bond in the CH3NCO molecule, so the reviewer's point is irrelevant. We add the phrase: so CH_3NCO should be easily converted by the Nr catalyst. (Line 288).

Was CIMS used (lines 260 for instance)? (and PTRMS in line 237?) If it was, then the details of its operation should be included.
The H_3O^+ CIMS and PTRMS are the same instrument and we feel its operation is adequately described by the two references given. We now use only H_3O^+ CIMS as a descriptor. (Lines245-246)

Results and discussion:
Biggest issue: all data must be shown either in the text or in the supplementary information.
As noted above, presenting every plot for every experiment would make the paper, or supplement too long. Accepted practice is to show key examples, and to have data available as part of the publication. We have greatly expanded the data that we show in the Supplement.

Figures 3, 4 & 5: missing error bars

We have now included error bars for Figures 3, 5, and 6, and note that the error bars on the points in Figures 4 and 7 are smaller than the width of the symbols. We note those features in the figure captions.

Line 394: specify small organic compounds
We have added three examples: such as acetylene, ethane and butane. (Line 419)

Table 1 is difficult to navigate. Merged cells could help, perhaps dividing the info into one table per compound since some columns are not necessary for all compounds. Perhaps rates can be presented in one table and thermodynamic data in another?
We have now divided Table 1 into 2 tables.

Lines 400-405: good discussion, but could benefit from reporting the quantitative data within the text.
We do not see the value in repeating numbers that are given in Table 1, it would make the text cumbersome and harder to digest.

Line 408: confusing "active hydrogen" terminology for an atmospheric chemist.
An "active hydrogen" is one attached to a O, N, or S atom, we have now added the text: (a hydrogen attached to an O, N, or S atom) (Lines 438-439).

Line 409: an addition reaction likely occurs at the C center.
Yes, this is almost saying the same thing, except with the additional information that the active H ends up on the N in the HNCO molecule. We give examples to make it clear, but we have added the phrase: where the active hydrogen ends up on the N and the other moiety ends up attached to the carbon (Line 439-440).

Hydrolysis rates R4 and R5 for CH3NCO are unclear to me. Does the hydrolysis go through a carbamic acid group (CH3-N(CO)-OH)? Does this group then have to be hydrolyzed with a subsequent water molecule?
We thank the reviewer for the question because it has prompted us to further study the literature to clarify our explanation of the CH_3NCO hydrolysis chemistry. The reviewer was correct in surmising a carbamic acid is formed (with one more H on the N atom than in the reviewer's suggested structure). We now note in the Introduction that R4 and R5 are the net reactions. (Line 156). In the Results and Discussion section we note that Castro et al. imply that the aqueous chemistry starts by hydration of CH_3NCO followed either by reaction with H_3O^+ (fast), or H_2O, (relatively slow), the net reactions being R(4) and R(5). We now write: The mechanism of CH_3NCO hydrolysis and other solution chemistry is discussed by (Al-Rawi and Williams, 1977; Castro et al., 1985). The hydrolysis of CH_3NCO is thought to proceed first by formation of a methyl carbamic acid:

$$CH_3NCO + H_2O \leftrightarrow CH_3NHC(O)OH \qquad (R13)$$

which is analogous to the way water adds across the N=C bond of HNCO. The methyl carbamic acid then either reacts with H_3O^+(faster) or H_2O (slower) to produce $CH_3NH_3^+$ and CO_2, or CH_3NH_2 and CO_2, yielding the net reactions (R4) and (R5):

$CH_3NCO + H_3O^+ \rightarrow CH_3NH_3^+ + CO_2$ (R4)
$CH_3NCO + H_2O \rightarrow CH_3NH_2 + CO_2$ (R5)

The Henry's law measurements in our work imply that if (R13) is happening, it must be to a quite minor extent, otherwise the H constant for CH_3NCO would be much larger than it is. Solution-based studies of MIC in the presence of strong acid anions (Al-Rawi and Williams, 1977; Castro et al., 1985) also imply that a complex mechanism takes place, (Lines 483-499)

Order of reaction numbering needs to be revisited to match the order the reactions were introduced.
We have insured the reaction numbering is correct. Note that several sets of reactions were first presented in the Introduction, so might appear to be mis-numbered when brought up again in the Results and Discussion.

There are also errors with the hydrolysis equations for XCN. For a hydrolysis reaction to occur, H_2O cannot be on the same side of the equation.
We have heard some purists claim that protons don't exist as such in aqueous solution and should always be designated H_3O^+. However, we have no strong attachment to this convention, so we have changed R6 to read:

$XCN + H_2O \rightarrow HOCN + H^+ + X^-$ (Line 538)

So I think R7 should read; XCN + OH- → HOCN X-.
Changed:

$XCN + OH^- \rightarrow HOCN + X^-$ (Line 539)

R8 is a tautomerization reaction and is therefore denoted with a doubled headed arrow ↔. Tautomerization does not require H+. R8 should read HOCN ↔ HNCO.
The reviewer is correct that R8 is a tautomerization reaction and so we have added the double arrow. However, as with almost all tautomerizations, this reaction does not happen in the gas phase at room temperature, but requires either a surface or a solution. Therefore, it is correct to have H+ on both sides of the equation because H+ adds to one side of the molecule and dissociates from the other side, the H atom does not migrate from one end of the molecule to the other. The key piece of information is that this equilibrium, by far favors HNCO, a feature covered by Belson and Strachan.

Brief discussion on anion complexation for XCN was unclear. Do the authors therefore expect a salting in/out effect on the solubility of these compounds then?

We reference the studies that have hypothesized anion complexation, but note that it did not apply to our studies. We have now added some text noting that this could be the subject of further work.:
however, such complexation should be considered in future condensed phase studies of XCN compounds. (Line 542)

Missing data for lines 531-534
Once again, we choose not to clutter the text up with numbers that can be readily seen in the Tables.

ICN discussion missing in paragraph starting at line 546
We were not able to measure the solubility of ICN in n-octanol with either the large or the small reactor. We now note this in the Methods section: Attempts to measure ICN solubilities in n-octanol were not successful using either reactor. (Line 337-338).

Atmospheric and environmental chemistry implication:
Figure 8: lines 601-602 described that data from other studies are presented, but it is unclear in Figure 8 who's data is which.
The lines noted details about what data for which compounds are used for Figure 8, we have added the temperature and fixed a typo, but we are not sure what other designations the reviewer believes are missing. The pHs designated by the shaded areas are generally understood to apply to those matrices. This sentence now reads: The results of these calculations are shown in Figure 8 for the H measurements at 298K reported here, k_{hydr} for HNCO reported by Borduas et al., (2016), k_{hdyr} for CH_3NCO from this work and k_{hydr} for ClCN from Bailey and Bishop (1973). (Line 653).

Lines 631-632: knowing that (Barth et al., 2013) data used formic acid, the authors can actually specific how their own revised values could affect their modeled results.
The reviewer is correct, we can now comment on the H_{eff} temperature dependence used by Barth et al., (2013), and do so by including a figure in the Supplemental Material (S13) showing the difference and include the following text: We can point out that our results yielded slightly lower H_{eff} (~22%) at the lowest temperature we measured, compared to the values used by Barth et al., (2013), see Figure S13. This would result in slightly slower removal rates in the Barth et al., model in low-temperature clouds. (Lines 684-686).

Technical comments: Line 60: attention to significant figures in reporting Ka.
The numbers reported are the error in the fit to our data, ($\pm 0.28 \times 10^{-4}$ M) propagated through log10 to obtain the uncertainty the pKa. But we see the reviewer's point here, we now round 0.28 up to 0.3 and, 0.06 up to 0.1 pH units. (Line 62, Line 390-391)

Line 64: specify the counter ion of NH4+
We now specify that it was NH_4Cl; as NH_4Cl, (Line 66).

The SI unit for seconds is "s", not "sec", and should be corrected throughout.
Done – please see red highlights in text.

Line 65: missing verb in second clause.

We do not see the problem, the verb "reaction" serves for the sentence ending on that line, and "were found to be" is the verb for the sentence that starts on that line.

Check syntax of lines 105-109. Best to attribute each reference with its relevant statement here.

We agree that the sentence, while correct, is awkward to read. So we have made it more concise: There are relatively few observations of HNCO in ambient air, showing "background" mixing ratios that range from 10pptv to over several ppbv depending on the nature of regional sources, and peak mixing ratios approaching a few ppbv, observed in areas impacted by local biomass burning (Line 111)

We disagree that the sentence needs to be parsed further as this was meant to be an introductory statement. To try to specify which paper shows what in detail does not add to the paper, as specific information from those references was not used in subsequent discussion. An exception to this is work of Zhao et al., which was dealt with at the end of the paper.

Arrows for all reactions should be including using symbols, like →

Done, please see red highlights in text.

Line 125: define pKas

We have now included the sentence: The pKa is defined as the negative Log_{10} of the dissociation constant of an acid, and can be thought of as the pH at which the acid and its conjugate base (in this case BH+ and B) are at the same concentration. (Lines 132-133)

Many references are based on personal communication, and I believe that in some circumstances work/reviews can be referenced instead.

We wish it were the case that there was published work to reference here. The BrCN and ICN data were not finalized and reported to the NASA website at the time our paper was submitted, and so by agreement, could not be referenced (nor explicitly described). That is no longer the case for BrCN, so we now reference the BrCN data on NASA data portal: NASA, 2019 (Line 175)

There is a much more thorough measurement of the OH + CH_3NCO rate constant that is considerably lower than the literature value, but unfortunately, it has not been published, so we are only able to refer to it in vague terms. We have now updated this text: however recent work indicates that secondary chemistry may have made this rate high by a significant amount (Papanastasiou, et al., manuscript in preparation, 2019). In addition, there are likely condensed-phase reactions that are faster than the simple hydrolysis reactions consider in this work. Never-the-less, it is useful to estimate the atmospheric loss rates implied by our work, as a baseline against which future atmosphere observations can be judged, and the importance of other heterogeneous processes can be assessed. (Lines 744-748).

For instance, indoor surfaces with chlorine to substantiate “J. Abbatt personal communication”: (Wong et al., 2017).

The reviewer is incorrect in surmising that Wong et al., 2017 describe the observation of cleaning of indoor surfaces producing HNCO. This observation was made during a project that took place in the Summer of 2018, the results of which were kindly communicated to us by one of the PIs of that project, J. Abbatt. Our understanding is that this new result has yet to be published, accordingly, we make no change to this statement.

Line 204: delete on iteration of “at several”

Done, (Line 212)

Line 244: specify the IUPAC name for Chloramine-T

This renders our description unnecessary so we include the name: N-Chloro-p-toluenesulfonamide sodium salt *and strike the description we gave,* (Line 252-253).

Lines 293: already been said, could delete for conciseness.

Done: (Lines 303)

Lines 330-331: it sounds like the manufacturer specifications had a slight temperature dependence?

Yes, we state that in the sentence.

Lines 339-346: repetitive

We eliminate this text, and slightly modify what is now the first sentence to read: Examples of the data generated by equilibration experiments are 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). Numerous other examples of both decay curves and decay rate versus ϕ/V are shown in the Supplementary Material for a range of different analytes and solutions. (Lines 358-361).

Line 567: should read “common”

We prefer: commonly used (Line 617).

Line 699: quantify “fairly readily”

We have now modified this section to read: The results of our solubility measurements indicate that ClCN will volatilize from the condensed phase fairly readily, e.g. within seconds of the application of a thin film of chlorine bleach cleaning solution, or the bubbling of air though a spa in which ClCN is dissolved. As a result, the atmospheric removal of ClCN should be considered. (Lines 764-765).

Be consistent in using chemical names vs formula. (CH3CN instead of acetonitrile for instance in line 577

We now ascribe to the convention of using the name and the formula when the compound is first introduced and then the formula after that. The exception is when *starting a sentence, then we use the name. The copy editor can correct us if that is not how the journal does it.*

Reviewer 2

This manuscript by Roberts and Liu presents a fundamental laboratory experiment to determine thermodynamic data required to predict atmospheric fates of HNCO, CH_3NCO, and three XCN species. HNCO and CH_3NCO are toxic volatile organic compounds for which an accurate understanding of their atmospheric fate is critical. In particular¨ ambient measurement of HNCO was first made possible a few years ago by Roberts and coworkers themselves. Although a number of studies have focused on the chemical behavior of HNCO since then, fundamental thermodynamic data, such as those presented here, are still lacking. XCN species are novel species whose atmospheric importance has been implied but has not been fully established.

The experiments were conducted with well-established methods, measurements and analyses were performed with cautions, and the choice of experimental conditions is thoughtful. Publication in ACP should be considered, but not before substantial revisions are made

Major comments:
1) The use of Henry's law constant.
Throughout the entire manuscript, I am concerned about the current use of effective Henry's law constant (H_{eff}) vs the intrinsic Henry's law constant (H_{HNCO} or H) It seems that the authors fully understand the difference between the two, though the usage of H and H eff is inconsistent and misleading. I would recommend the authors first use a few sentences in the introduction or method to clarify the difference between H eff and H, and then revisit each H and H_{eff} throughout the manuscript to revise them accordingly
Here are some particular examples:

> -Line 309 and Eq (1). My understanding is that the H determined using the experimental method and Eq (1) is in fact H_{eff}. The authors should clarify that.
>
> -The only intrinsic Henry's law constant appears is in Eq (4) and related discussions. The authors decide to temporarily use H_{HNCO} here.

We have taken the reviewer's suggestion and use the correct designation of H_{eff} for HNCO in the introduction (Line 116), and have a more thorough explanation of effective Henry's coefficient in the Results section and are careful to use the proper terms in the text (see text highlighted in red) label the Figures correctly. The use of H_{HNCO} is no longer necessary, so we use H in this equation. The revised section reads as follows:
The dependence of aqueous solubility of HNCO on pH is expected given it is a weak acid;

$HNCO_g \leftrightarrow HNCO_{aq}$ $H = [HNCO]_{aq}/[HNCO]_g$ Eq. (2)
$HNCO_{aq} + H_2O_{aq} \leftrightarrow H_3O^+ + NCO^-$ $K_a = [NCO^-][H^+]/[HNCO]$ Eq. (3)

so that what is measured is the effective Henry's coefficient, H_{eff}, which involves the sum of all forms of HNCO in solution:

H_{eff} = {[HNCO]$_{aq}$ + [NCO-]}/[HNCO]$_g$ Eq. (4)

Substituting for [NCO^-] using the rearranged form of Eq(3), and using Eq(2) we get the relationship for H_{eff}:

H_{eff} = H(1 + K_a/[H^+]) Eq. (5)
Lines (375-387).

We also mention that we measure H_{eff} in our experiments but the distinction is only import in the case of the weak acid HNCO. The text reads: In practice we measure the effective Henry's coefficient in our experiments, but the distinction is only important for the weak acid, HNCO, as described in the Results and Discussion section below. (Lines 328-329).

2) Atmospheric implication (Section IV)© is one of the most important sections in the manuscript and requires some revisions. In particular:

-While the focus of this study is heterogeneous processes, the authors mention about the gas-phase fates of HNCO and CH3NCO in a rather sporadic manner. I was under an impression that the gas-phase loss of HNCO and CH3NCO is less important than the heterogeneous process, until I saw the OH rate coefficient of CH3NCO (3 6e-12 cm3 molec-1 sec-1) and realized that it is actually very important for CH3NCO. I would suggest the authors extend the discussion of atmospheric fate to include gas-phase loss processes for a more complete picture.

As described in the response to reviewer 1, this is a difficult issue for us to address, since there is a thorough study of the OH + CH_3NCO rate constant that has resulted in a significantly lower rate constant, and addresses the probable reason for the high result in the single measurement reported in the literature. Unfortunately, it has not been published yet so we cannot quote it directly. We have modified this section to note that the literature value is in question, citing a personal communication (D. Papanastasiou). Moreover, there is the real possibility that condensed phase reactions other than hydrolysis could compete with the OH reaction rate. Accordingly, it is useful to estimate the heterogeneous loss processes of CH_3NCO due to the chemistry that we currently know. We have added to this paragraph:
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 = 3.6×10^{-12} cm^3 $molec^{-1}$ s^{-1} (Lu et al., 2014), however recent work indicates that secondary chemistry may have made this rate high by a significant amount (Papanastasiou et al., manuscript in preparation, 2019). In addition, there are likely condensed-phase reactions that are faster than the simple hydrolysis reactions consider in this work. Never-the-less, it is useful to estimate the atmospheric loss rates implied by this work, as a baseline against which future atmosphere observations can be judged, and the importance of other heterogeneous processes can be assessed.
(Lines 744-748)

> -The introduction to the loss processes, e.g., deposition velocity, uptake coefficient, etc., is very insightful and resourceful. However, the authors perform the actual analysis at a rather abstract level after a full-bodied introduction. In particular, the fate of HNCO is summarized into a couple of numbers in Table 2, which in a sense self-negates all the detailed analyses performed by authors themselves. Given all the HNCO data at different pH and temperatures etc., HNCO deserves a more detailed discussion in a separate paragraph, and perhaps with additional diagrams.

We agree that our results allow for a better description of HNCO loss processes compared to the previous studies, e.g. (Barth et al., 2013), however a detailed analysis is beyond the scope of this paper. Simple calculations don't allow us to refine the highly polluted case modeled by Barth et al., so we prefer to use that number in our Table 3 as a limiting case. The possible impact of higher solubility in organic substrates on the aerosol loss processes is now explored briefly by estimating the lifetime against reaction for mixed organic/aqueous phase particles. This section now reads: Given that aerosol particles in most polluted atmospheres are at least half organic carbon by mass (Jimenez and et al., 2009), it is useful to estimate what effect an increased solubility of HNCO might have on its removal lifetime. If take our 1000 $\mu m^2/cm^3$ surface area aerosol from the above calculation, assume a 50/50 organic to aqueous distribution and that the solubility of HNCO in the organic fraction is the same as n-octanol, we can arrive at a weighted average Henry's solubility of 55 M/atm. If we combine that with the same reaction rate corresponding to pH1, then the lifetime of HNCO against reaction to this aerosol drops to about 2 days, a significant effect.
(Lines 724-730).

> -It is surprising that the in-cloud rxn value of HNCO in Table 2 is directly taken from another study. Why don't the authors derive this value from their own data from this study using Eq. 16? I thought that was the whole purpose of doing all the analyses for HNCO.

We have now modified this section with the material added above, but wish to keep the number from the Barth et al., 2013, as it was calculated using a fully coupled model.

> -HNCO and other compounds' water solubility varies significantly across temperatures and pH What condition is used to derive logKow in Table 2? No explanation is provided. When the Henry's law constant of HNCO varies to such an extent, is Kow of HNCO helpful at all?

We listed the temperatures in column 2 of the Table and we now make it clear that we use the intrinsic H coefficients calculated from our work. The reviewer is correct to wonder how K_{ow}s for weak acids can have application at physiologic pH, a point we should have explained further. We have now added text and a reference to explain that membrane transport theory uses K_{ow}s and pK_as of weak acids to estimate transport rates. In other words, such models account for the weak acid equilibrium and the solubility differences between aqueous and membrane media. Our results show directly that HNCO is more efficiently transported by membranes than a common weak acid, formic acid. We have now included this material in the section on K_{ow}: However, transport models of biological systems account for these acid base equilibria along with using the K_{ow} to estimate transport rates (Missner and Pohl, 2009). 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 HC(O)OH, so should have larger membrane permeabilities. (Lines 625-626).

3) Miscellaneous typos, mistakes, etc. Each of them is minor by itself, but the overall quality of this manuscript should be improved to achieve a professional level.

Minor and technical comments:

-Line 204 "at several at several"

This has now been fixed, see response to reviewer 1 above.

-Line 284: as the authors point out, the selectivity of the detection method is indeed important. Did the authors try using CIMS and PTRMS which should be able to verify the selectivity of the Nr method?

We did not use CIMS or PTRMS to verify the selectivity of our Nr method since it is well established that the solution-phase chemistry of these compounds leads to highly soluble products that do not come out of solution under the conditions used here.

-Line 314 "phi/V"

Corrected, (Line 324).

-Line 324 "cc/min" should be made consistent with "ml/min" used previously (Line 297)

We prefer to use cc instead of mL, so all the units have been made consistent. Please see text noted in red throughout.

-Line 345 redundant

This section was removed in changes suggested by reviewer 1.

-Line 348 "volumetric flow rate to solution volume" is already defined as phi/V previously

Now changed to ϕ/V, (Line 359).

-Line 351 "lass rate"

Corrected: (Line 364).

-Line 365 should define effective Henry's law coefficient as H_{eff} here

As noted above, we have moved this discussion to the Introduction.

-Line 386 394. Please consider citing this paper for salting in/out and Setschenow constants: Wang et al. EST 2014 10.1021/es5035602

We now add a sentence on the results of Wang et al., who found that Setschenow constants for ammonium sulfate are larger than those for NaCl: Interestingly, Wang et al., (2014) found that Setschenow constants for ammonium sulfate {$(NH_4)_2SO_4$} are typically larger than those for NaCl, a feature which might impact the uptake of HNCO to aerosol particles having substantial $(NH_4)_2SO_4$ content. (Lines 420-422).

> -Line 411 R10: out of curiosity, H_2O can be technically treated as a type of ROH. Any suggestion on why the reaction mechanisms of HNCO towards H_2O and ROH are different?

This is a really good question. The initial mechanisms are the same, both HOH and ROH add across the N=C bond in the HNCO molecule. The difference is that HOH makes carbamic acid [$H_2NC(O)OH$] which is unstable and decomposes to NH_3 and CO_2, and ROHs make carbamates ($H_2NC(O)OR$, carbamic acid esters), which are stable molecules. We now have added a sentence in this section to that effect: Note that this is really the same mechanism as the neutral hydrolysis of HNCO, except that the addition of water forms carbamic acid, $H_2NC(O)OH$ which is unstable and decomposes to NH_3 and CO_2. (Lines 445-446).

> -Line 624-625: By using an extremely polluted condition, I guess the authors are trying to derive the lower limit of Aerosol Dep. Lifetime. This should be clarified somewhere, perhaps as a notes to Table 2.

That was correct, we wished to estimate a lower limit to lifetime against aerosol deposition. We have now added a clause to that sentence: … to obtain a lower limit to the lifetime against this process, (Line 676-677)

> -Line 682 check the unit of k

The reviewer is correct that we had the units of the rate constant wrong, that has now been corrected; (Line 774-775).

> -Figure 4: The figure contains data for H_{eff} HCN, but nothing is mentioned in the caption.

We now mention this in the caption with text: The green line was calculated from the intrinsic H coefficient reported by Sander, (2015), and its pKa,(9.3). (Line 1178-1179).

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

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Abstract

Condensed phase uptake and reaction are import 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. These nitrogen species are of emerging interest in the atmosphere as they have either biomass burning sources, i.e. HNCO and CH_3NCO, or like the XCN species, have the potential to be a significant condensed-phase source of NCO^- and therefore HNCO. Solubilities and first-order reaction rate 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~~ and had an intrinsic Henry's law solubility of 20 (±2) M/atm, and a K_a of 2.0 (±0.3) $\times10^{-4}$ M (~~which corresponds to~~ pK_a = 3.7 ±0.1) at 298K. The temperature dependence of HNCO solubility was very similar to other small nitrogen-containing compounds, such as HCN, acetonitrile (CH_3CN), and nitromethane, 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, as NH_4Cl, was measured at pH=3, and found to be 1.2 (±0.1) $\times10^{-3}$ $M^{-1}s^{-1}$, ~~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), features that have implications for multi-phase and membrane transport of HNCO. The first-order loss rate of HNCO in n-octanol was determined to be relatively slow 5.7 (±1.4) $\times10^{-5}s^{-1}$. 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) M/atm at 298K to 2.8 (±0.3) M/atm at 310K. 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} s^{-1} from 298 to 310K. The aqueous solubilities of XCN ~~was~~ 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 (Li et al., 2000; Roberts et al., 2011). 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 (Keller-Rudek et al., 2013). 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 (Boenig and Chew, 1999; Broughton, 2005; McMaster et al., 2018; Wang et al., 2007). 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, which are biomass burning products, and cyanogen chloride, ClCN, cyanogen bromide, BrCN, and cyanogen iodide, ICN, which could be condensed-phase sources of cyanate ion (NCO^-) and therefore HNCO.

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, showing "background" mixing ratios that range from 10pptv to over several ppbv depending on the nature of regional sources, and peak mixing ratios approaching a few ppbv, 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 shows behavior typical of weak acids, where the effective Henry's coefficient H_{eff} varies with pH, and so HNCO is only slightly soluble at pHs characteristic of atmospheric aerosol (pH= 2-4) and 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 as 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). The pKa is defined as the negative Log_{10} of the dissociation constant of an acid, and can be thought of as the pH at which the acid and its conjugate base (in this case BH+ and B) are at the same concentration.

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 (California, 2008).

There have been only a few studies of the gas phase loss rates of CH_3NCO including reaction with OH radical, which appears to be slow based on the mostly recent measurements (Lu et al., 2014) (Papanastasiou et al., in preparation, 2019), reaction with chlorine atoms (Cl) which might be as much as 20% of OH under some atmospheric conditions (Papanastasiou et al., in preparation, 2019), and UV photolysis which has a negligible contribution to atmospheric loss (Papanastasiou et al., in preparation, 2019). 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, exhibiting the following overall reactions;

$$CH_3NCO + H_2O + H^+ \rightarrow CH_3NH_3^+ + CO_2 \qquad (R4)$$

$$CH_3NCO + H_2O \rightarrow CH_3NH_2 + CO_2 \qquad (R5)$$

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),(NASA, 2019). 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 also 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 to the strength of X-CN bonds (Davis and Okabe, 1968). 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;

$$XCN + H_2O \rightarrow HOCN + H^+ + X^- \quad (R6)$$

$$XCN + OH^- \rightarrow HOCN + X^- \quad (R7)$$

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);

$$HOCN + H^+ \rightarrow HNCO + H^+ \quad (R8)$$

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 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 in the range pH 2-4, temperature in the range 279-310K, and salt concentration up to 2.5M NaCl. 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, in the range 298-310K, 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 pH 2 and 7, and the solubility in n-octanol was also determined at several temperatures, 298 and 310K. 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 of siloxanes (3% by mole), 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 (H_3O^+ CIMS) (Koss et al., 2018; Yuan et al., 2016), which showed that it had no impurities detectable above the 1% (as N) 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:

$$HCN + HOCl \rightarrow ClCN + H_2O \qquad (R9)$$

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 (*N*-Chloro-*p*-toluenesulfonamide sodium salt, 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 commercially-prepared 10ppmv gas-phase standard of HCN in N_2 (GASCO, Oldsmar, FL), 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/100cc 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%), (H_3O^+ CIMS), 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 on 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 were on the order of 250-350 ppbv in 1 SLPM in mixing ratio. Analysis by iodide ion chemical ionization mass spectrometry {Warneke, 2016 #1366} 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) so CH_3NCO should be easily converted by the Nr catalyst. 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 cc. Liquid volumes used in the experiments ranged from 20 to 50 cc, and the volumetric flow rates used ranged from 170 to 1070 ambient cc/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/s) to liquid volume (V, cm^3), the effective Henry's Law solubility H_{eff} (M/atm), and the first-order loss rate (k):

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

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 ϕ/V of $1/H_{eff}RT$, where R is the ideal gas constant, and T the temperature (K), and an x-intercept of k, the first-order loss rate (s^{-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. In practice we measure the effective Henry's coefficient in our experiments, but the distinction is only important for the weak acid, HNCO, as described in the Results and Discussion section below.

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 cc 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. Attempts to measure ICN solubilities in n-octanol were not successful using either reactor.

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 solutions 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).~~ Examples of the data generated by equilibration experiments are 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 ϕ/V (Figure 2). Numerous other examples of both decay curves and decay rate versus ϕ/V are shown in the Supplementary Material for a range of different analytes and solutions. 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 loss 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 Tables 1&2 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, and its dissolution is accompanied by an acid-base equilibrium;

$$HNCO_g \leftrightarrow HNCO_{aq} \qquad H = [HNCO]_{aq}/[HNCO]_g \qquad \text{Eq. (2)}$$

$$HNCO_{aq} + H_2O_{aq} \leftrightarrow H_3O^+ + NCO^- \qquad K_a = [NCO^-][H^+]/[HNCO] \qquad \text{Eq. (3)}$$

so that what is measured is the effective Henry's coefficient, H_{eff}, which involves the sum of all forms of HNCO in solution:

$$H_{eff} = \{[HNCO]_{aq} + [NCO\text{-}]\}/[HNCO]_g \qquad \text{Eq.(4)}$$

Substituting for $[NCO^-]$ using the rearranged form of Eq(3), and using Eq(2) we get the relationship for H_{eff}:

$$H_{eff} = H(1 + K_a/[H^+]) \qquad \text{Eq. (5)}$$

The plot of H_{eff} vs $1/[H+]$ is shown in Figure 3, the slope of which is $H \times K_a$, and the intercept is the intrinsic Henry's Law constant, H. The resulting fit ($R^2 = 0.99$) gave a H = 20 (±2) M/atm, and a K_a of 2.0 (±0.3) $\times 10^{-4}$ M (which corresponds to $pK_a = 3.7 \pm 0.1$). 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. 5 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;

$$d\ln H_{eff}/d(1/T) = -\Delta H_{soln}/R \qquad \text{Eq. (6)}$$

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 (-4.1 kJ/mole), and nitromethane (-33.3 kJ/mole) (Sander, 2015), but different than that of formic acid (HC(O)OH) (-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:

$$-\text{Log}(H_{eff}/H_{eff0}) = k_s \times [I] \qquad \text{Eq. (7)}$$

where H_{eff} is the Henry's coefficient at a given ionic strength, I, and H_{eff0} 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 $0.097 \pm 0.011\ M^{-1}$. The magnitude of the salting out effect on HNCO is similar or slightly smaller than those found for other small organic compounds in NaCl, such acetylene, ethane and butane (Clever, 1983; Schumpe, 1993), Interestingly, (Wang et al., 2014) found that Setschenow constants for ammonium sulfate $\{(NH_4)_2SO_4\}$ are typically larger than those for NaCl, a feature which might impact the uptake of HNCO to aerosol particles having substantial $(NH_4)_2SO_4$ content.

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;

$$k_{hydr} = \frac{k_1[H^+]^2 + k_2[H^+] + k_3K_a}{K_a + [H^+]} \qquad \text{Eq. (8)}$$

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 8 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” (a hydrogen attached to an O, N, or S atom)(Belson and Strachan, 1982), through simple addition across the N=C bond, where the active hydrogen ends up on the N and the other moiety ends up attached to the carbon. For example, alcohols react to yield carbamates, i.e. esters of carbamic acid:

$$HNCO + ROH \rightarrow H_2NC(O)OR \qquad (R10)$$

Note that this is really the same mechanism as the neutral hydrolysis of HNCO, except that the addition of water forms carbamic acid, $H_2NC(O)OH$ which is unstable and decomposes to NH_3 and CO_2. In the same fashion, $HNCO/NCO^-$ can react with ammonia in solution to yield urea

$$HNCO + NH_3 \leftrightarrow H_2NC(O)NH_2 \qquad (R11)$$

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

$$HNCO + RNH_2 \leftrightarrow H_2NC(O)NHR \qquad (R12)$$

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) $\times10^{-3}$ s^{-1} is faster than the hydrolysis at pH3, 0.66 (±0.06) $\times10^{-3}$ s^{-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).

$$\frac{d[HNCO+NCO]}{[HNCO+NCO]} = -(k_{hydr} + k_{11}[NH_4{}^+])dt \qquad \text{Eq. (9)}$$

We calculate a value of 1.2 (±0.1) $\times10^{-3}$ $M^{-1}s^{-1}$ for k_{11} from our measurements which is much faster than the rate constants reported by previous studies, 5 $\times10^{-6}$ $M^{-1}s^{-1}$ (Jensen, 1959) and 1.5 $\times10^{-5}$ $M^{-1}s^{-1}$ (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 MIC 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 MIC solubility, at least that 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 MIC, 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. The mechanism of CH_3NCO hydrolysis and other solution chemistry is discussed by (Al-Rawi and Williams, 1977; Castro et al., 1985). The hydrolysis of CH_3NCO is thought to proceed first by formation of a methyl carbamic acid:

$$CH_3NCO + H_2O \leftrightarrow CH_3NHC(O)OH \qquad \text{(R13)}$$

which is analogous to the way water adds across the N=C bond of HNCO. The methyl carbamic acid then either reacts with H_3O^+ (faster) or H_2O (slower) to produce $CH_3NH_3^+$ and CO_2, or CH_3NH_2 and CO_2, yielding the net reactions (R4) and (R5):

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

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

The Henry's law measurements in our work imply that if (R13) is happening, it must be to a quite minor extent, otherwise the H constant for CH_3NCO would be much larger than it is. Solution-based studies of MIC in the presence of strong acid anions (Al-Rawi and Williams, 1977; Castro et al., 1985) also imply that a complex mechanism takes place, involving a reversible complexation, (shown here for HSO_4^-):

$$CH_3NCO + HSO_4^- \leftrightarrow CH_3NH\text{-}C(O)\text{-}OSO_3^- \qquad (R14)$$

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 R14 equilibrium. Again, 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:

$$k_{MIC} = k_5 + k_4[H_3O^+] \qquad (Eq\ 10)$$

to derive the following values for k_5 =1.9 (±0.6) ×10^{-3} s^{-1}, and k_4 = 0.13 (±0.07) $M^{-1}s^{-1}$. These values are in reasonable agreement with the value for k_5 given by Al-Rawi and Williams, (1977), 1.47 x10^{-3} s^{-1} considering those measurements were at 1M KCl, and the value for k_4 = 0.16 $M^{-1}s^{-1}$ 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 2. The ClCN solubility was essentially the same as that measured for MIC 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 0.95cc). 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 (±41) 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 MIC:

$$XCN + A^- \leftrightarrow [XCN \bullet A]^- \qquad (R15)$$

$$XCN + H_2O \rightarrow HOCN + H^+ + X^- \qquad (R6)$$

$$XCN + OH^- \rightarrow HOCN + X^- \qquad (R7)$$

This complexation can be ignored in our study for ClCN and BrCN since the experiment was performed in DI water, however, such complexation should be considered in future condensed phase studies of XCN compounds. Accordingly, the expression for the ClCN and BrCN hydrolysis rate constant is;

$$k_{XCN} = k_w + k_{OH}[OH^-] \qquad (Eq.11)$$

Bailey and Bishop (1973) found $k_w = 2.58 \times 10^{-6}\ s^{-1}$ and $k_{OH} = 4.53\ M^{-1}s^{-1}$ at 299.7 K, for ClCN, which corresponds to 3.03×10^{-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 ($\pm 4.2 \times 10^{-4}\ s^{-1}$). 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 $1.9 – 9.2 \times 10^{-5}\ s^{-1}$, (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, $4.4\ (\pm 7.6) \times 10^{-5}\ s^{-1}$, 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. Tridecane was used because it is the heaviest n-alkane that is still a liquid at 273.15K, and it has purely non-polar character, i.e. no functional groups, so is a slightly different model for non-polar matrices.

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 human 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 (R10), 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 and BrCN have about the same relative differences in solubility in n-octanol (a factor of 3-4) as they did H_2O. The higher solubility of BrCN relative to ClCN could again be due to its higher dipole moment and polarizability (Maroulis and Pouchan, 1997). The first-order loss rates of ClCN and BrCN could be determined from the flow reactor experiments and were 1.3 (±0.4) $\times 10^{-3}$ s^{-1} and 9 (±2) $\times 10^{-5}$ s^{-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 used 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;

$$K_{ow} = H_{oct}/H_{H2O} \qquad \text{(Eq.12)}$$

The results are listed in Table 4 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. However, transport models of biological systems account for these acid base equilibria along with using the K_{ow} to estimate transport rates (Missner and Pohl, 2009). 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 HC(O)OH, so should have larger membrane permeabilities. Similarly, the n-octanol partition coefficient of CH_3NCO is 6.8 times larger than that of CH_3CN. 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):

$$\gamma_{rxn} = \frac{4HRT\sqrt{kD_a}}{<c>} \qquad \text{(Eq.13)}$$

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^2 s^{-1} for HNCO and 1.6 x10^{-5} cm^2 s^{-1} for CH_3NCO and ClCN, 1.2 x10^{-5} cm^2 s^{-1} for BrCN, and 1.0 x10^{-5} cm^2 s^{-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 at 298K reported here, k_{hydr} for HNCO reported by Borduas et al., (2016), k_{hdyr} for 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:

$$v_d = \frac{1}{\frac{1}{v_t} + \frac{1}{\gamma\frac{<c>}{4}}} \qquad \text{(Eq.14)}$$

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/s for a reasonably mixed boundary layer (Wesely and Hicks, 2000). For compounds for which γ is quite small, the chemical term predominates.

$$v_d \cong \gamma\frac{<c>}{4} \qquad \text{(Eq.15)}$$

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 3, 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;

$$k = \frac{A\gamma<c>}{4} \qquad \text{(Eq.16)}$$

where A is the aerosol surface area. If we take the γs from Figure 8, and assume highly polluted conditions to obtain a lower limit to the lifetime against this process, A = 1000 µm^2/cm^3 and pHs between 1 and 2, then the lifetimes listed in Table 3 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 undoubted 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. We can point out that our results yielded slightly lower H_{eff} (~22%) at the lowest temperature we measured, compared to the values used by Barth et al., (2013), see Figure S13. This would result in slightly slower removal rates in the Barth et al., model in low-temperature clouds. 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 3. 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:

$$k = k_l L_c HRT \qquad \text{(Eq.17)}$$

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 3 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_{eff} was assumed equal to that of HC(O)OH, 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_{eff} 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. Given that aerosol particles in most polluted atmospheres are at least half organic carbon by mass (Jimenez and et al., 2009), it is useful to estimate what effect an increased solubility of HNCO might have on its removal lifetime. If take our 1000 $\mu m^2/cm^3$ surface area aerosol from the above calculation, assume a 50/50 organic to aqueous distribution and that the solubility of HNCO in the organic fraction is the same as n-octanol, we can arrive at a weighted average Henry's solubility of 55 M/atm. If we combine that with the same reaction rate corresponding to pH1, then the lifetime of HNCO against reaction to this aerosol drops to about 2 days, a significant effect.

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 $k = 3.6 \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1} (Lu et al., 2014), however recent work indicates that secondary chemistry may have made this rate high by a significant amount (Papanastasiou, et al., manuscript in preparation, 2019). In addition, there are likely condensed-phase reactions that are faster than the simple hydrolysis reactions consider in this work. Never-the-less, it is useful to estimate the atmospheric loss rates implied by our work, as a baseline against which future atmosphere observations can be judged, and the importance of other heterogeneous processes can be assessed. 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, e.g. within seconds of the application of a thin film of chlorine bleach cleaning solution, or the bubbling of air though a spa in which ClCN is dissolved. As a result, the atmospheric removal of ClCN 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 ($<3 \times 10^{-15}$ cm^3 $molec^{-1}$ s^{-1},(Davies and Thrush, 1968)) and the reaction of Cl atom with ClCN at high temperature is also quite slow ($<1.0 \times 10^{-14}$ cm^3 $molec^{-1}$ s^{-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 ($<2 \times 10^{-14}$ cm^3 $molec^{-1}$ s^{-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 S13 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 3 shows a general trend. The lifetimes become shorter as the halogen atom goes from Cl to Br to ICN, 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. Depending on the mechanism of condensed phase XCN reactions, this chemistry could be a condensed phase source of NCO^- and therefore HNCO similar that observed by Zhao et al. (2014) in coastal clouds.

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 4). 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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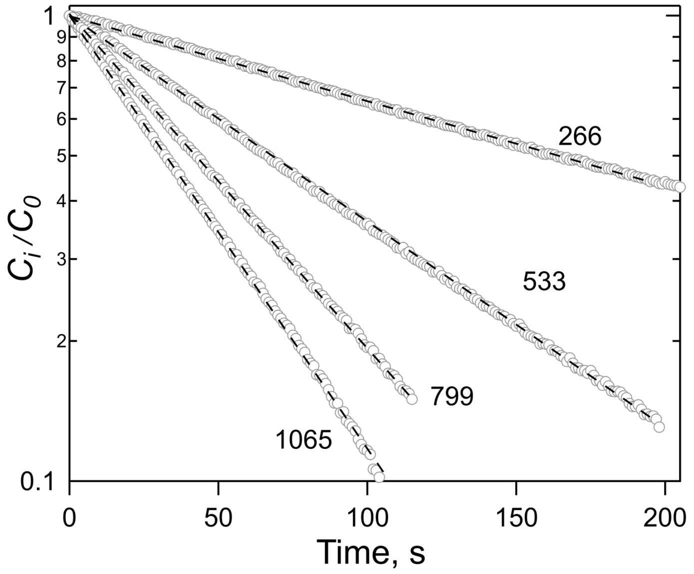

Figure 1. Plots of the ratio of HNCO concentration at time t, C_i, to the initial concentration, C_o, versus time for a series of flow rates, noted as ambient cc/min. The solvent was tridecane ($C_{13}H_{28}$) and 299 K.

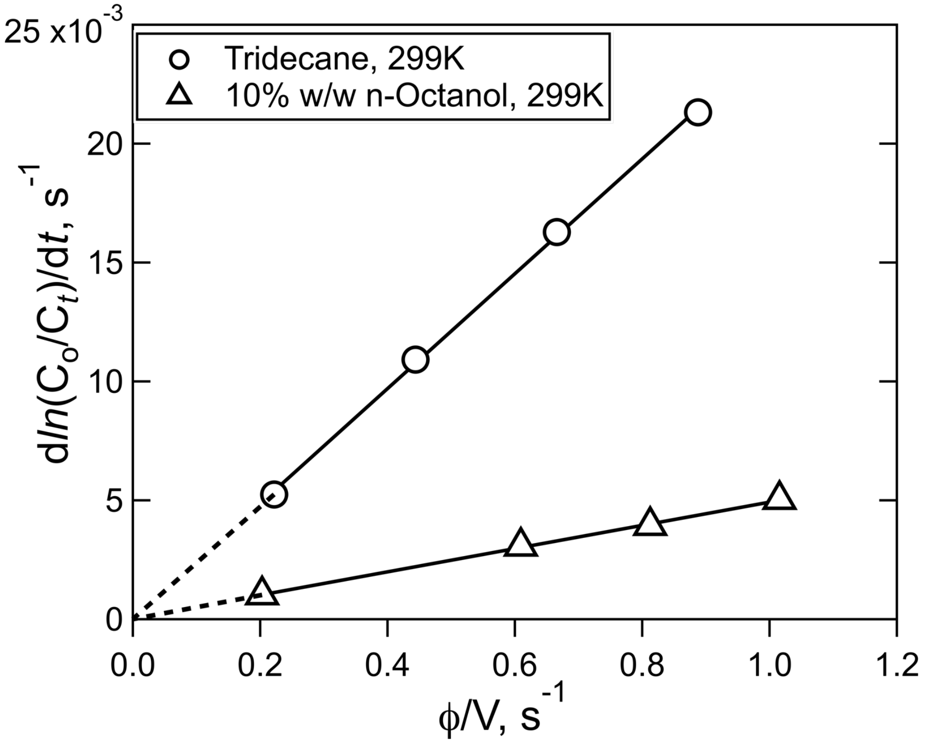

Figure 2. Plots of HNCO loss rate versus the ratio of volumetric flow rate, ϕ, to solution volume, V, for the experiment shown in Figure 1, (circles), and the experiment with 10% w/w n-octanol in tridecane at 299 K (triangles). The error bars in the individual rates were smaller than the width of the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

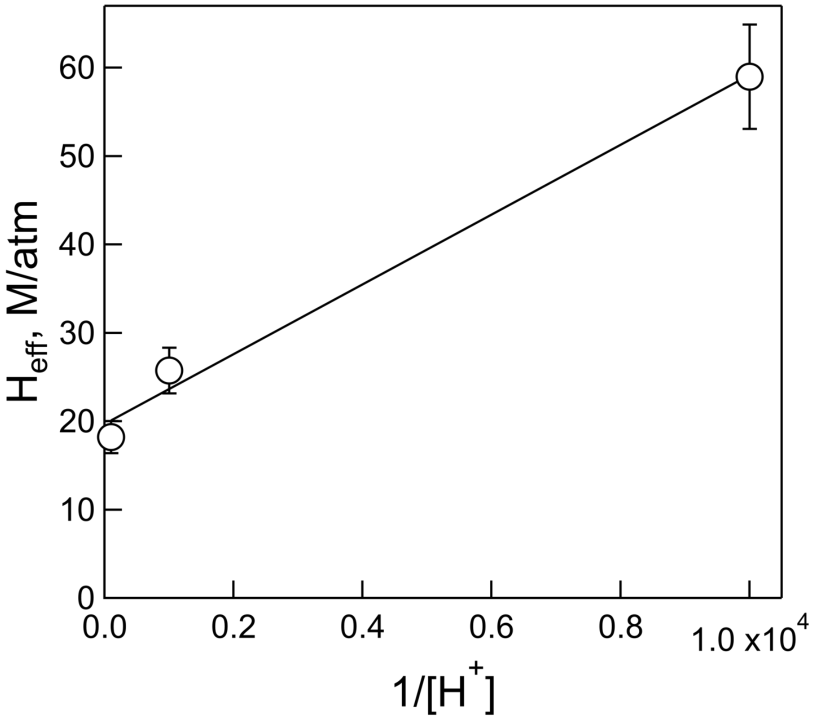

Figure 3. Plot of effective Henry's coefficient of HNCO vs 1/[H+] for the measurements at pH=2, pH=3 and pH=4, and 298 K.

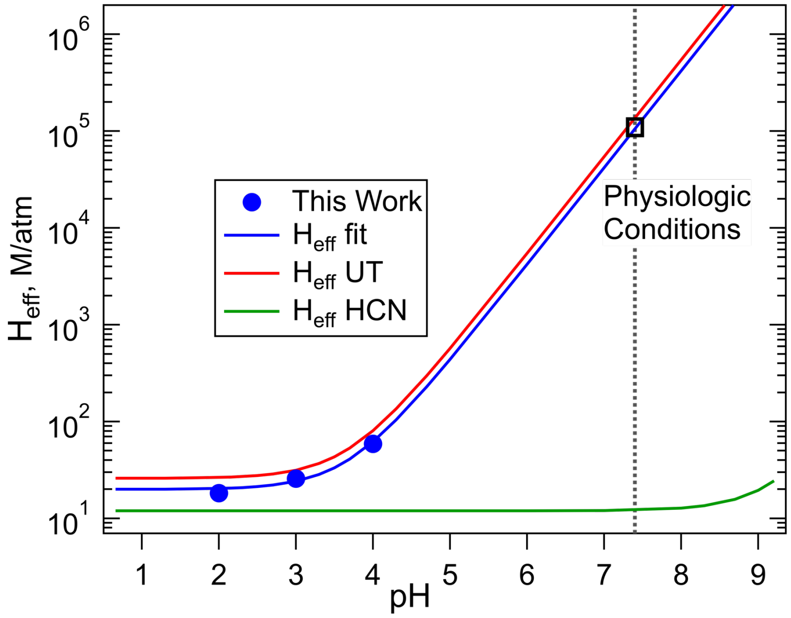

Figure 4. Comparison of effective Henry's coefficients of HNCO measured in this work (blue) with those reported by Borduas et al., 2016, plotted versus pH, according to Equation 4. The error bars on our H_{eff} values are smaller than the width of the symbols. The green line was calculated for HCN from the intrinsic H coefficient reported by Sander, (2015), and its pKa, 9.3.

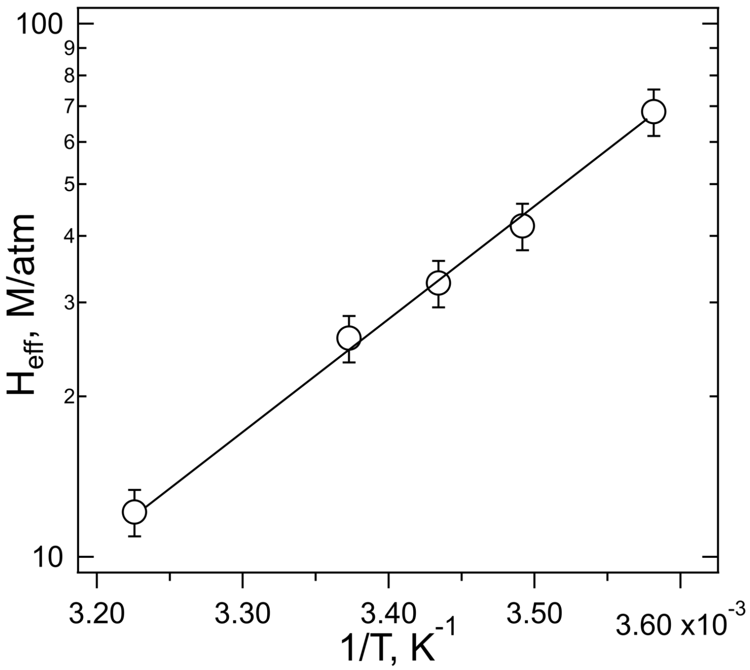

Figure 5. The plot of ln H_{eff} vs 1/T for the experiments performed with HNCO at pH=3. R^2=0.997

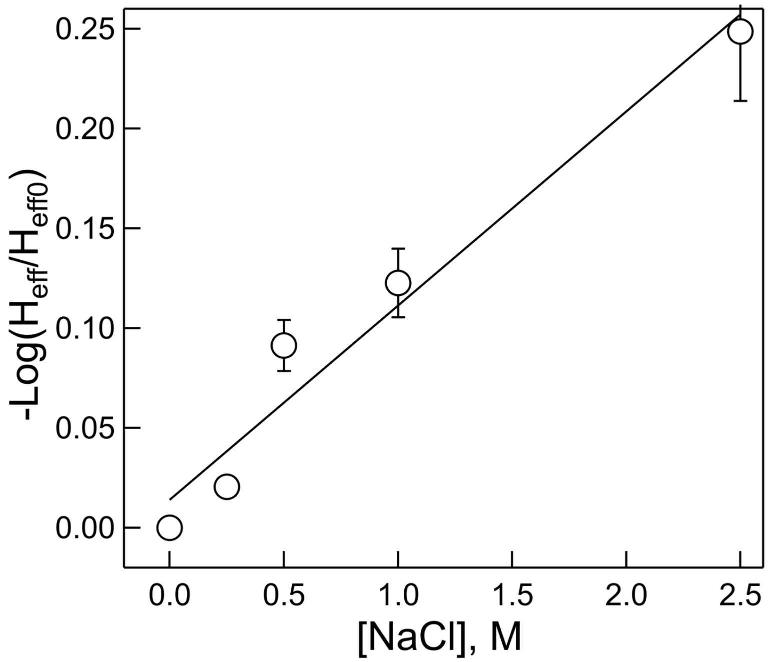

Figure 6. Dependence of the effective Henry's coefficient (H) at a given salt concentration, relative to that with no added salt (H_{eff0}) versus NaCl molarity. R^2 = 0.960

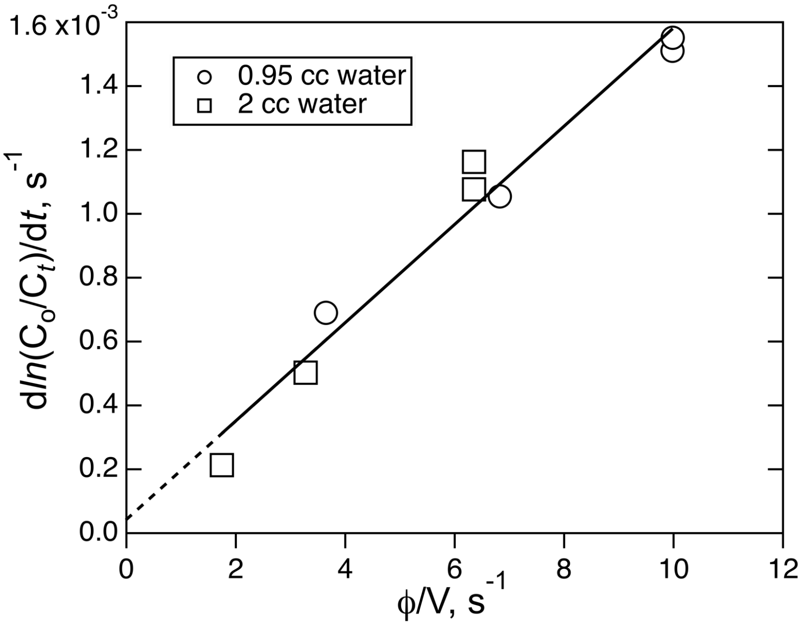

Figure 7., The Plot of ICN loss rate versus the ratio of volumetric flow rate, ϕ, to solution volume, V, for the experiment involving the solubility of ICN in water with the small reactor. The line is the least-square fit to the data ($R^2 = 0.968$)

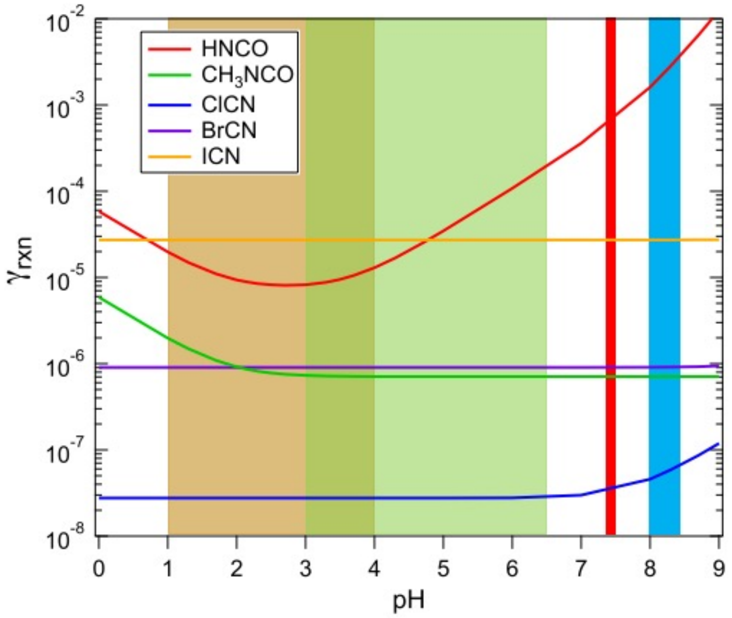

Figure 8. The uptake coefficients of HNCO, CH_3NCO, ClCN, BrCN, and ICN as a function of pH for aqueous solution at approximately 298 K. The shaded areas show the range of pHs characteristic of: aerosols (light brown), cloud/fog water (green), human physiology (red), and ocean surface water (light blue).

Table 1. Summary of solubility and loss rate measurements of HNCO and CH_3NCO.

Solute	Solvent	Temp. (°K)	pH	Salt, Reactant	H_{eff}, M/atm	Literature H	k^I, ($x10^3$), s^{-1}	Literature k, ($x10^3$), s^{-1}
HNCO	H_2O	279	3.0		68 ±7	73[a]	0.22	0.24[a] 0.17[b]
		286.5	3.0		42 ±4	51[a]	0.38	0.43[a] 0.41[b]
		291	3.0		33 ±3	40[a]	0.66	0.63[a] 0.72[b]
		296.5	3.0		26 ±2.6	31[a]	1.02	0.96[a] 1.32[b]
		310	3.0		12 ±1.2	17[a]	4.15	2.6[a] 5.6[b]
		298	2.0		18 ±1.8		2.2 ±0.1	
		298	3.0		26 ±2.6		1.02 ±0.13	
		298	4.0		59 ±5.9		0.72 ±0.11	
		298	3.0	0M NaCl	26 ±2.6			
		298	3.0	0.25M NaCl	24.6 ±2.5			
		298	3.0	0.5M NaCl	20.9 ±2.1			
		298	3.0	1.0M NaCl	19.4 ±2.0			
		298	3.0	2.5M NaCl	14.5 ±1.5			
		292	3.0	0.45M NH_4Cl	31.5 ±3.2		1.2	0.005 - 0.015[c]
	Tridecane (TD)	298	-		1.7 ±0.17		<0.043	
	TD + 10% n-Octanol	283	-		13.2 ±1.6		0.16 ±0.18	
	TD + 10% n-Octanol	298	-		8.3 ±0.8		<0.03	
	n-Octanol	298	-		87 ±9		<0.015	
	n-Octanol	310	-		51 ±5		0.057 ±0.014	
CH_3NCO	H_2O	298	2.0		1.3 ±0.13		3.2 ±0.3	2.5[d], 3.1[e]
		298	7.0		1.4 ±0.14		1.9 ±0.6	1.34[d], 1.47[e]
	n-Octanol	298	-		4.0 ±0.5		2.5 ±0.5	
	n-Octanol	310	-		2.8 ±0.3		5.3 ±0.7	

a. Calculated from the temperature and pH dependent data reported by Borduas et al., (2016).

b. Calculated from the temperature and pH dependent data reported by Jensen, (1958).

c. These were calculated from rates measured at higher pHs, assuming the mechanism is HNCO + NH_3 => $H_2NC(O)NH_2$

d. From k_{H+} and k_w reported by Williams and Jencks (1974a)

e. From k_{H+} for HCl and k_w reported by Castro et al., (1985)

Table 2. Summary of solubility and loss rate measurements of XCN compounds.

Solute	**Solvent**	**Temp. (°K)**	**pH**	**H_{eff}, M/atm**	**Literature H**	**k^I, (x10^3), s^{-1}**	**Literature k, (x10^3), s^{-1}**
ClCN	H_2O	299.5	7.0	1.4 ±0.14	0.6[a], 0.52[b]	0.0 ±0.42	3.03 x10^{-3}[c]
	H_2O	273.15	7.0	4.5 ±0.4		0.015 ±0.016	
	n-Octanol	299.5		1.9 ±0.2		1.3 ±0.4	
BrCN	H_2O	296	7.0	8.2 ±0.8		6.2 ±3.7 x10^{-2}	1.9 – 9.2 x10^{-2}[d]
	H_2O	273.15	7.0	32.7 ±3		2.4 ±0.5 x10^{-2}	
	n-Octanol	297		31 ±3		9 ±2 x10^{-2}	
ICN	H_2O	296	7.0	270 ±54		4.4 ±7.6 x10^{-2}	~3.4 x10^{-2}[e]

a. Measured value at 293K, reported by Weng et al., (2011).

b. Modelled value at 298K, reported by Hilal et al., (2008).

c. From k_w and k_{OH} reported by Bailey and Bishop (1973).

d. Estimated from Heller-Grossman et al., 1999, and Vanelslander, et al., 2012.

e. Estimated from Gerritsen et al., (1993).

Table 3. Estimates of HNCO, CH_3NCO, and XCN compounds against loss due to heterogeneous processes.

Process	HNCO	CH_3NCO	ClCN	BrCN	ICN
BL deposition	1-2 days	0.5 yrs	yrs	0.5 yrs	5-10 days
Aerosol dep.	6-12 days	2-4 months	yrs	0.6 yrs	8 days
In-cloud rxn	2-6 hrs[a]	2 months	10-20 wks	1-3 wks	1-3 days

[a] from the highly polluted case described by Barth et al., (2013).

Table 4. Octanol/Water partition coefficients for HNCO, CH_3NCO, ClCN, BrCN and related compounds.

Compound	Temperature	LogK_{ow}
HNCO[a]	298	0.64
	310	0.63
CH_3NCO	298	0.49
ClCN	299.5	0.13
BrCN	297	0.61[b]
HC(O)OH	298	-0.54[c]
CH_3NO_2	293	-0.33[c]
HCN	?	0.66[d]
CH_3CN	298	-0.34[c]

a. This uses the intrinsic H calculated from Eq(5), and our results.

b. based on extrapolated H_{H2O} at 297K

c. (Sangster, 1989)

d. (EPA, 1989)

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

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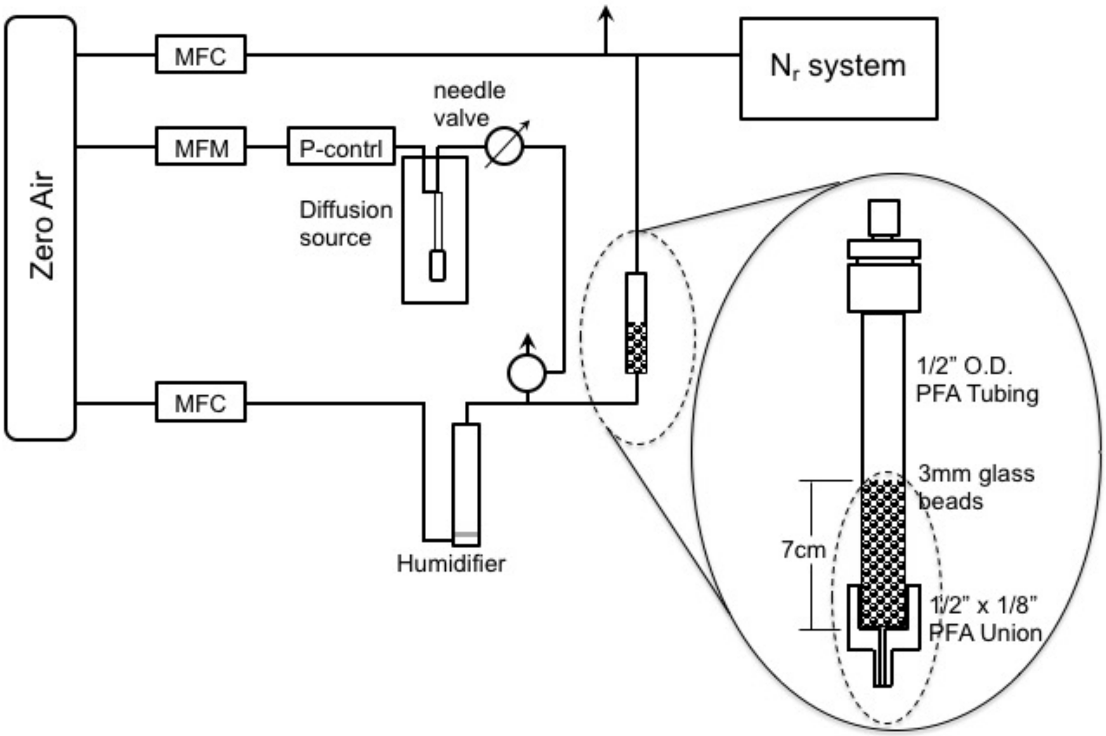

Figure S1., The small-scale Teflon PFA reactor used for ICN solubility measurements.

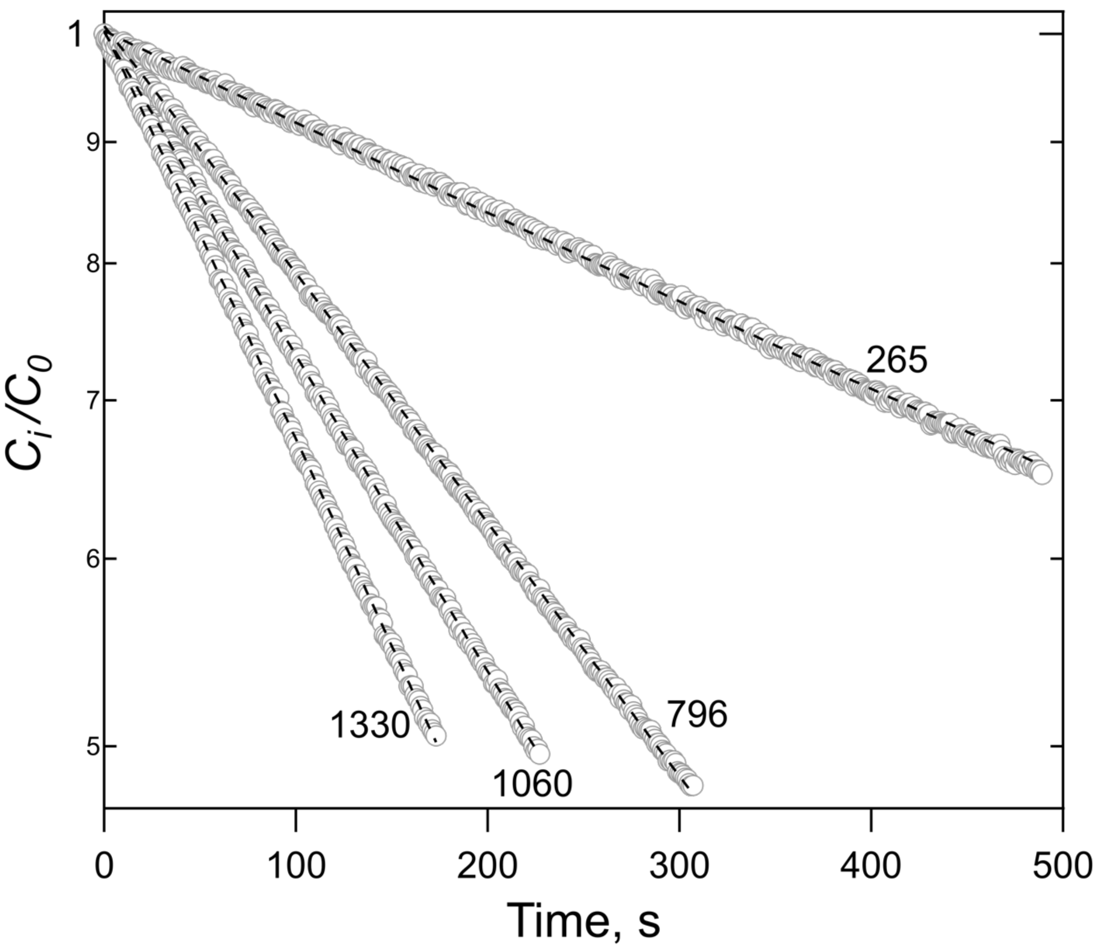

Figure S2. The decay curves corresponding to the measurement of HNCO solubility in 21.9 cc of 10% n-octanol in tridecane at 299K, for which the results are shown in Figure 2 of the main paper. The dashed lines are exponential fits and the numbers shown are the flow rates in amb cc/min.

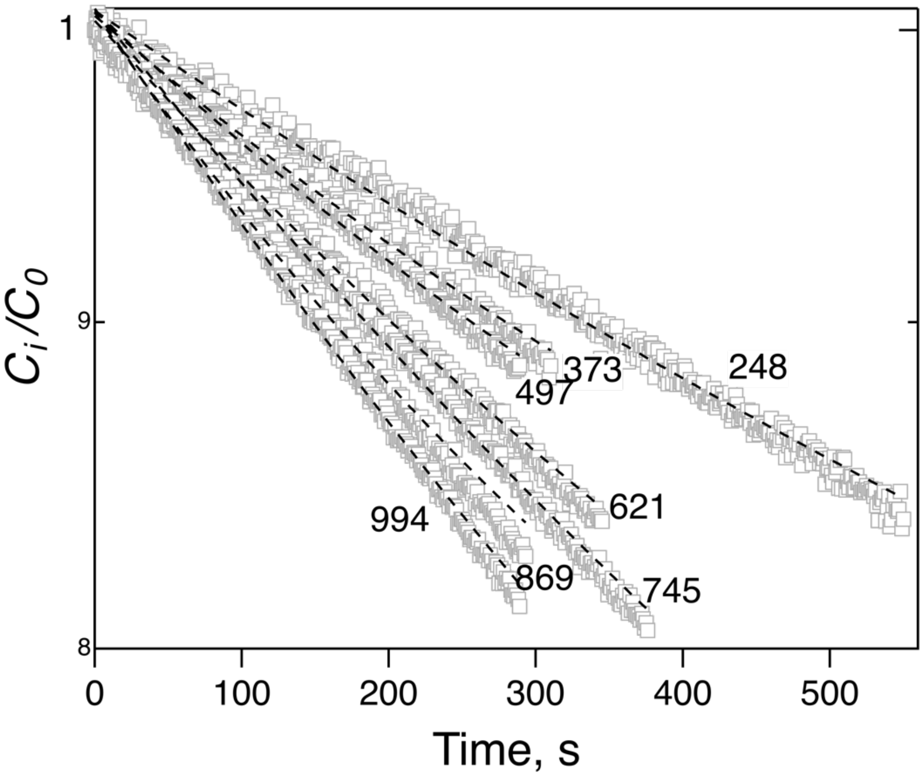

Figure S3. The decay curves corresponding to the measurement of HNCO solubility in 20 cc of H2O at pH3 and 279K. The dashed lines are exponential fits and the numbers shown are the flow rates in amb cc/min.

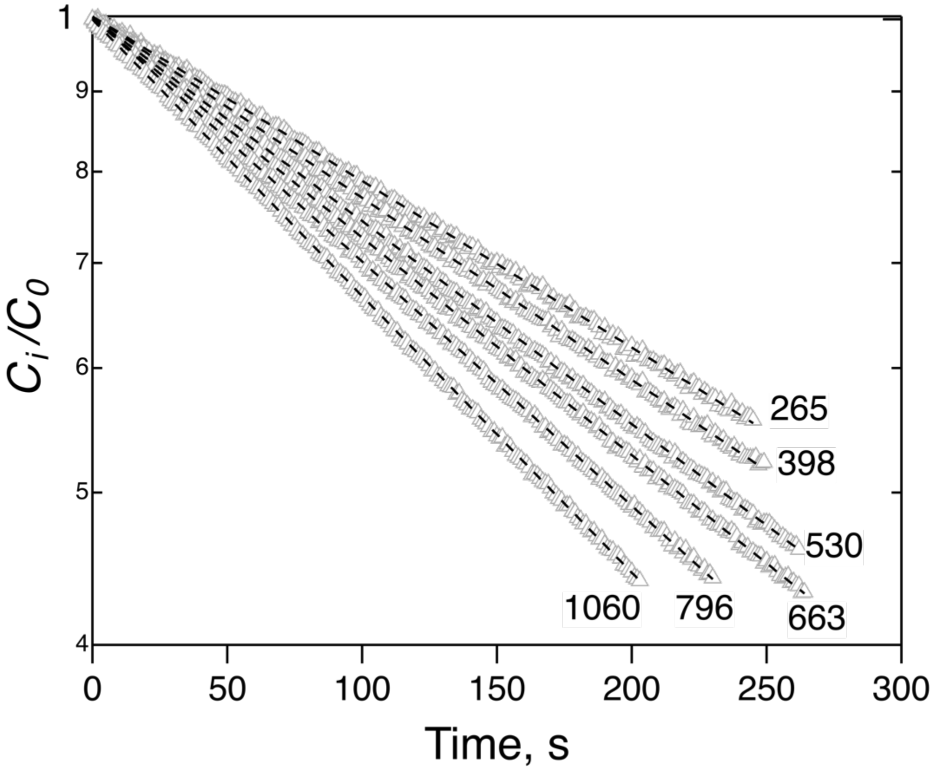

Figure S4. The decay curves corresponding to the measurement of HNCO solubility in 20 cc of H_2O at pH2 and 298K. The dashed lines are exponential fits and the numbers shown are the flow rates in amb cc/min.

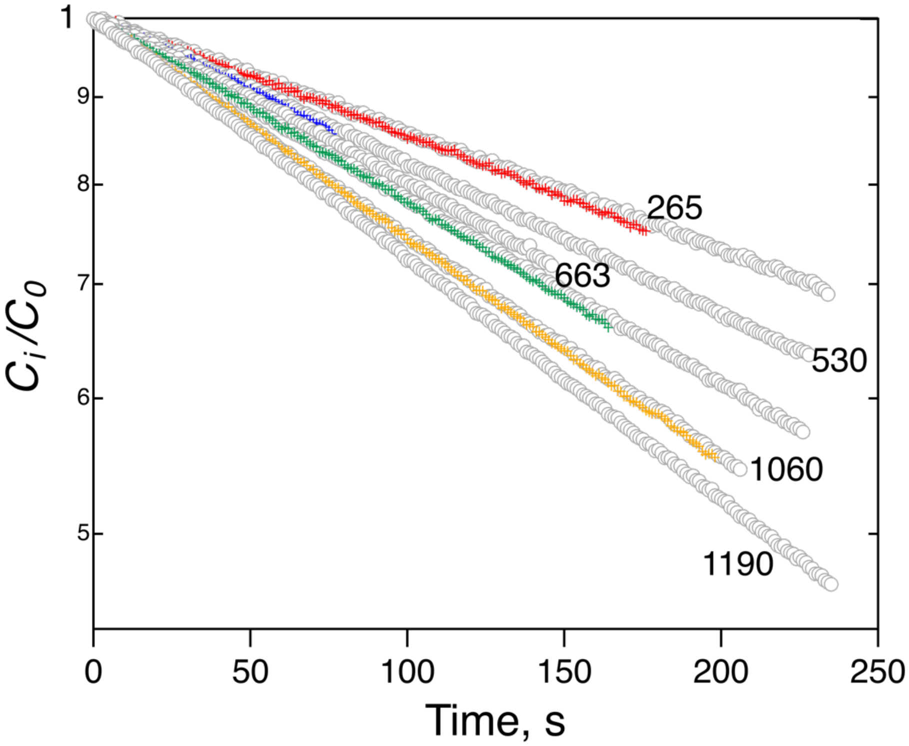

Figure S5. The decay curves corresponding to the measurement of HNCO solubility in 20 cc of H2O at 1M NaCl, pH3 and 298K. The numbers shown are the flow rates in amb cc/min.

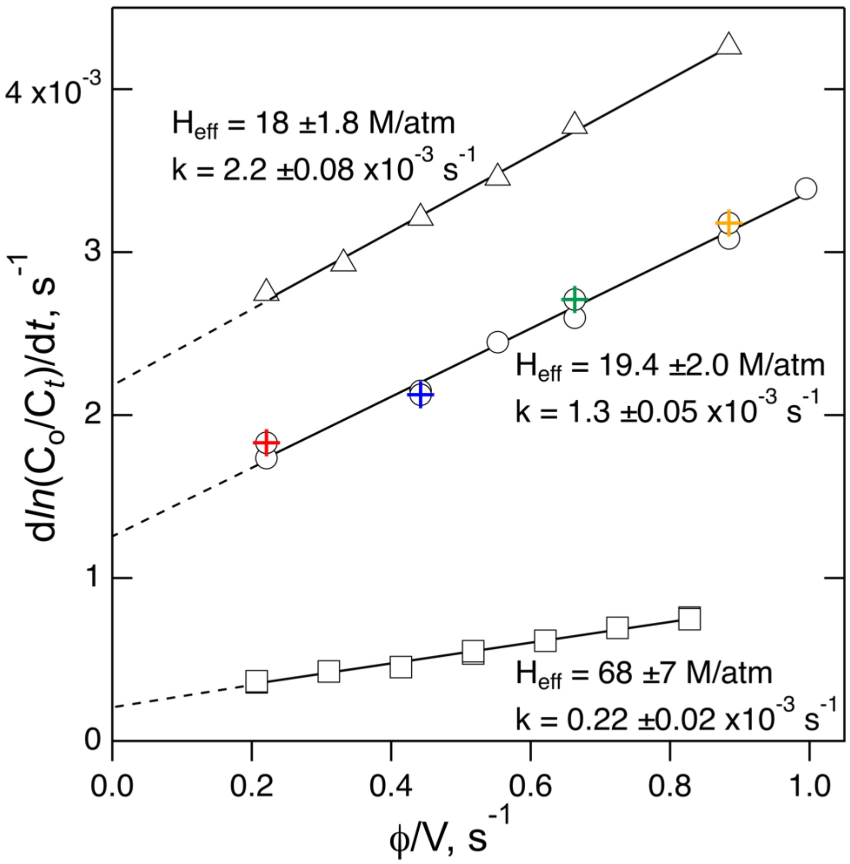

Figure S6. Summary of the decay rate data from Figures S3, S4, and S5, versus ϕ/V, and the associated H and k calculated from the fits. The errors in individual rate measurements are smaller than the width of the symbols.

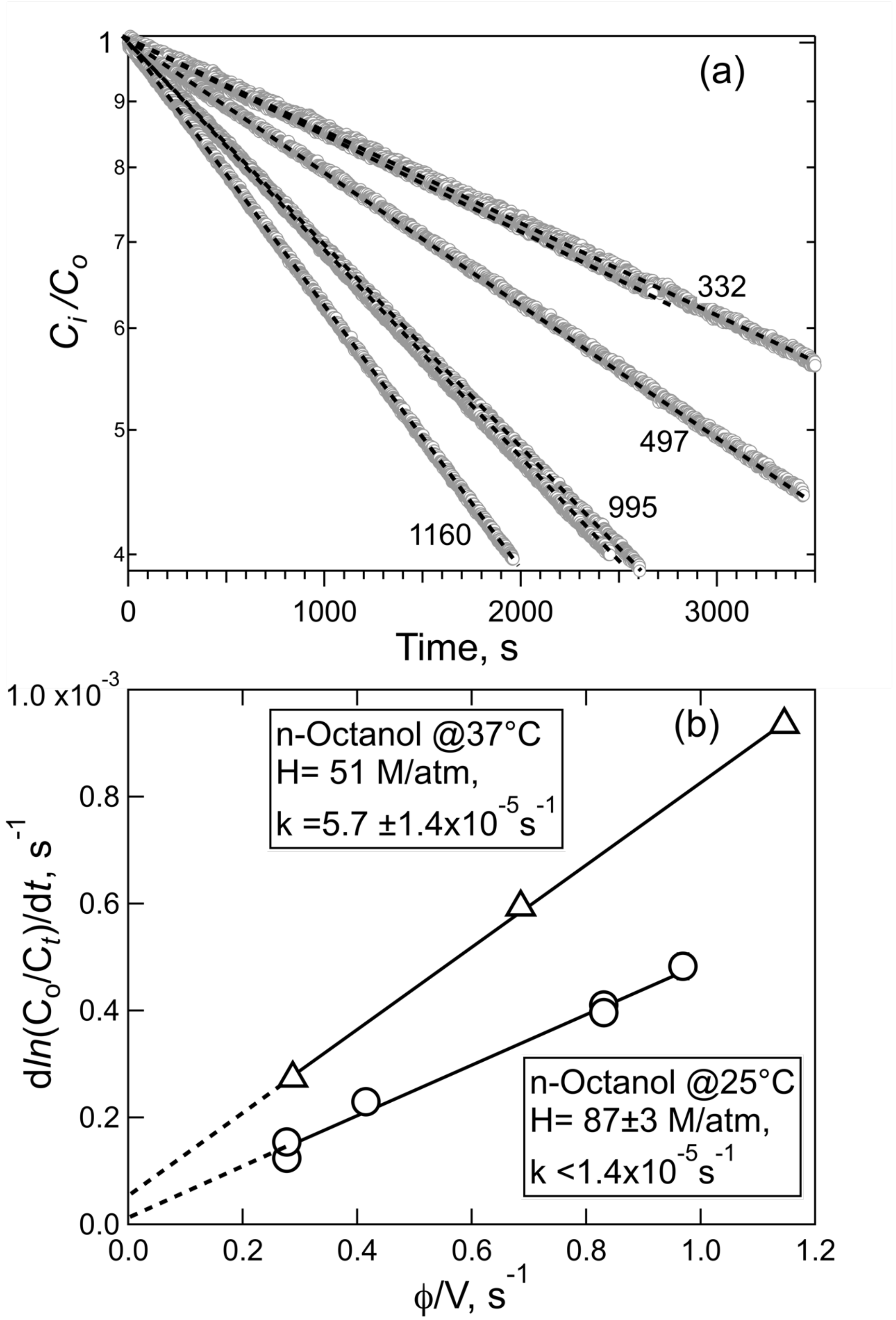

Figure S7. (a) The decay plots for the experiment with HNCO in 20cc n-octanol at 298K. The dashed lines are exponential fits and the numbers shown are the flow rates in amb cc/min. (b) The summary of decay rates versus ϕ/V for both 298K (circles) and 310K (triangles). The errors in the individual decay rate determinations are smaller than the width of the symbols.

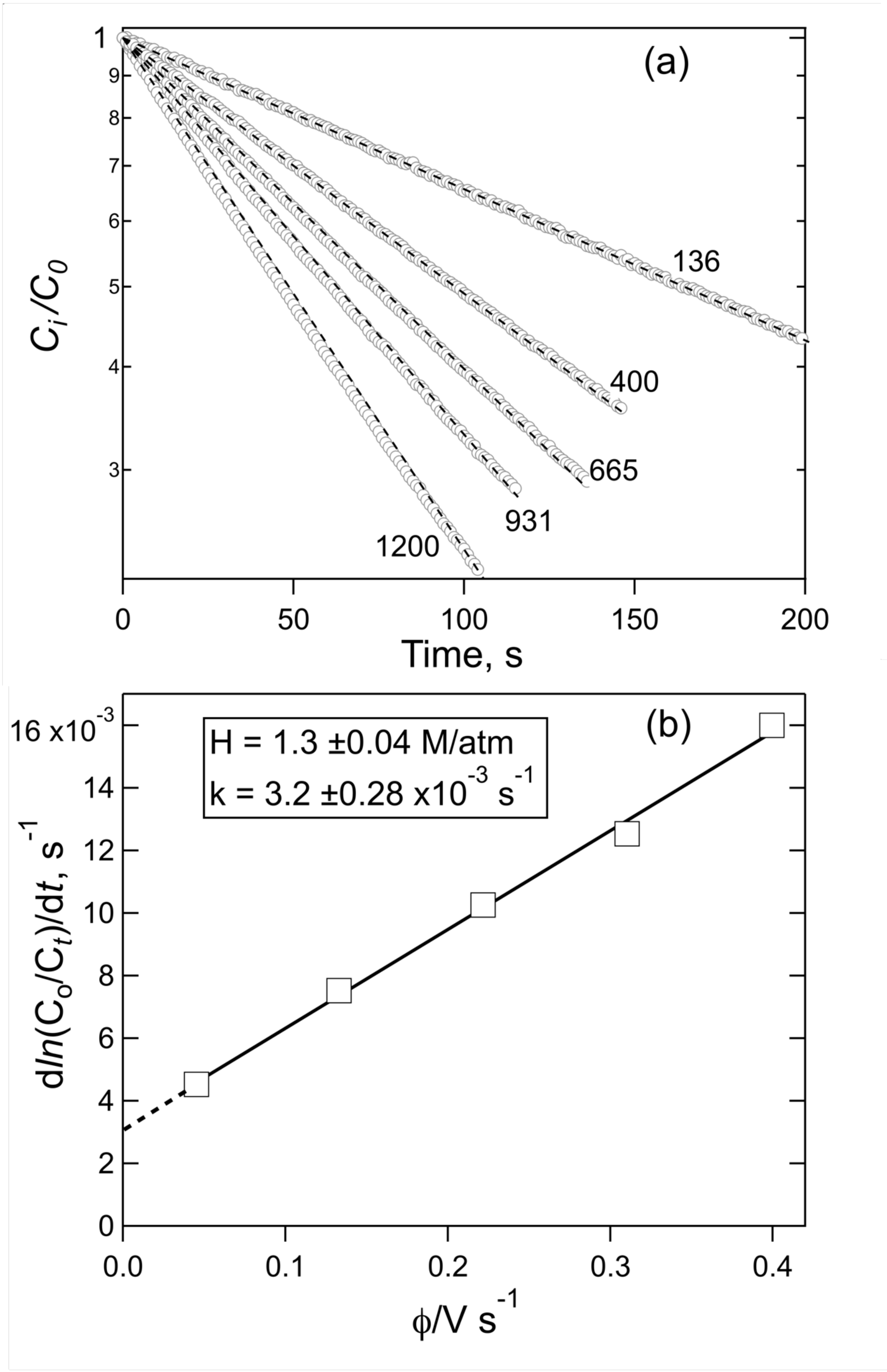

Figure S8. (a) The decay plots for the experiment with CH_3NCO in 50cc H_2O at pH2 and 298K. The dashed lines are exponential fits and the numbers shown are the flow rates in amb cc/min. (b) The summary of decay rates versus ϕ/V for the data in panel (a). The errors in the individual decay rate determinations are smaller than the width of the symbols.

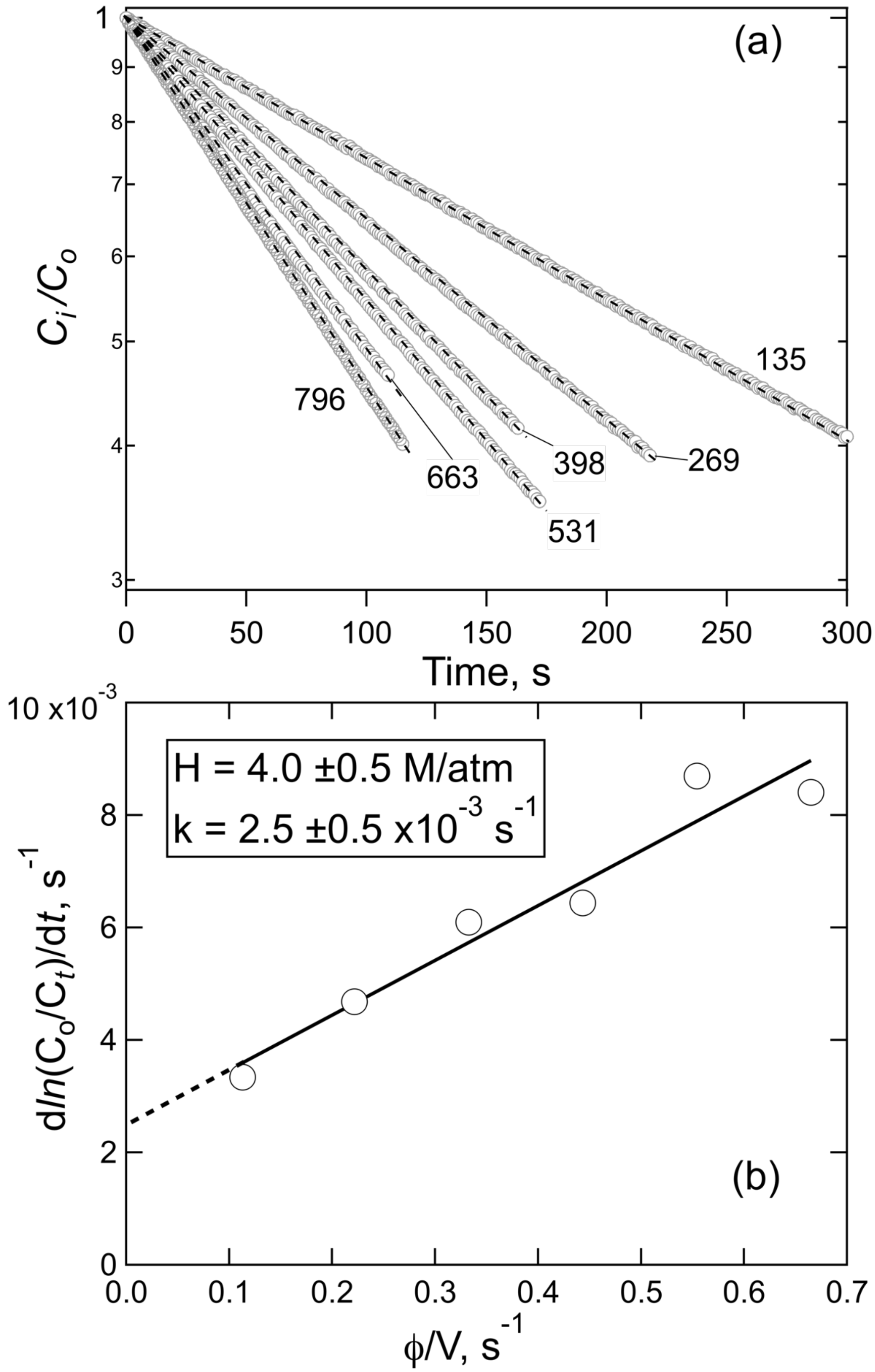

Figure S9. (a) The decay plots for the solubility experiment involving CH_3NCO in 20 cc of n-octanol at 298K. The dashed lines are exponential fits and the numbers shown are the flow rates in amb cc/min. (b) The plot of the CH_3NCO loss rates versus ϕ/V under the range of flow rates used. The errors in the individual decay rate determinations are smaller than the width of the symbols.

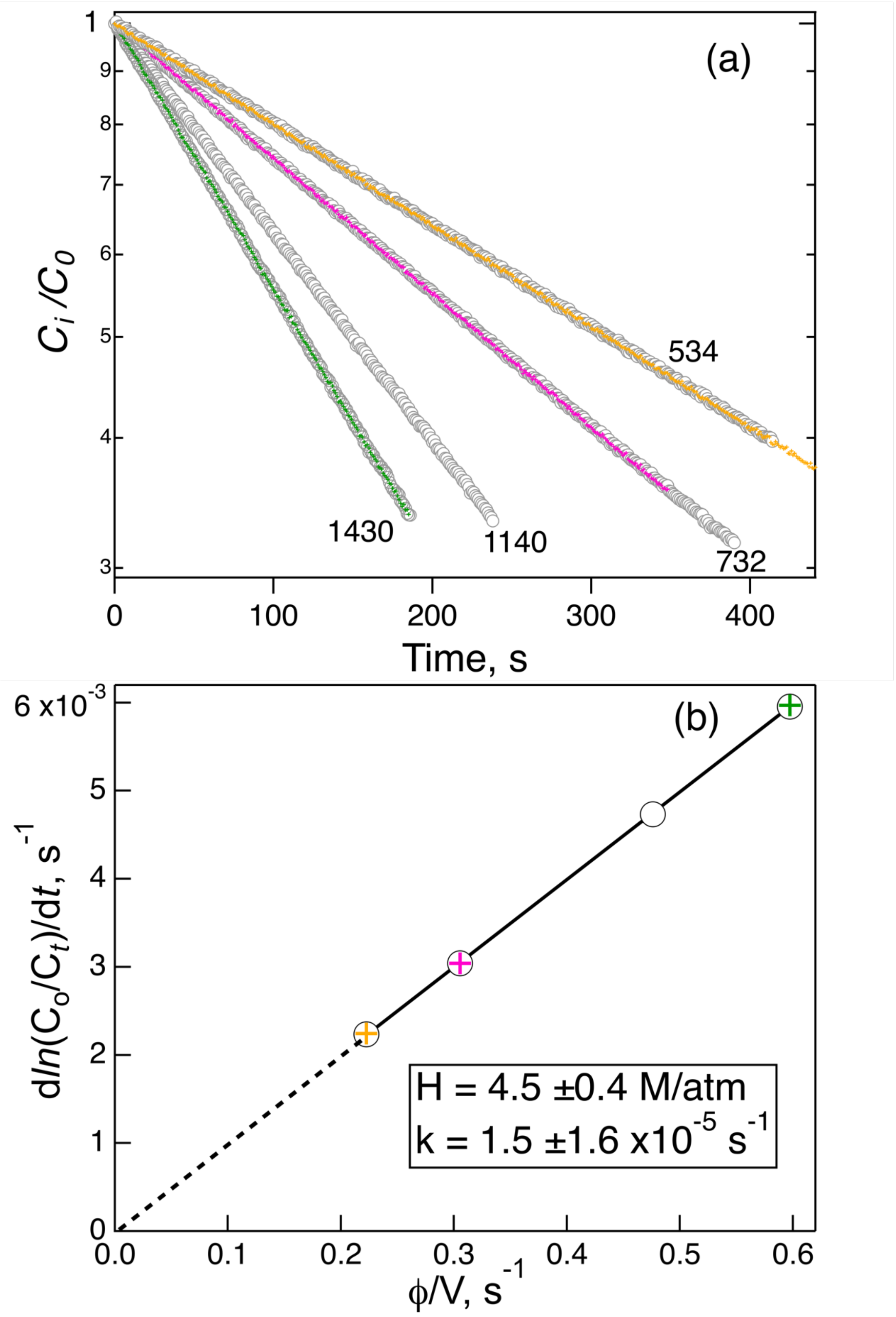

Figure S10. (a) The decay plots for the solubility experiment involving ClCN in 40 cc of H_2O at 273.15K. The numbers shown are the flow rates in amb cc/min, and duplicate runs are shown in colors. (b) The plot of the ClCN loss rates versus ϕ/V under the range of flow rates used. The errors in the individual decay rate determinations are smaller than the width of the symbols.

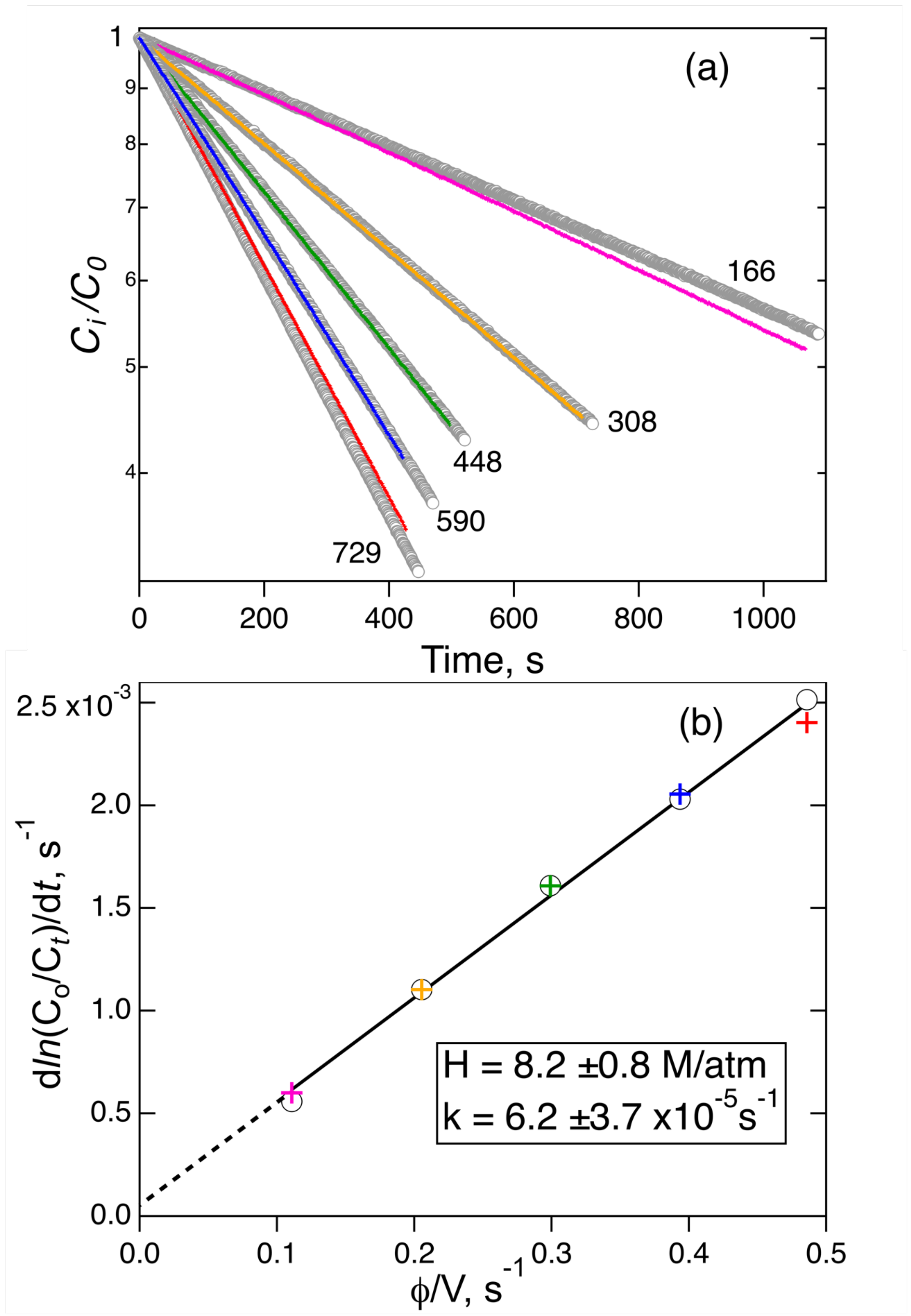

Figure S11. (a) The decay plots for the solubility experiment involving BrCN in 25 cc of H_2O at 296K. The numbers shown are the flow rates in amb cc/min, and duplicate runs are shown in colors. (b) The plot of the BrCN loss rates versus ϕ/V under the range of flow rates used. The errors in the individual decay rate determinations are smaller than the width of the symbols.

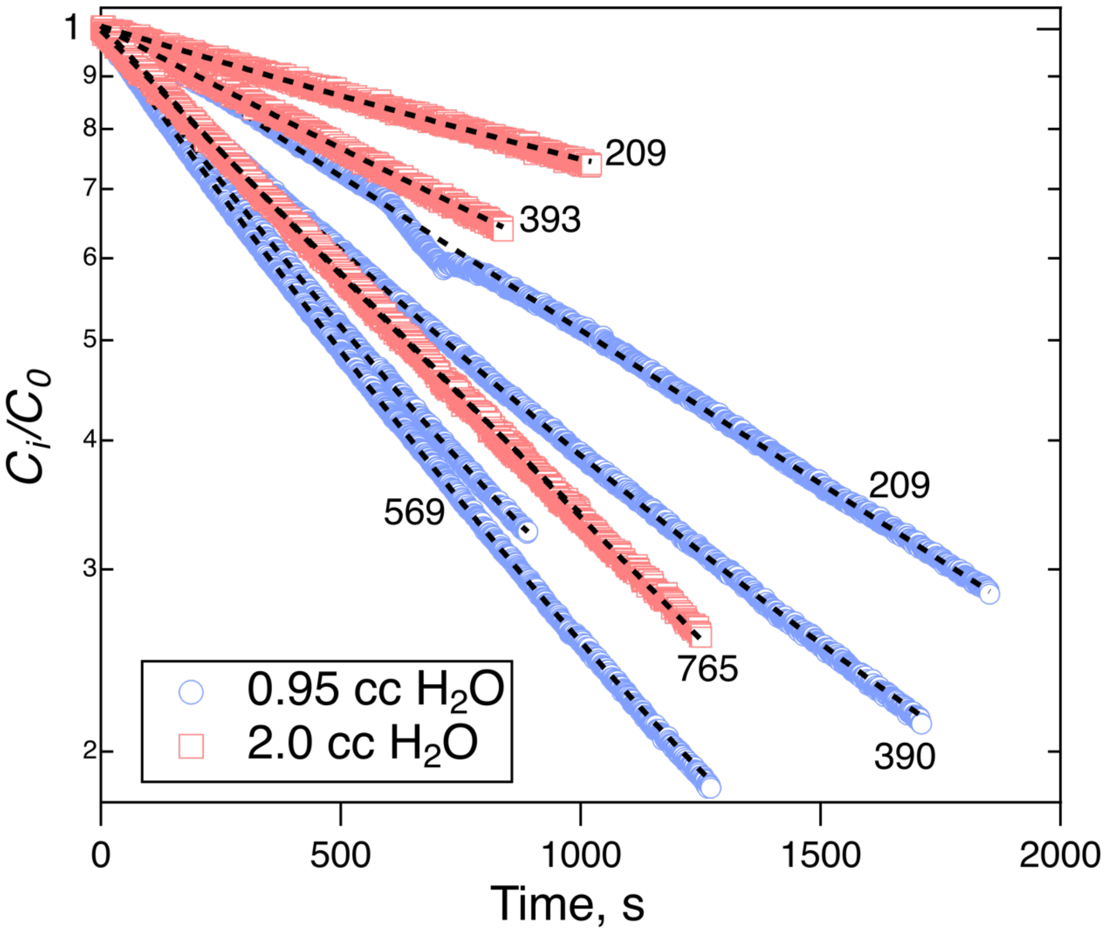

Figure S12. The decay plots for the solubility experiments shown in Figure 7 of the main paper involving ICN in 0.95 and 2.0 cc of H_2O at 298K. The dashed lines are exponential fits and the numbers shown are the flow rates in amb cc/min.

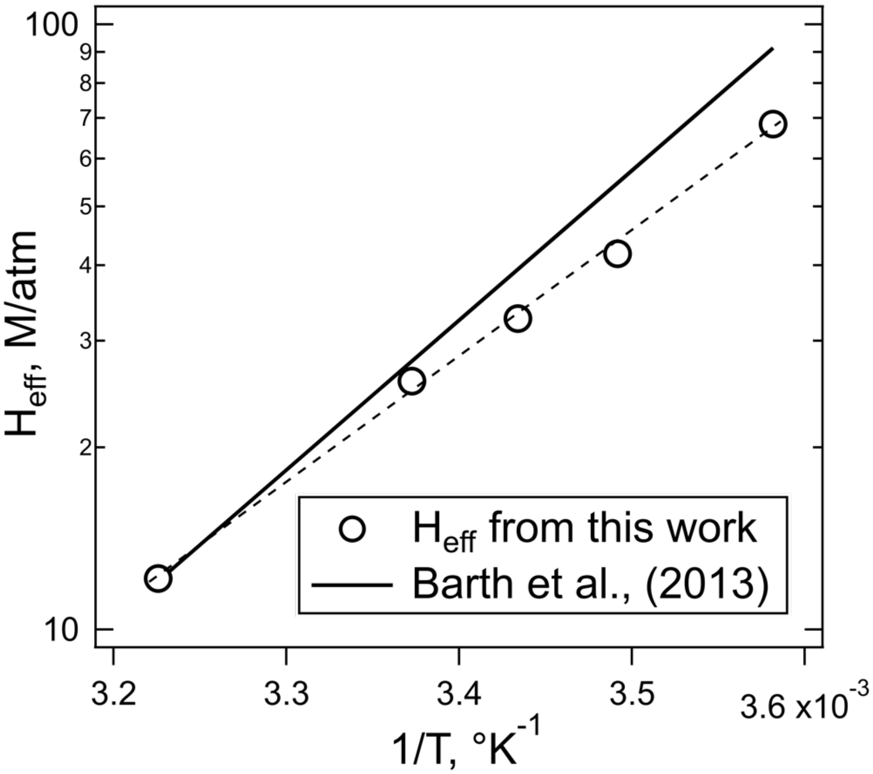

Figure S13. Comparison of the temperature dependence of H_{eff} for HNCO at pH3 between this work (circles and dashed line) with that used by the model of Barth et al., (2013) (solid line), which was based on the assumption that it was the same as for HC(O)OH.

Unlike HNCO and CH_3NCO, some of the XCN compounds have absorbances in the near UV-vis that could lead to photolysis in the lower atmosphere, Figure S14. The UV-vis spectra and photon fluxes estimated from the NCAR TUV model (NCAR, 2018) can be used to calculate photolysis rates, by integrating over the wavelength region where the absorption is significant, and assuming a quantum yield of 1. The absorption spectra are such that ClCN will not be photolyzed in the troposphere, BrCN has some slight absorption in the actinic region and ICN has substantial absorption. The lifetimes against photolysis at 0km altitude, 40°N, on June 30. 2015, were estimated to be 135 days for BrCN, and 9 hours for ICN.

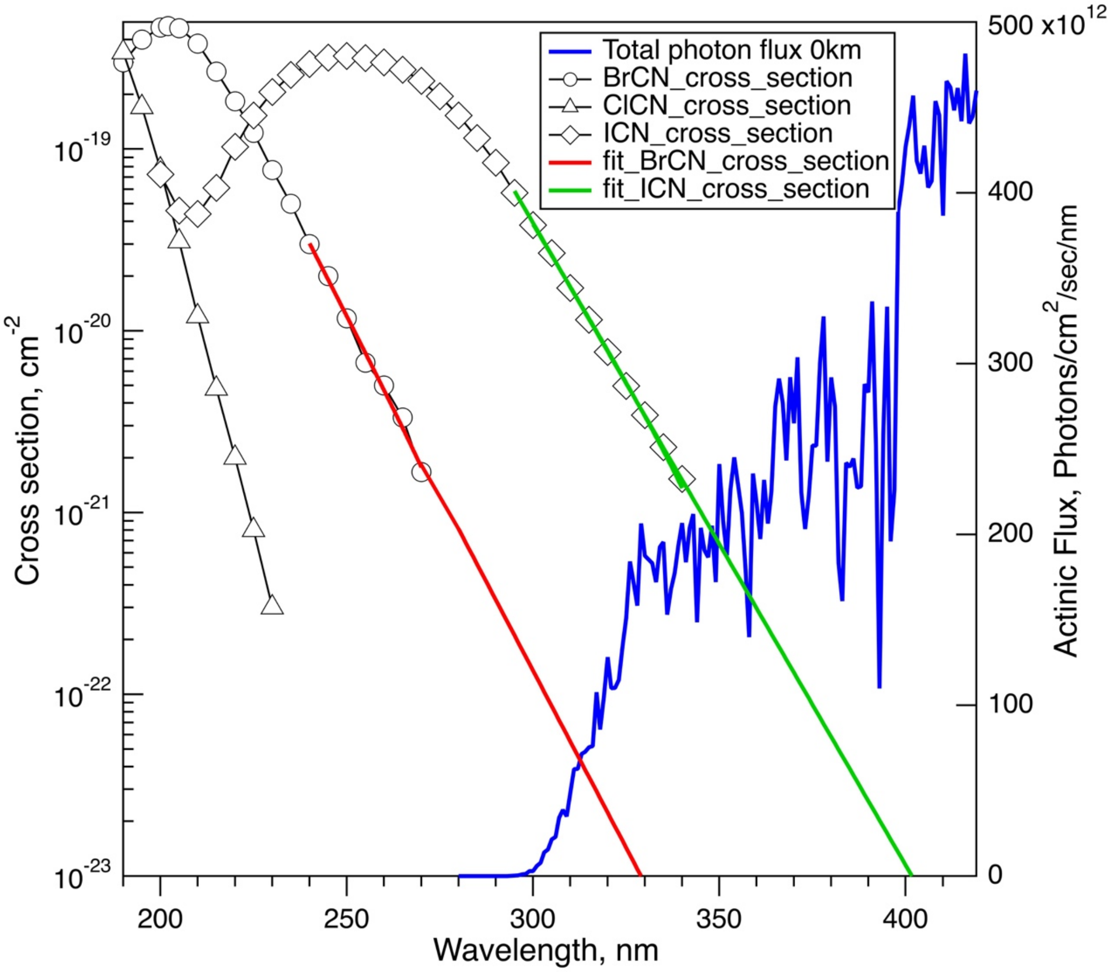

Figure S14. The UV-vis absorption spectra of ClCN, BrCN, ICN, (Barts and Halpern, 1989; Felps et al., 1991; Hess and Leone, 1987; Russell et al., 1987) and the photon flux spectrum estimated from the NCAR TUV model for 40° N, surface on June 30, 2015 (NCAR, 2018). The extrapolation assumes the cross-sections are ln-linear over the portions that tail into the actinic region.

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