

***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 #1

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General Comments

This paper addresses the question of how ammonium sulfate is able to catalyze aldol condensation of carbonyl compounds, a discovery which was announced in a 2007 GRL paper from this group. Aldol condensation can create conjugated molecules which absorb UV and visible light, and could be a major source of oligomerized material in aerosols. As the authors show, this chemistry is therefore likely important to the understanding the formation and aging of atmospheric organic aerosol. The authors have run aldol reactions on acetaldehyde with a wide variety of salts in order to determine whether the ammonium ion or the sulfate ion was responsible for the effects observed

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previously. Bulk experiments are performed at concentrations greater than 0.1 M. The mixtures are then analyzed by HPLC/high-resolution MS to detect aldol condensation products and by UV-Vis spectroscopy to monitor the increase in absorption. Kinetics data is extracted from the increase in absorption at single wavelengths. The manuscript is for the most part clearly written, and the experiments are described or referenced with enough information that others could reproduce them.

These studies unequivocally determine that the ammonium ion is involved in the production of light-absorbing products, rather than the sulfate ion. The claim that the ammonium ion is a catalyst for aldol condensations may be correct, but it is not fully supported by the evidence presented, because the light-absorbing compounds that are quantified in Figs. 1, 3 and 4 are not necessarily only those detected by HRMS and shown in Fig. 2, as the authors seem to assume. Without stronger experimental proof of catalysis or elimination of alternative hypotheses, many of the claims made in this paper may eventually turn out to be false, including the title claim. Acceptance of this paper, given its data interpretation, should therefore be conditional on stronger proof of ammonium catalysis.

Specific comments:

In order to establish that ammonium is a catalyst, one of the following must be demonstrated: 1) the concentration of ammonium does not change during the reaction (in a case where ammonium ions are not in huge excess), 2) the aldol condensation products that do not incorporate nitrogen, such as those shown in Figure 2, account for essentially all of the measured absorbance, or 3) the production of nitrogen-free aldol condensation products is substantially increased in the presence of ammonium salts.

An increase in production rates of light-absorbing molecules and non-quantitative detection of nitrogen-free aldol condensation products are not enough to demonstrate catalysis, because alternative explanations exist. Ammonium (or ammonia) could react with carbonyl compounds, creating light-absorbing (but N-containing) products that

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have different absorbance spectra than those of the base-catalyzed (N-free) reaction (as is indeed seen in Figure 3). At the same time, some fraction of the reactant is producing nitrogen-free aldol condensation products in a pathway that is not affected by the presence of the ammonium ion.

The authors also find that carbonate ions appear to be active in the chemistry. However, they note on p. 7 that carbonate appears to be functioning simply as a base catalyst. Its activity is thus a direct function of pH, as can be seen in the data by the faster reactivity in Na_2CO_3 solution relative to the less basic $(\text{NH}_4)_2\text{CO}_3$. Based on the abstract, one might think that $(\text{NH}_4)_2\text{CO}_3$ would be the most catalytic salt, since it contains both ions that the authors claim are catalytic. The authors correctly note on p. 7 that the main environmental relevance of carbonate catalysis in aldol condensation would be in alkaline, carbonate rich environments, such as soil.

The title is far too broad. A more appropriate title would be, Ammonium and carbonate ions are efficient catalysts for aldol condensation reactions in atmospheric aerosol.

p. 4 equation (3): The transformation from increase in absorbance to reactant concentration assumes that the gain in absorbance at one wavelength is always proportional to the loss of the reactant molecule. This assumption should be explicitly stated, and preferably supported. The deflection of the data near the origin in Figure 1a suggests that this assumption may not always be true.

p. 6 line 5: The statement that the reaction occurred only in the presence of ammonium ions could be verified (and quantified) by readers if the data for NaCl and sodium sulfate were included in Table 1. Without it, one tends to focus on the effect of the counter ion. I concluded upon first looking at the data that fluoride and sodium ions are the most reactive / catalytic.

p. 10 line 16: The comparison between ammonium-catalyzed aldol condensation and other atmospheric processes must be quantitative to be convincing. Although aldol condensation reactions occur around the clock, that alone does not make them more sig-

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nificant than oxidation by radicals. The authors should compare lifetimes with respect to oxidation by OH (typically hours) with the lifetimes that they measure (days). Even if the authors were correct that ammonium-catalyzed aldol condensations are faster overall than other sink reactions for carbonyl compounds, it would still not be correct to generalize this conclusion to apply to all organic compounds.

p. 11 line 6: When the authors begin to estimate the quantities of products formed via ammonia-catalyzed aldol condensation reactions in the atmosphere, they are making a new, unstated assumption: the mass yield of the absorbent products is not only proportional to carbonyl compound loss (as expressed in equation (3)), but is actually 100%. Since the yields of the products do not appear to have been quantified in the laboratory, this estimate is only an upper limit. As such, it is not conservatively estimated. This needs to be clarified.

Technical corrections

p. 6 line 15-16: if these are absorbance maxima listed, this should be stated.

p. 7 line 13: change compounds to carbonyl compounds to clarify the subject of this sentence.

p. 9 line 11: typo on reference author

p. 10 line 13: delete the word ones

p. 10 line 13: The inference from Table 2 doesn't make sense. Do the authors mean to refer to Table 1?

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

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