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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Solubility and Solution-phase Chemistry of Isocyanic Acid, Methyl Isocyanate, and Cyanogen Halides" *by* James M. Roberts and Yong Liu

Anonymous Referee #1

Received and published: 11 December 2018

General comments: The manuscript presents necessary thermodynamic data for relevant atmospheric compounds including HNCO, CH3NCO, 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, CH3NCO, ClCN, BrCN and ICN in the atmosphere against deposition, particle uptake and in cloud reactions/hydrolysis.

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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.

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).

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.

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. 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).

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).

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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.

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.

Line 57: specify reaction rates with water

Line 61: specify which “other small nitrogen-containing compounds”

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

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.

Line 177: unclear statement about electronegativity. Clarify the link between slow OH/Cl reaction rates and electronegativity

Line 205: specify range of pH and temperatures (in general try to be more quantitative)

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. Examples include line 231 (3% of siloxane – 3% of signal intensity? By mass?); line 238 (1% level impurity); line 235 (how was 10 ppmv mixing ratio quantified?); line 259 and so on.

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.

Was CIMS used (lines 260 for instance)? (and PTRMS in line 237?) If it was, then the details of its operation should be included.

Results and discussion:

Biggest issue: all data must be shown either in the text or in the supplementary information.

Figures 3, 4 & 5: missing error bars

Line 394: specify small organic compounds

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?

Lines 400-405: good discussion, but could benefit from reporting the quantitative data within the text.

Line 408: confusing “active hydrogen” terminology for an atmospheric chemist.

Line 409: an addition reaction likely occurs at the C center.

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?

Order of reaction numbering needs to be revisited to match the order the reactions were introduced.

There are also errors with the hydrolysis equations for XCN. For a hydrolysis reaction to occur, H2O cannot be on the same side of the equation. So I think R7 should read XCN + OH- $\rightarrow$ HOCN X-. R8 is a tautomerization reaction and is therefore denoted with a doubled headed arrow $\leftrightarrow$. Tautomerization does not require H+. R8 should read HOCN $\leftrightarrow$ HNCO.

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?

Missing data for lines 531-534

ICN discussion missing in paragraph starting at line 546

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.

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.

Technical comments: Line 60: attention to significant figures in reporting Ka.

Line 64: specify the counter ion of NH4+

The SI unit for seconds is "s", not "sec", and should be corrected throughout.

Line 65: missing verb in second clause.

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

ment here.

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

Line 125: define pKas

Many references are based on personal communication, and I believe that in some circumstances work/reviews can be referenced instead. For instance, indoor surfaces with chlorine to substantiate “J. Abbatt personal communication”: (Wong et al., 2017)

Line 204: delete on iteration of “at several”

Line 244: specify the IUPAC name for Chloramine-T

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

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

Lines 339-346: repetitive

Line 567: should read “common”

Line 699: quantify “fairly readily”

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

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