Atmospheric Chemistry and Physics Discussions

Interactive Comment

Interactive comment on "Uptake of hypobromous acid (HOBr) by aqueous sulfuric acid solutions: low-temperature solubility and reaction" *by* L. T. Iraci et al.

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Received and published: 25 April 2005

In this paper Iraci *et al.* present effective Henry's law coefficients for hypobromous acid in sulphuric acid, determined using a Knudsen cell based method. This method is well established for determining effective Henry's law coefficients of acidic gases and small organic molecules in sulphuric acid at low temperatures. Their results are in excellent agreement with the only previous systematic study of these coefficients for HOBr in H_2SO_4 at low temperatures (T < 238 K, obtained using a coated flow-tube based technique), but are in significant disagreement with the only previous study at

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higher temperatures (T $>$ 250 K). In addition to confirming existing low temperature measurements, this short paper extends the range of conditions used over those published hitherto. Parameterisations of the effective Henry's law coefficient as a function of temperature are presented, as are values for ΔH and ΔS. An appraisal of heterogeneous HOBr chemistry in sulphuric acid aerosols in the lower stratosphere is also given.

The paper is well written (I have found no typographical errors) and on the whole the authors present clear arguments to support their interpretation of their data.

Although the inclusion of more data would strengthen the paper, it already contains sufficient new information to make publishing in this journal both appropriate and desirable. I am therefore recommending that this paper be published, after the following questions and comments have been addressed.

1) A comprehensive temperature range is covered for both 45 and 70 wt % acid, as is a reasonable temperature range for 61 wt % H_2SO_4 (although not extending the range covered by Waschewsky and Abbatt). Why then is the number of datapoints for the "novel" composition of 55 wt% limited to three? Considering the scatter on the various datasets, why is it more appropriate to average the data for 55 wt % with the data for 60 and 70 wt% rather than with the data for 45 wt %? Measurements at colder temperatures for 55 wt % H_2SO_4 solutions would have removed this uncertainty and measurements at 50 wt% over a range of temperatures would also have been useful.

2) What fraction of the experimental data was rejected by the protocol used to identify suspicious and biased data?

3) Are the values of β sensible, given the probable (small) size of the diffusion component and of the accommodation coefficient? In fact, is it possible to extract any information about α from the data?

4) How much does a mismatch of 10 %, 60 % or 100 % between the solution water

vapour pressure and the gas phase water vapour pressure change the wt % of the sulphuric acid? (page 1219, line 19-20)

5) Water vapour is present in the flow from the HOBr source. How much is present and would this amount significantly change the H_2SO_4 wt%?

6) The partial pressure of HOBr used in these experiments of between 1×10^{-5} and 2×10^{-4} Torr ($\approx 5 - 100 \times 10^{11}$ cm^{-3}) is quite high. What was the typical partial pressure used, and was there any variation of the observed uptake coefficients with initial HOBr partial pressure? Also was there any dependence of the amount of gas-phase Br$_2$O with HOBr partial pressure, or cell temperature?

7) In addition to reaction with HOBr, could the presence of large amounts of HBr affect the uptake of HOBr in H_2SO_4?

8) Was the uptake of HBr examined and if so what did it look like? Was the form of the HBr uptake different for an experiment with a non-zero 'k', compared to an experiment were k was zero?

9) For ease of comparison with figure 1, a raw mass spectrometer trace for HOBr in figure 3 would be useful. In addition I think the 3 parameter fit should also be shown in figure 3.

10) The difference in ΔH and ΔS between 45 wt % and 55-70 wt % sulphuric acid is large. Has similar behaviour been observed in the solubility of any other gas in H_2SO_4? (Section 3.1, 3.2)

11) What did subsequent uptakes onto previously exposed samples look like? Waschewsky and Abbatt noted that using a previously exposed surface led to a reduction of up to a factor of two in the observed uptake coefficient. I assume that a difference was observed as otherwise it would not be necessary to stir the solution between experiments. If the uptake behaviour does change for repeated exposures there must be more chemistry going on than just the reaction of HOBr with HBr and itself,

as these reaction partners are present in roughly the same amounts for each repeat exposure.

12) From figure 4(a) it appears that the dominant gas-phase product is Br_2O (assuming similar MS sensitivities between Br_2O and Br_2). Can this observation be consistent with your assertion that reaction with HBr is the dominant loss process for cases where the fitted k was non-zero? What is known about the solubility of Br_2 in H_2SO_4 under these conditions?

13) The temperature dependence of k is the same as that of log H^* for HBr. However it is also the same within error as the temperature dependence for log H^* for HOBr.

14) In the stratospheric implications section you set the bimolecular rate coefficients for HOBr + HX (X = Cl, Br and OBr) to the same value. The aqueous phase rate coefficient for HOBr + H^+ + Cl^- is known to be approximately a factor of three smaller than the rate coefficient for HOBr + H^+ + Br^-. Although I agree that the conditions under which these coefficients were measured were very different from 66 wt % H_2SO_4 and temperature assumed here, this ratio is at least as reasonable as setting the coefficients to the same value. In addition if k^{II}(HOBr + HBr) = k^{II}(HOBr + HOBr) then reaction of HOBr with HBr could not be the dominant loss process in your experiments where [HOBr] = 3-8 × [HBr]. If you are correct and reaction with HBr is the dominant loss in your experiments then the rate coefficient for the self reaction is almost certainly at least a factor of 10 less than for the reaction HOBr + HBr. It would be interesting to see how your predictions are altered if the rate coefficients were to be set to k^{II}(HOBr + HBr) = 10 × k^{II}(HOBr + HOBr) = 3 × k^{II}(HOBr + HCl).

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