Atmos. Chem. Phys. Discuss., 11, C14597–C14605, 2012
www.atmos-chem-phys-discuss.net/11/C14597/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "The adsorption of peroxynitric acid on ice between 230 K and 253 K" *by* T. Ulrich et al.

T. Ulrich et al.

thomas.ulrich@psi.ch

Received and published: 23 January 2012

T. Ulrich, M. Ammann, S. Leutwyler and T. Bartels-Rausch

Here we give a response to the comments of Anonymous Referee #1 to our manuscript submitted to ACP. We thank the referee for the useful comments and for the detailed list of questions and suggested corrections. We apologize for the extra time and effort that might have been needed to evaluate the manuscript due to the sometime confusing use of the English language. We took the opportunity to edit the language and structure of the whole manuscript. In a revised version we would not only make changes as requested by the referee, but additionally restructure, rewrite, and shorten throughout the manuscript. In the following the comments and questions of the reviewer are cited and answered.

Specific comments:

1 - Page C12207, Line 5: “It will be easier and clearer for the readers if the authors divided section 2 (pages 26818-2682) into titled sub-sections rather than lumping everything in one huge section. It will also be better if the authors were more organized. For instance, have a section describing the general setup. Then have another section of chemicals used, a section about ice preparations, a section about CWFT-CIMS and a section about the photolysis reactor, etc.”

Response: We fully agree that section 2 (pages 26818-26823) was difficult to read, as it was not clearly structured. Adding titles to each paragraph helps to keep the focus in each paragraph.

2 - Page C12207, Line 10: “Page 26821, Line 15 to 18 is confusing, in line 15 the authors stated that, NO could not be quantified since CO interfered with NO detection, but this interference was not observed when CO was passed through the molybdenum. Is there a contradiction here, since in line 15 the authors stated that they were only able to detect NO after all the NOy species were passed through the convertor. Can the authors please clarify this point better? Are the authors here talking about NO generated from the conversion of NOy? and if CO interfered with the detection of NO does not this mean that it interfered with the NOy detection after they were converted to NO.”

Response: We agree that a better understanding of the NO2 quantification could be useful. The text should be edited. The instrument (Monitor Labs ML 9841) only measures NO. To quantify NOy all species have to be converted to NO by a molybdenum converter. As soon we use the converter, there is no interference with CO anymore. We quantified NO and NO2 prior to the addition of CO. In those experiments NO was near the detection limit of the NOx analyzer at around 2*109 molecules cm-3. It is true that we can not differentiate between NO and NO2 as soon CO is added. In the revised version we account for this issue and talk only of NOx when we are not able to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

differentiate:

In this photolytic HO2NO2 synthesis the levels of by-products are generally rather low. HNO3 and HONO levels of 1×1011 molecules cm-3 were determined for an initial NOX concentration of 3.4×1012 molecules cm-3 in the photolysis chamber (Fig. 2, 295-330 min). This is lower than observed in our previous study (Bartels-Rausch et al., 2011). The reason for this might be a more selective and direct detection mode of HNO3 and HONO. In the previous study both species were only indirectly determined. The low levels of by-products are supported by a comparison of the rate constants showing that CO scavenges OH much faster than it reacts with either NO or NO2. The ratios of rate constants of R5/R3 and R6/R3 are 0.001 and 0.06 respectively (Atkinson et al., 2004). Due to interference in the chemiluminescence detection, we cannot quantify NO once CO is added to the gas flow and we can also not differentiate between NO and NO2.

NO and NO2 do not interact with the ice at temperatures of our experiment (Bartels-Rausch et al., 2002), thus their presence does not influence the adsorption measurements of HO2NO2.

Figure 2. Time traces of HO2NO2 (blue solid line, left axis) and the by-products NOx (black dotted line, left axis), HONO (green dash dotted line, left axis), HNO3 (red dashed line, left axis), and H2O2 (turquoise solid line, right axis). Times at which traps were active are indicated by horizontal bars: Red: HO2NO2 trap (heating system), green: Ti(IV) denuder, blue: Cooling trap. Concentrations are given without the dilution in front of the CWFT. The data were obtained at initial concentrations of 3.4×1012 molecules cm-3 NO2, 5.4×1015 molecules cm-3 O2, 1.6×1016 molecules cm-3 CO, and 2.36×1018 molecules cm-3 water vapor.

3 - Page C12207, Lines 18-21: “Pages 26823 -26824, the authors had to use a Ti (IV) denuder to reduce the interference of H2O2, however the use of the denuder although eliminated 99% of H2O2 it increased the HNO3 levels by 240% this is why a cooling trap was needed to reduce the HNO3 levels. Once I reached page 26824 lines 11-

17, the authors stated that without purification levels of HNO3 stayed within 10% of HO2NO2 concentration and that's why Ti(IV) denuder is not needed. This is really confusing so did the authors use a denuder in their experiments or not."

Response: The Ti(IV) denuder was used for all adsorption experiments. This point needs to be strengthened throughout the manuscript. In the revised version, we structure the text newly, having one part for the synthesis without purification and one part only about the purification. We feel that the information of the pure synthesis is useful as it allows comparing the performance of the synthesis to our previous work.

4 - Page C12207, Line 24: "Page 26825 line 24, the authors stated that error estimates were based on experiments performed at 230K, is there a reason why did they use 230 K and what about experiments performed at 253 K?"

Response: We agree that the explanation for the error should be exacter. In the revised document all error are given as 95 % confidence interval. Also we added a section where we discuss the uncertainties of the measurements:

The uncertainty of nads, KLinC, the exponent of the Arrhenius temperature dependency and the ΔH0ads was determined by the 95 % confidence interval of the fit through 22 data points. The reported error represents random variations between individual experiments and is expressed as 2 times the standard deviation in each direction. The 95 % confidence interval of the fit agreed well with the confidence interval of 5 repeated experiments at 230 K. A rough estimation of the individual contributions to the total uncertainty revealed that fluctuations in nads, which are 19 % of the mean value and instrumental fluctuations, which are 5 % of the mean value, contribute to an half of the total uncertainty of nads. Other random fluctuations like the temperature of the CWFT or the fluctuations of the flow through the CWFT have a lower impact on the error.

Co-adsorption has been identified as a possible systematic error for the analysis of the breakthrough curves and the determination of KLinC of HO2NO2. The estimation of the effect of co-adsorption relies on parameters that had to be assumed, which might have an uncertainty by themselves. An error in nmax of H2O2 and of HO2NO2 was found to be negligible. In the interval of nmax from 2 ×1014 molecules cm-2 to 4 ×1014 molecules cm-2, KLinC only changed by 7.4 % at 230 K. The gas phase concentration of H2O2, which was tested in the ± 50 % interval, changed KLinC by 7 % at 230 K. This deviation is also within the experimental scatter. A change in KLinC of H2O2 within a + 150 % - 66 % interval, leads to a change in KLinC of 22 %. This effect was the greatest, but still inside the bounds of error of experimental scatter. In summary the estimation of the parameters is robust, and the conclusion, that co-adsorption is negligible, is valid.

5 - Page C12207, Lines 24-28: "Page 26826, line 17 neither McNeill et al 2006 nor Ullerstram et al 2005 reported information about CF3COOH a reference is needed here."

Response: This is correct, the reference for Symington et al. (2010) should be included.

6 - Page C12207, Line 28: "Page 26828 lines 25-27, the authors stated that HNO3 desorbs at higher temperatures (+25K). Is this the temperature or is it 25 degrees higher than that of HO2NO2?"

Response: We agree that this statement can be misleading. We clarify that HO2NO2 desorbs at around 225 K while HNO3 desorbs at around 246 K. The revised section reads:

It is also in agreement with Li et al. (1996) who observed that HNO3 desorbs at higher temperatures (246 K) than HO2NO2 (225 K) in temperature programmed desorption experiments.

7 - Page C12208, Line 1: Page 26829, lines 20-23. Are the authors discussing their results or still talking about the Sokolov data?"

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Response: We agree that the sentence can be confusing. We clarify that we are talking about our data and not the data of Sokolov et al.(2002). The revised document is structured newly, not mentioning the study of Sokolov et al. (2002) in this part anymore:

The good correlation illustrates the importance of both the acidity and the solubility on the partitioning to ice. Apparently similar molecular properties determine the tendency for uptake into water and the adsorption on ice for these acidic trace gases. This even holds for acidic organic trace gases.

8 - Page C12208, Line3: Page 26831 line1, by long experiments do you mean long term uptake experiments?"

Response: We did not execute long term uptake experiments. We waited until no more uptake was visible for HO2NO2 and the intensity before the activation of the CWFT was reached. For colder temperatures it was sometimes more difficult to identify this point, simply because the breakthrough took longer. In some of these cases we waited longer than necessary to identify full recovery. Those experiments took about 45 minutes. The revised version reads:

In all experiments the HNO3 signal remained at background level, while the onset of the recovery for the H2O2 signal was only visible in longer experiments (> 45 min).

9 - Page C12208, Line 4: "what do the authors mean by the upper 1.1 nm of the ice?"

Response: It is true that the probing depth of XPS and NEXAFS are not the same. The upper 1.1 nm are the probing depth of XPS at the energies applied in that study, but the results refer to the NEXAFS measurements. We apologize for this misunderstanding. The NEXAFS probing depth should be in the same order of magnitude. The text should be edited, changing 1.1 nm probing depth to the upper mono-layers of water molecules. The edited version reads:

In agreement, solid ice was still observed at the surface in presence of nitrate at concentrations similar to this study (Krepelova et al., 2010).

10 - Page C12208, Line 5: “Page 26842, table 1 I would suggest that the authors change the citation of references from number to letters so that is can be less confusing to the reader.” Response: We agree with that statement. The table should be edited: Table 1. Solubility, acidity (pKa), and adsorption enthalpies (DHads). The solubility is given as molecular Henry constant at 298 K (H298).

See Fig 1

a: (Durham et al., 1981), b: (Becker et al., 1996), c: (Lelieveld and Crutzen, 1991), d: (Chameides, 1984), e: (Amels et al., 1996), f: (Regimbal and Mozurkewich, 1997), g: (Marsh and McElroy, 1985), h: (Chen et al., 1979), i: (Liss and Slater, 1974), j: (Wilhelm et al., 1977), k: (Hwang and Dasgupta, 1985), l: (Hoffmann and Jacob, 1984), m: (Yaws and Yang, 1992), n: (Servant et al., 1991), o: (Gaffney and Senum, 1984), p: (Bowden et al., 1996), q: (Bartels-Rausch et al., 2002), r: (Kerbrat et al., 2010b), s: (Thibert and Dominé, 1998), t: This study, u: (Pouvesle et al., 2010), v: (von Hessberg et al., 2008), w: (Sokolov and Abbatt, 2002).

Technical comments: 1 - Pages C12208-C12209: “Page 26817, lines 15- 16 change the sentence to read probability that a gas molecule kinetically collide rather than a molecule that gas-kinetically collide. 2- Page 26828 line 14, omit “and” before “Arrhenius type”. 3- Page 26828 line 20, add “the following references” after on data from. 4- Page 26829 line1, replace better by more. 5- Page 26829 line18, replace is mainly that by is mainly what, same page line 22, omit “-“ after ice. 6- Page 26830 line 2, add a period after the word “each” and before “where slope” so the sentence now reads “each. The slope and uncertainty..” Same page, line 3, replace “:While” by “. The slopes”. Same page lines 4-5 rewrite so it reads “The slopes of the HNO3-HONO and the HNO3-HO2NO2 pair were not different, which might be due to...”. Line 7, replace were statistically by was statistically.”

Response: We thank the reviewer for these useful comments.

2 - Page C12208, Line 21: “the uncertainties of what??? were given by 95% confi-

dence??”

Response: We agree that the error of the measurements was described poorly. A new section for discussion of the measurement uncertainty is included, see above

3 - Page C12209, Line 11: “does the symbol [-] means unitless?”

Response: Yes.

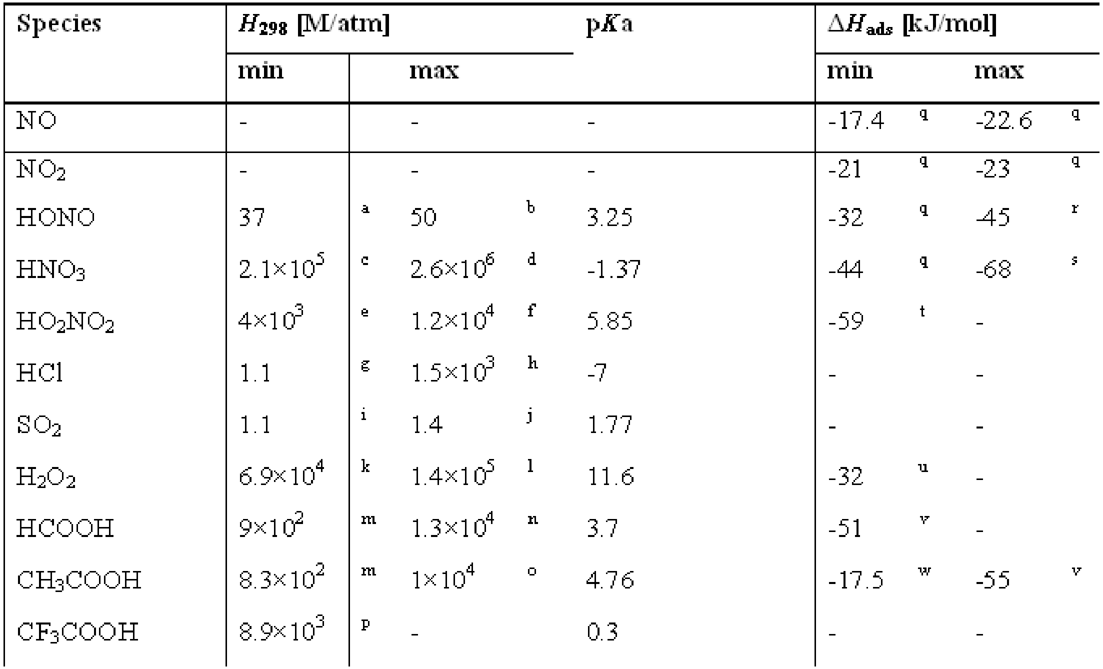
Interactive comment on Atmos. Chem. Phys. Discuss., 11, 26815, 2011.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Species	H_{298} [M/atm]		pKa	ΔH_{ads} [kJ/mol]	
	min	max		min	max
NO	-	-	-	-17.4[q]	-22.6[q]
NO_2	-	-	-	-21[q]	-23[q]
HONO	37[a]	50[b]	3.25	-32[q]	-45[r]
HNO_3	2.1×10^5[c]	2.6×10^6[d]	-1.37	-44[q]	-68[s]
HO_2NO_2	4×10^3[e]	1.2×10^4[f]	5.85	-59[t]	-
HCl	1.1[g]	1.5×10^3[h]	-7	-	-
SO_2	1.1[i]	1.4[j]	1.77	-	-
H_2O_2	6.9×10^4[k]	1.4×10^5[l]	11.6	-32[u]	-
HCOOH	9×10^2[m]	1.3×10^4[n]	3.7	-51[v]	-
CH_3COOH	8.3×10^2[m]	1×10^4[o]	4.76	-17.5[w]	-55[v]
CF_3COOH	8.9×10^3[p]	-	0.3	-	-

Fig. 1.