

***Interactive comment on* “Common inorganic ions are efficient catalysts for organic reactions in atmospheric aerosols and other natural environments” by B. Nozière et al.**

Anonymous Referee #3

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This is an interesting and topical article that is of potential importance to aerosol chemistry and the fate of VOCs in the atmosphere. Therefore, the manuscript is principally suited for ACP. However, there are several points that are yet unclear and need to be revised before the paper is acceptable. In particular, I have problems with some of the analysis and the interpretation/application of the experimental results to the atmospheric situation.

1) The concentration units are used very inconsistently throughout the paper: % and wt.% and mol% and M are being used, sometimes even in the same table. Also, M is not defined (I assume you mean mol L⁻¹). Please use ONE consistent scale

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throughout, preferably mole fraction or mol kg⁻¹ as this does not require the knowledge of solution densities.

2) P.3, lines 21-22: 'Concentrations were introduced...' Are these the concentrations after mixing, or were these solutions added to the salt solutions? Please be more precise.

3) P.8, lines 23-25: I do not understand why the ammonium activity coefficients were not calculated for the nitrate and bisulfate solutions. These are also provided by AIM. For example, at 308 K the ammonium activity coefficient is 0.4014 in AIM, while you assume 0.69 (This is almost a factor of 2!). In contrast, ammonium chloride, bromide and fluoride are not provided at the temperatures specified in Tab.1. Please specify exactly how the activities were obtained.

4) Table 1, Figure 4 and related text. The ion activities must not have units. Please specify on which concentration scale the activity coefficients were calculated, i.e. on the mole fraction scale or molality scale (note that the activity coefficients are dimensionless quantities by themselves). AIM usually provides the activity coefficients in mole fraction. Depending on which scale you use the actual values are different. Hence, it is important also for calculating the activities specified in Tab.1 and shown in Fig.4.

5) In the first paragraph on page 7, it is stated that 'ammonium-catalyzed reactions do not follow the classical acid- or base catalysis mechanisms'. The current manuscript does not provide evidence for this statement. In fact, I could well imagine the ammonium ions to act as proton donors in the aldol-reaction in the enol mode in a pre-equilibrium with the protonated O-atom.

6) Why haven't there been any experiments investigating the pH-dependence? In a very recent paper by the same authors (Noziere et al., 2009) the ammonium catalysis of glyoxal reactions was shown to very strongly depend on pH!

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7) There seems to be a logarithmic (not linear!) dependence of k as a function of the ammonium ion concentration. Is there any explanation for this fact?

8) Also, there is a very strong dependence on the ammonium counter-ions. Is there any explanation for this fact? Could it be due to the kinetic salt effect which is based on the overall ionic strength of the aqueous medium stabilizing or destabilizing the excited states of reaction intermediates. So plotting $\log(k)$ versus the square root of the ionic strength might shed some light on the involved intermediates. These effects must be known as the anions in the atmosphere are quite variable.

9) The main problem that I have with this paper is that quite bold interpretations are made, and the simple first order rate constants obtained in the present experimental study are applied to the atmospheric situation without even knowing the underlying chemical mechanisms. This is an extremely dangerous game to play and I would be very hesitant to make such statements without resolving points 5)-8) above.

Technical comments:

1) Title, abstract and elsewhere in the text: I have a problem saying that the NH_4^+ and CO_3^{2-} ions are 'inorganic' ions. Along the same lines one might argue that CO_3^{2-} is an organic ion. Either way, this specification is not required and I suggest to remove it.

2) There are several places where the English could be improved. For example in the abstract:

P.2, lines 8-9: The reactions were found to be as fast 'in tropospheric ammonium sulfate composition' as in concentrated sulfuric acid.

P.2, line 22: 'such as aldol condensation' instead of 'such aldol condensation'

P.3, line 11: 'work' instead of 'works'

P.11, line 16: 'as has been' instead of 'as as been'

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