

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

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Reply to the reviewers on 'Common inorganic ions are efficient catalysts for organic reactions in atmospheric aerosols'

Reply to referee 1

General comments

A few comments on this first paragraph:

- our study involves several different ammonium salts, not only ammonium sulfate as mentioned in the first sentence,

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- the experiments included other carbonyl compounds than acetaldehyde: acetone, propanal, butanal, glyoxal (see Table1, Fig.3, and Fig. 4),

- we are not claiming that these reactions are a source of oligomers in general. This might be misleading as there are probably many different types of oligomers in aerosols, and different people have different definitions for oligomers. Therefore, we are only claiming that these reactions produce light-absorbing compounds.

1 - Role of ammonium ions: catalyst or reactant ?

The definitions proposed by the referee to distinguish between a catalyst and a regular reactant are close to the official definition, the later being the following:

1) a substance that takes part in the mechanism, but does not stay bonded to the final products. A direct consequence of this is, indeed, that its concentration does not vary during the reaction, but a more direct criterion is that the final products do not contain this substance,

2) it affects the rate constant of a reaction (usually increases it) by lowering its activation energy (Atkins, Physical Chemistry, 5th Ed. pp. 914-915). It is essential here that the criterion is on the rate constant, not simply the rate of the reaction, the latter being anyway increased by any reactant (unless the kinetics is zeroth order).

In this work, we demonstrate that non-nitrogen containing products are formed (and, respectively, non-carbonate containing ones in carbonate catalysis): crotonaldehyde, 2,4-hexadienal, and 2,4,6-octatrienal with acetaldehyde, and the oxygen-containing oligomers for glyoxal (more detailed in Noziere et al., JPC A 2009). In all cases, it is clear that none of the salts in the solutions are contained in these final products, which fulfills point 1) of the definition. We also performed a kinetic analysis specifically to extract rate constants and demonstrate that they increase with the concentration of these ions (Figure 4), which fulfills point 2) of the definition. Note that this kinetic analysis was based on non-nitrogen containing products (2,4,6-octatrienal) and is therefore

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safe from artifacts from non-catalytic pathways.

The fact that other pathways producing N-containing compounds also take place does not contradict the fact that catalytic pathways also exist. The contribution of each different pathway to the overall reaction is another debate. But rough estimates of the yields for the light-absorbing compounds in our experiments suggest that they were substantial (see answer to Question 7 below) while the yield of N-containing imidazoles in these reactions is reported to be small in the literature, 4 - 9 percent (Prasanthi, V., et al., Asian Journal of Chemistry, 19, 5778, 2007 and reference therein).

Finally, the identity of the light-absorbing products in this work (crotonaldehyde, 2,4-hexadienal, and 2,4,6-octatrienal for acetaldehyde) has been well demonstrated in our previous papers (Noziere et al., GRL 2007 and Noziere and Cordova, JPC A, 2008) by using standards for these compounds and verifying that they corresponded to the absorption bands. These are well-known aldol condensation products for acetaldehyde. We also performed ^1H NMR analysis of the crude reaction mixture, which established the presence of crotonaldehyde and 2,4-dihexadienal. Therefore the identity of the reaction observed in this work as aldol condensation was straightforward. Similarly, the oligomers identified with glyoxal are also well established products of acetal formation, as observed by Liggio et al., EST, 2005 with acid catalysis for instance.

2- Carbonate ion catalysis

We are not sure to understand this question. The abstract does not mention $(\text{NH}_4)_2\text{CO}_3$. It is always tricky to predict the efficiency of a combination of catalysts (here ammonium and carbonate ions together), which is why we preferred to make the measurements and not comment on them.

3- Title

Replacing 'Common inorganic ions' by 'Ammonium and carbonate ions' is fine with us. But we demonstrate that these catalysts are effective not only for aldol condensation

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but also for acetal formation with glyoxal. It is also well known in chemistry that catalysts for aldol condensation and acetal formation also work for many other types of reactions. Thus, keeping 'organic reactions' is justified.

4- Beer-Lambert law

The fact that the increase in absorption (or absorbance) is proportional to an increase in the corresponding product concentration is the definition of the Beer-Lambert law, mentioned at the beginning of Section 2.1.

The small delay near $t=0$ in Fig. 1 has already been explained in detail in Noziere and Cordova, JPC A 2008, and is due to the fact that the product monitored (here 2,4,6-octatrienal) is a third-generation product. There is therefore a delay between the beginning of the reaction and its formation.

5- Reaction in NaCl and Na₂SO₄

We can add the results in NaCl and NaSO₄ in Table 1, but since no reaction was observed these entries will only give upper limits for the rate of reaction (for instance $< 10^{-8} \text{ s}^{-1}$).

6- Comparison with OH reaction

This part will be re-written for more clarity. We will also add a row in Table 2 with the rate of these compounds by reaction with liquid-phase OH radicals. Yes, the rate constants for OH reactions are fast, but since the radicals are in much lower concentration (10^{-15} M) than the salts the overall rates of reaction are not necessarily faster. For glyoxal, ionic catalysis is, in some cases, faster than OH reaction.

If the referee means gas-phase OH reactions, these are not the subject here. As we explained in conclusion (and again, this will be re-written for clarity) these ionic reactions are mostly relevant for the primary organic material already present inside particles and never exposed to gas-phase OH radicals. Acetaldehyde, acetone, propanal, butanal are used as proxy for this primary material in this study. Glyoxal is an exception, as

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the only compound likely to transfer from the gas. But Volkamer et al, GRL, 2007 have demonstrated that its reaction with OH can not explain its concentrations in Mexico City and that heterogeneous or multiphase processes contribute significantly to its removal from the gas (and to 95 percent of its removal at night). But see Noziere et al., JPC A, 2009 and Galloway et al., ACPD, 2009 for better discussions of the case of glyoxal.

7- Yield of light-absorbing products

These estimates assume that all or most of the carbonyl compound reacted is transformed in light-absorbing products so, yes, they are upper limits. We could not determine precisely the yields for the light-absorbing products, but estimates based on their UV absorption indicated that they were substantial: 50 percent or more in NH₄F and Na₂CO₃ solutions (see details below). However these figures are very approximate because the absorptions of crotonaldehyde and hexadienal were often saturated, and it was not possible to determine the amounts of unreacted acetaldehyde, as its absorption overlapped with the products. Also, these yields seemed to vary with the reaction conditions (pH), and need to be determined with more precision. We will re-write this part to make clear that these estimates are upper limits.

Estimates of the yield of light-absorbing products:

In NH₄F and Na₂CO₃ solutions containing initially 0.2 M of acetaldehyde, the absorption index of crotonaldehyde, hexadienal, and octatrienal at the end of reaction reached up to 10⁻³, 5 10⁻⁴, and 10⁻⁴, respectively (very approximate for the first two because of saturation). Their absorption cross section (0.026 M⁻¹, 0.053 M⁻¹, and 0.095 M⁻¹, respectively, in absorption index units) give individual concentrations of 0.038 M, 0.009 M, and 0.002 M, respectively. Taking into account that crotonaldehyde contains two molecules of acetaldehyde, hexadienal 3, and octatrienal 4, the equivalent of acetaldehyde accounted for by these absorptions was thus of the order of 0.1 M. Thus, if all acetaldehyde had reacted the yield would be 50 percent but if some acetaldehyde was left, it would be larger. Lower product concentrations seemed to be obtained in ammo-

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mium sulfate but, again, it was impossible to determine the corresponding amount of acetaldehyde reacted.

All technical corrections have been noted and will be taken into account.

Reply to Referee 2

1- Ammonium as a catalyst or co-reactant

Please, see answer to the same question for Referee 1 (Question 1) above.

2- Comparison with OH reactions

This question was also answered in Question 6 for Referee 1 above. We will add the rate for the liquid-phase OH reaction in Table 2 to show the comparison. In the case of glyoxal, ammonium catalysis seems to be faster than OH reaction, but this depends strongly on pH.

3- Quoting other works

Yes, these works will be quoted.

4- Henry's constants

This part will be re-written for clarity. We already pointed out in our previous papers that these ionic reactions should be mostly relevant for primary material, and not for the uptake of organic gases and SOA formation, except for glyoxal. That said, this requires a discussion which is easier to make at the end of the paper. In particular, one can be more specific about the value of the Henry's coefficient for which these reactions might become significant for the uptake of organic gases and SOA formation (such a discussion is proposed in Noziere et al., JPC A, 2009).

1b- We will try to arrange this

2b- A larger portion of the mass spectrum was not given because the signal to noise

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was quite large.

3b- We will try to give more information. For instance, for all compounds, direct injection on ESI-HRMS (Bruker Daltonics MicroTOF) was performed.

4b- This question was also answered in Question 1 for Referee 1: the products found with acetaldehyde (crotonaldehyde, 2,4-hexadienal, and 2,4,6-octatrienal) are its well-know aldol condensation products, therefore the identification of the reaction was straightforward.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1, 2009.

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