Atmos. Chem. Phys. Discuss., 5, S770–S777, 2005
www.atmos-chem-phys.org/acpd/5/S770/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

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

L. T. Iraci et al.

Received and published: 14 May 2005

We thank the Reviewers for their comments and expertise. As there was nearly complete overlap in their comments, we have combined our responses into a single document.

1) Referee #2, point #1: The temperature range of the 55 wt% H_2SO_4 experiments was limited by practical, rather than experimental or theoretical reasons. We invested much effort in measuring well the warm end of the 70 wt% line and in confirming the surprising temperature dependence of the 45 wt% data, such that time ultimately became a limiting factor in the scope of the study. The Reviewer's comment about

including the 55 wt% data into the 61-70 wt% set, rather than into the 45 wt% set, is a fair one. We chose the former based on other laboratories' demonstration of lack of acidity dependence for 58-70 wt% solutions. Due to the overlapping scatter in our 45 and 55 wt% measurements, we did not expect that measurements at 50 wt% H2SO4 would have shed any light on the situation.

2) Referee #2, point #2: After we removed data sets with obvious experimental difficulties (unstable HOBr flow rates, etc.), five additional data sets were omitted based on the statistical screening tests. Three of these five were already suspect, but two had not been subjectively identified as unusual. A sentence to this effect has been added in the Appendix.

3) Referee #2, point #3: Since the mass accommodation coefficient, alpha, should be between zero and unity, beta should be $>=$ 1, as the gas-phase diffusion term is a positive number. This constraint was imposed on the fitting procedure, and our beta values ranged from 1.0 to 277, with most in the range 10 - 80, as can be seen in Table S1. As the gas-phase diffusion term is considered negligible in Knudsen cell experiments, these beta values correspond to a values of 0.1 - 0.013. The only predictive relationship found for beta is in the 45 wt% data set. At warmer temperatures, beta is larger, with an exponential dependence on T. No other trends in beta have been identified, and thus we chose not to discuss the intercept term and its possible interpretation.

4) Referee #2, points #4 and 5; and Referee #1, point #2: The amount of water delivered with the HOBr varied depending on many factors, including the age and acidity of the sample, the flow rate needed to deliver HOBr at detectable levels, etc.. Water pressures in the Knudsen cell supplied by the mixed gas stream were usually on the order of 1-5 mTorr, which was often too high for the more acidic and colder conditions. The possible change in acid composition due to a mismatch in water partial pressure depends on how badly it is matched, the diffusion coefficient for additional water to be mixed down into the solution, and other parameters. Let us evaluate the experiment presented in Figure 3 for uptake of HOBr into 70 wt% H2SO4 at 212 K. This is

a good example of the difficulty in delivering sufficient HOBr while maintaining as low a water partial pressure as possible. The equilibrium water vapor pressure over this solution is 0.16 mTorr, and the gas stream delivering HOBr contained ˜1.1 mTorr of water. When this gas was exposed to H2SO4, the water partial pressure dropped to ˜0.66 mTorr (a loss of ˜60%). This change in signal can be converted to the number of water molecules taken up by the solution. Accounting for surface area, exposure time, and diffusion depth, we estimate that the surface (˜12 um) of the acid solution may have become as dilute as 68 wt% H2SO4. A sentence indicating the magnitude of this possible change has been added to the manuscript. While it is certainly possible that these small variations in the acidity contribute to the scatter in the data, unfortunately we cannot ascribe all the variability to changes in H2SO4 content, particularly because many of the data points shown in Figure 2 are averages of multiple independent exposures.

5) After a detailed re-examination of much of the experimental data, we offer the following responses to several comments addressing the partial pressures of HOBr used. a) Referee #2, point #6 "typical" partial pressure of HOBr: This is a difficult question to answer precisely, as the amount of HOBr present in the gas stream varied from one synthesis to another and as each batch aged (decomposed). Furthermore, the MS electron multiplier (SEM) sensitivity degraded over time, and the filaments and SEM were changed during the course of the experiments. With all that said, it is our best estimate that most of the experiments reported here were conducted between 3 x 10-6 and 3 x 10-5 Torr of HOBr, with experiments spread across that entire range as a function of experimental parameters such as aperture size, SEM voltage, and quality of HOBr sample. It is probable that some experiments were conducted at both higher and lower partial pressures as well, expanding the range of conditions from 2 x 10-7 to 6 x 10-5. Of course, these estimates are subject to the assumption of comparable MS sensitivities for HOBr and HBr, as discussed on pg 1219. That discussion has been slightly modified as noted here, based on the present re-assessment of experimental conditions.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

b) Variation in uptake coefficient with initial HOBr MS signal: No correlation is present between beta (the uptake coefficient at time zero) and the MS signal for HOBr (a surrogate for partial pressure) for the 45 or 70 wt% data sets.

c) Dependence of Br2O formation on partial pressure of HOBr (also Referee #1, point #4): Br2O production was observed in experiments which had a relatively narrow range of conditions. For 70 wt% H2SO4, the coldest uptakes (which were the experiments which showed Br2O and Br2 formation) were actually performed with some of the lowest HOBr signal levels, and thus the lowest partial pressures. The temperature dependence was clear (production when cold, no production when warm), but any dependence of Br2O production on HOBr pressure alone could not be discerned from the data collected. That, coupled with such small amounts of Br2O observed in the gas phase, prevents us from saying anything quantitative about the effect of HOBr partial pressure on product formation. Two sentences have been added to the second paragraph of section 3.2 to convey this information.

d) Dependence of Br2O formation on the temperature of the cell walls: With the exception of a small area above the liquid sample, which is influenced by the cold bath in which the liquid is submerged, the glass surfaces of the Knudsen cell were at room temperature in all experiments, with or without observed Br2O generation. We expect no influence of wall temperature on the Br2O production from solution and have no specific information regarding this effect.

e) Referee #1, point #1, Does partial pressure affect uptake measurements, particularly when Br2O is seen to form?: To answer this question strictly in terms of HOBr levels, we must remove the strong temperature dependence in the observed solubility. As mentioned above, we have insufficient data for experiments which produced Br2O to separate the effect of HOBr pressure from the effect of lower temperature. However, if we broaden the question to examine the effect of HOBr pressure on solubility regardless of Br2O liberation, we have more data to examine. Among the 11 exposures of HOBr to 70 wt% H2SO4 at 233 K, the pressure of HOBr was varied ˜3-fold. While this is not a wide range of conditions, no trend is seen in H* with HOBr pressure.

f) The 25% uncertainty in H* values due to possible HOBr generation from Br2O in the delivery gas was estimated from the typical experiment shown in Figures 1 and 4b. Assuming roughly equal MS responses for all brominated species, the Br2O signal of ˜4 x 10-10 Amps was taken to estimate a delivered concentration which was approximately 15% of the concentration of HOBr (˜2.7 x 10-9 Amps). Complete hydrolysis of Br2O would therefore liberate HOBr roughly equal to 30% of the delivered HOBr. Since other experiments showed a slightly lower contribution from Br2O (˜10%), we felt a 25% uncertainty in H* due to available HOBr in solution was an appropriate estimate for the study as a whole. {A note about isotopic ratios: bromine has two natural isotopes of nearly equal abundance. The Br2O peak at 176 amu accounts for half of the Br2O available. The peaks at 174 and 178 amu each has one quarter. The HOBr peak at 98 amu also represents half of the total HOBr concentration, thus the two peaks can be directly compared without correction for other isotopes.}

g) Referee #1, point #5: The text at the beginning of section 4 has been tempered to reflect possible differences in behavior between laboratory and atmospheric conditions.

6) Referee #2, point #7: The only effect which we anticipate would be a change in acidity (or water activity) due to the uptake of HBr. But in such small amounts (relative to H2SO4), HBr should not affect the pH (or excess acidity, or whichever acidity scale one prefers to use) or the solvating properties of "H2SO4 + H2O." Granted, HBr is a stronger acid than H2SO4, but it would cause only a small shift in the dissociation of H2SO4. For example, at 220 K and 70 wt% H2SO4 with H*(HBr) = ˜2 x 104 M/atm, when P(HBr) ˜ 1 x 10-4 Torr (1.3 x 10-7 atm), the solution concentration of HBr is 2.6 x 10-3 M; H2SO4 is 12.0 M under the same conditions. Thus, we do not believe the trace amount of HBr will affect the ability of the solvent to accept HOBr, and no significant change in ionic strength will occur, precluding any "salting in" or "salting out" effects. Beyond these effects, I am unaware of any surface properties or other processes involving HBr which should be considered.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

7) Referee #2, point #8: Due to the high solubility of HBr in less acidic H2SO4 solutions, the observed uptake of HBr was always significant and essentially independent of time for our 45 and 55 wt% solutions. As shown by Williams et al. [J. Geophys. Res., vol. 100, p.7329, 1995], the Knudsen cell technique is poorly suited for measurements of HBr solubility in $<=$ 60 wt% H2SO4. In our 61 wt% experiments, time dependence was sometimes evident. In the 70 wt% solutions at colder temperatures, we regularly saw time dependence but did not analyze those results for H*(HBr), due to the complex solution phase chemistry occurring in those systems.

8) Referee #2, point #9: Both are good suggestions, and we have changed Figure 3 as requested.

9) Referee #2, point #10, enthalpy and entropy differences between 45 wt% H2SO4 and other solutions: To my knowledge, such an observation has not been made for any other inorganic acid solute studied below 50 wt% H2SO4. However, a more negative entropy and enthalpy of dissolution in the most dilute acid studied has also been seen in our laboratory for methanol [Iraci et al., J. Phys. Chem. A, vol.106, p. 4054, 2002] and acetaldehyde [Michelsen et al., J. Geophys. Res., vol. 109, doi:10.1029/2004JD005041, 2004], although the difference in enthalpy is most significant for HOBr. Using a flow tube technique, Kane et al. [J. Phys. Chem. A, vol. 103, p. 9259, 1999] found DS for uptake of acetone into 40 wt% H2SO4 to be a factor of two more negative than in 70 wt%. In our previous work, we have wondered if the relatively narrow temperature range limited our ability to determine the intercept of the fit line, as doing so requires significant extrapolation. The extended temperature range studied here gives us additional confidence in this observation for HOBr.

10) Referee #2, point #11 and Referee #1, point #3: Unlike flow tube experiments, we do not desorb any gases which are taken up during an exposure before starting the next. Thus, stirring between uptakes insures that the solution nearest the gas-liquid interface is not already saturated with analyte from the previous experiment. We believe this to be especially important for the more viscous solutions (higher acidity,

lower temperature), where liquid-phase diffusion is slowest. In addition, as noted in response #4 above, a mismatch of the water partial pressure above a solution may lead to small changes in the acidity of the surface layers of a sample; mixing between exposures provides reassurance that any small changes are not propagated from one experiment to the next. We do have one pair of exposures (the first is marked "l" in Table S1, and the second is "k") which were performed sequentially, without stirring during the ~160 sec which elapsed between them. As can be seen from the H* values in Table S1, the solubility measured in each case is the same, within experimental uncertainty. The second exposure had smaller uptake coefficients, while still demonstrating the same time dependence. Thus, it had a larger b value, perhaps suggesting a reduced a for uptake on a "dirty" solution. Our thanks to both Reviewers for reminding us to highlight these findings for this pair of experiments. The footnote to Table S1 has been amended to include this information.

11) Referee #2, points #12 and 13: Your points regarding the dominant reaction pathway are well-made. The absence of a dependence of k on the partial pressure of HOBr, coupled with the similarity of the T-dependence of k and of H* for HBr, drew us to the conclusion that k was driven by [HBr]. However, the points you raise have caused us to question our original conclusion. To our knowledge, nothing is known about the relative solubilities of Br2O and Br2 under these conditions. This, coupled with your observation that the signal for liberated Br2O exceeds that for Br2 in Figure 4a causes us to re-evaluate our assignment of HOBr + HBr as a dominant loss mechanism under laboratory conditions. Inspection of the data from experiments which liberated Br2O and Br2 shows that the integrated signal from Br2O was always comparable to or exceeded that of Br2. Thus we may presume that Br2O was produced in equal or greater amounts than Br2. We have removed the statement in section 3.2 which suggests HOBr + HBr dominates under laboratory conditions and have instead suggested that the two channels produce roughly equal amounts of Br2O and Br2. Given the expected solution concentrations of HOBr and HBr, this suggests that the rate constant for HOBr + HOBr may be one-third to one-eighth that of HOBr + HBr. We have added

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

a statement to that effect.

12) Referee #2, point #14 and Referee #1, point #6: Given the expertise of and agreement between the referees, we thank them for their advice and are happy to increase the rate constant for HOBr + HBr in our implications section. We have also reduced the rate constant for HOBr self-reaction, given the discussion in item #11 above. Table 1 has been recalculated to reflect these changes, and the text has been updated. No significant changes to our conclusions result. We have also highlighted our assumption of volume-dependent (rather than surface dependent) reactions.

13) Referee #1, point #7: This is an excellent suggestion to make Figure 2 more useful to the reader. We have amended the figure caption and legend to include the solution compositions of Waschewsky & Abbatt (1999) and Hanson (2003).

We thank the Reviewers again for their efforts; our manuscript has benefited from their time and assistance.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 1213, 2005.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper