Atmos. Chem. Phys. Discuss., 4, S1177–S1180, 2004
www.atmos-chem-phys.org/acpd/4/S1177/

Atmospheric
Chemistry
and Physics
Discussions

# *Interactive comment on* "A study of the phase transition behavior of mixed ammonium sulfate – malonic acid aerosols" *by* C. F. Braban and J. P. D. Abbatt

**C. F. Braban and J. P. D. Abbatt**

Received and published: 12 July 2004

The purpose of this comment is to suggest that letovicite forms in the studied system. Ammonium sulfate and malonic acid can combine to form an acidic sulfate solid, namely letovicite (triammonium hydrogen disulfate). The authors rule out the formation of letovicite on lines 24 of page 2954 through line 7 of page 2955. Principally, the authors state that bisulfate has a peak at 1300 cm$^{-1}$ whereas the observed spectra do not show a peak in this region. In fact, the principal peak of bisulfate is 1200 cm$^{-1}$, and I will assume that the manuscript has a typo.

*Yes, it is a typo. Thank you for pointing it out!*

In lines 16-18 on page 2958, the authors state that Figure 1C is similar to Figure 2C. I wish to dispute this statement, specifically in regard to the peak at 1100 cm$^{-1}$, which

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

is significantly broader in Figure 1C than in Figure 2C. Moreover, shoulders are clearly apparent in Figure 1C. I suggest that the peak in Figure 1C is consistent with letovicite peaks as shoulders at 1210 cm$^{-1}$ and 1095 cm$^{-1}$ around a central ammonium sulfate peak at 1115 cm$^{-1}$.

*We agree that there is more structure in the low RH, Figure 1C spectrum, which could be consistent with formation of some letovicite. See discussion below.*

The suggestion of the formation of letovicite is also consistent with the behavior seen in Figure 5. Namely, whereas pure crystalline ammonium sulfate deliquesces at 80% relative humidity, pure crystalline letovicite deliquesces at 69.5%. A step change consistent with this change in dominant solid at 10 to 30 wt% is apparent in Figure 5.Of course, this interpretation based upon pure compounds does not take into account malonic acid and hence the shift to a eutonic relative humidity, as mentioned by Braban and Abbatt.

*This is correct. It is unfortunate that the two phase transitions fall within error at the same RH, so that it is not possible to differentiate between either, or discern whether both transitions are occurring.*

With this comment, I wish to suggest that the evidence presented in the manuscript appears to unduly rule out the formation of letovicite. If this solid forms, some of the implications discussed by Braban and Abbatt may also be affected (e.g., lines 10-16 on page 2960).

As an example of a possible complication, consider first a solution composed of 10% nitric acid (as an analog to malonic acid) and 90% ammonium sulfate. If the only solids allowed to form are letovicite and ammonium sulfate, then both of these solids form at low relative humidity, and an aqueous layer of slightly acidified ammonium sulfate remains.

This complex behavior is possible because the solution contains nitrate, proton, ammonium, sulfate, and water. That is, because nitric acid and ammonium sulfate dissociate, the system has five components instead of three so that solids like letovicite, which do not lie on the central axis of composition mixtures of nitric acid and ammonium sulfate, can form. When this finding is applied to a system for which malonic acid is substituted for nitric acid, it is reasonable (in the absence of a phase diagram but consistent with Gibbs phase rule) to suggest that ammonium sulfate and letovicite both crystallize and a residual aqueous layer of slightly acidified ammonium malonate remains.

*This example system is very illustrative and useful. The main difference between it and the system studied in the paper is the availability of protons. Malonic acid, even in fairly dilute aqueous solutions, is only weakly dissociated (see paper text). Similarly, in the presence of sulfate, it will remain largely undissociated: the Ka of bisulfate (pKa $=$ 1.99) is close to an order of magnitude larger than that of malonic acid (pKa $=$ 2.85). Thus, the driving force for whether letovicite ($(NH_4)_3H(SO_4)_2$)will want to form is not as strong, i.e. there is not as much bisulfate present in solution as in the example given by Prof. Martin. That being said, we fully agree with the point made above that there are features in the peak in Figure 1C at close to 1100 cm$^{-1}$ which are consistent with the presence of letovicite. In support of this we also note that in x-ray diffraction experiments which are detailed in a forthcoming paper (Braban and Abbatt, in prep) low levels of letovicite were observed in dry particles in which a small fraction of malonic acid was present with ammonium sulfate. The evidence against the presence of large amounts of letovicite in the particles is the absence in Figure 1C of a strong peak that appears between 1500 and 1600 cm$^{-1}$ in spectra of ammonium malonate and bimalonate particles (Braban and Abbatt, in prep), and the absence of a weak-to-medium strength peaks at close to 880 cm$^{-1}$ that are characteristic of letovicite (Schenkler et al., submitted; Scot Martin, private communication). Given the evidence to date, we believe that small amounts of letovicite may indeed have formed but, given the absence of the malonate peak between 1500 and 1600 cm$^{-1}$, it is likely that substantial amounts of solid ammonium sulfate also form. If letovicite does form, it is true that the resulting supersaturated solution would be acidic in nature and we had not previously*

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

*considered this. Prof. Martin's attention to these details is really very useful, and the suggestion that letovicite may have formed in these solutions will be incorporated into the final version of the manuscript.*

---

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 2949, 2004.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper