Atmospheric Chemistry and Physics Discussions

Interactive
Comment

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

B. Nozière et al.

Received and published: 6 March 2009

Replies to Referees 3 and 4

Before to reply, we would like to communicate the general information that the international patent application for the discovery of the ammonium catalysts reported in this manuscript (PCT/SE2008/051091) has now been approved as 'novel, innovative, and applicable' by the International Search Authority (ISA) with an anteriority date of 01/10/2007 in favor of the inventors, Barbara Noziere and Armando Cordova. This patent should be made public in April 2009.

Also, a note on the replies below: as it was not possible to upload figures in this document, we kindly ask the referees to follow the link to the webpage where the figures

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

relevant to these replies have been posted. Some of the quality has been lost during the conversion into web documents, but we hope that all the necessary information is still clear. We apologize for the inconvenience.

————————————————————— Replies to Referee 3

1) In general, we have tried to use Molar units (mol L-1) for concentration throughout the manuscript, as these are the relevant units for chemistry, especially for kinetics. However for salts or acids, concentrations in wt percent are also given because these are commonly used in atmospheric studies. We have tried to give their Molar equivalent in the text, but we will go through the text and Tables again to verify the consistency of the units. We will also indicate that 'M' is mol L-1.

2) The concentrations mentioned there are the final ones (same as in Table 1). We will modify the text to make this clear.

3) At the time these activities were calculated (over a year ago), we did not see that the AIM models included ammonium nitrate mixtures (was this updated recently ?). In any case, we will now do these calculations for the nitrate and bisulfate solutions, as we want to have the most accurate possible values. The activities coefficients for NH4+ in the various solutions were determined as follow: runs were performed with the AIM Model II for ammonium sulfate over the range of concentration 2-4 M, and with Model III (thus, at room temperature) for ammonium chloride over 1.8-6 M. These runs provided two curves describing the variations of the activity coefficients with concentration in these solutions, which were used to estimate the activities in the other solutions, in particular ammonium fluoride. For ammonium bromide and nitrate solutions, however, which were studied close to saturation, we chose the value of the activity coefficient which was close to saturation in ammonium chloride, 0.69.

It is clear that these values are very approximate, and only a best guess until more accurate ones become available. An alternative would be to present the results as function of concentration, but this would probably not be relevant in these concentrated

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

salt solutions.

However, the only consequence of using inaccurate activity values here is to modify the shape of the variations of the rate constants in Figure 4 (which is directly linked with Question 7 below). But the main conclusion that these rate constants increase with ammonium ion concentration/activity and therefore that ammonium ions act as catalyst, remains valid.

4) In Table 1 and Figure 4 the quantities shown are activities (products of the activity coefficients by the concentrations), not activity coefficients. They have therefore the same units than concentrations. We have used the values of the activity coefficients provided by the model as they were (believing they were dimensionless). We had done the same in a previous study of acid catalysis (Esteve and Noziere, JPC A, 2005) and the results seemed to make sense.

5) Yes, ammonium ions can, in principle, donate a proton but, as discussed in the introduction and illustrated in Table 2, such acid catalysis pathway would be negligible in the ammonium solutions studied this work (pH = 4-8). This is well established by the rate constants for the acid catalyzed aldol condensation reported by many previous studies (Baigrie et al., JACS 1985, Esteve and Noziere, JPC A 2005; Casale et al., Atmos. Environ.,2007 among others). The results of these studies imply that acid-catalyzed reactions would have apparent first-order constants of the order of 10-8 s-1 in the ammonium solutions studied in this work, which is negligible compared to the reactions measured. Table 2 has for objective to further illustrate this point by showing that acid catalysis would affect only 0.1 percent of the carbonyl composition of tropospheric aerosols while ammonium catalysis would affect 20 percent or more under the same conditions. Similarly, the base-catalyzed aldol condensation becomes significant only above pH =9 (which is he case in the carbonate solutions studied in this work). This is why the possibility of a contribution of base- or acid catalysis mechanism to the reactions observed in this work is excluded.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The exact nature of the mechanism of ammonium catalysis remains to be studied more, as this type of catalysis is reported here for the first time (hence the patent). The suggestion made in the text that it might be similar to the amino acid catalysis mechanism, which includes enamine and iminium intermediates, is based on the long experience of the co-authors of this manuscript with nitrogen-based catalysts (amino acids and amines) and that indeed iminium intermediates were formed as established by HRMS. Moreover, the exact same products were formed by the inorganic ammonium ions as when amino acids were used as catalysts.

6) The pH (or pKb) dependence is currently being studied and will be presented elsewhere. The main objective of the present manuscript is to report the identification of new catalysts for tropospheric aerosols, ammonium and carbonate ions, which should be enough for a publication.

7) We are not claiming that the variations of the rate constants in Figure 4 are linear. They seem indeed exponential, which we can not explain for now. Our best interpretation is that the correct ions activities have to be used to obtain a linear variation (or a second-, or third-order one, in any case not exponential). This was the case with acid catalysis (Esteve and Noziere, JPC A, 2005).

8) Yes, this effect is discussed lines 8-12 on p. 10. Although it is still under investigation, we expected it to be due either to pH or to the pKb of the solutions, the first having been shown for glyoxal (Noziere et al., JPC A, 2009), and the second for the amino acid catalysis of the same reaction (Noziere and Cordova, JPC A, 2008). But we exclude an effect of ionic strength here as solutions of ammonium fluoride, chloride, and bromide of the same concentration have the same ionic strength, and Figure 4 clearly shows that the rate constants in these solutions would be very different. This was briefly commented in lines 8-12 of p. 10. The mechanism for this reaction remains to be studied in detail. However, the similarity to amino acid catalysis and the presence of enamine intermediates, suggest that the activated complex would not carry significant charges and should not be significantly stabilized or de-stabilized by the charges in

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

solutions. No effect of ionic strength is thus expected (Noziere and Cordova, JPC A, 2008).

9) We did not assume that the kinetics of these reactions was first order, we demonstrated it with a kinetic analysis. The whole point of measuring rate constants is precisely that the latter do not vary with concentrations and can be applied to other conditions than those at which they have been measured in laboratory. Besides, the conditions under which the rates constants have been studied in this work (concentrations of ammonium ions and carbonyl compounds) are exactly those relevant in aerosols, as explained in the manuscript, and applying the results to aerosols could not be more straightforward.

Technical comments

1- The term 'inorganic' is extremely important here, especially for the ammonium ions, as organic-substituted ammonium ions (of formula N(R1)(R2)(R3), where R1, R2, R3 are organic groups) have been widely studied in chemistry, especially in catalysis. The originality of the discovery reported in this work, and the justification for the patent, is that simple, non-organic ammonium ions work as catalysts, which was not known before, while organic ammonium ions were known as catalysts.

Carbonate ions are not considered as organic (just as CO or CO2). This distinction between organic carbon (produced by the biosphere) and inorganic (or mineral, i.e. non-living) carbonates is essential in the global carbon cycle and an important aspect of the storage of CO2 in the climate system.

The other technical comments have been noted and will be taken into account.

———————————————————— Reply to referee 4

Main question: Potential impact of N-containing products (or of any other light-absorbing product) on the kinetic analyses

Yes, we do have all the facts to support that our kinetic analyses were not impacted by

other light-absorbing compounds than the compounds of interest, but did not provide all the details in the manuscript to keep the presentation of the results concise and also because similar discussions had been presented in our previous works, to which the reader was referred. But these arguments are the following:

1) We are sure of the identity of the aldol products absorbing at the wavelengths of our analyses (crotonaldehyde at 229 nm, hexadienal at 272 nm, and octatrienal and 320 nm), because these products and their absorption have been carefully characterized in our previous studies using standards compounds (Noziere et al., GRL, 2007; Noziere and Cordova, JPC A., 2008). Pure standards for crotonaldehyde and hexadienal were obtained from Sigma Aldrich, and the standard for octatrienal was synthesized and analyzed by NMR analysis.

We also know that the absorption bands of these products were not significantly distorted by unaccounted products in the ammonium experiments because they were identical to the bands observed in our studies of the amino acid catalysis of these reactions (Noziere and Cordova, JPC A., 2008).

2) We could exclude the possibility that unaccounted products have contributed to some of these bands by applying the kinetic analysis to all 3 bands and obtaining the same rate constants, within experimental uncertainties (Figure A, and similar discussion in Noziere and Cordova, JPC A, 2008). If other light-absorbing products had contributed to some of these bands, the rate constants obtained at these wavelengths would be significantly different than at the others.

For Figure A, please follow the link: `http://people.su.se/~bnozi/FiguresReplyAcpd-2008-0558.html`

3) The HRMS analyses of the crude product mixtures performed in this work did not reveal any other major compounds than the expected aldol condendation products. In particular, N-containing hetrocyclic products were not found. Notably, when 20 mol percent of NH4F was used as a catalyst for the self-aldol condensation of n-heptanal,

the corresponding product was formed in 80 percent conversion and isolated in 75 percent yield by silica-gel column chromatography. No other products were observed by NMR analysis of the crude reaction mixture.

4) To our knowledge, N-containing hetrocyclic products have only been reported for acetal reaction (and with glyoxal) but never in aldol condensation. This is consistent with our product analyses.

5) The N-containing compounds reported in the reaction of glyoxal, such as imidazole carboxaldehyde, can not be mistaken for aldol condensation products in the analyses as they absorb at a different wavelengths (Figure B). Their contribution to the spectra would have distorted the absorption of these aldol products, as an extra absorption band between hexadienal and octatrienal for instance, which was not observed.

For Figure B, please follow the link: `http://people.su.se/~bnozi/`
`FiguresReplyAcpd-2008-0558.html`

6) Finally, the absorption of these N-containing compounds was found to be very small in our glyoxal experiments (Figure C), and would be negligible -a few percents- compared to the absorption of the aldol condensation products (compare Figure B and C). The kinetic analyses of the glyoxal reaction would not be affected by these compounds either, as these analyses were performed at a wavelength where N-containing compounds such as imidazole do not absorb much (209 nm).

For Figure C, please follow the link: `http://people.su.se/~bnozi/`
`FiguresReplyAcpd-2008-0558.html`

Our estimate for the absorption cross section for imidazole carboxaldehyde (0.08 M-1 in absorption index units or log epsilon = 4.54) indicates that they could have been present at concentrations up to the mM range in our glyoxal experiments. This would represent a few percent of the initial concentration of glyoxal only, and might explain that they were not detected in the product analyses of the glyoxal experiments. This is

also consistent with the low yields for this imidazoles reported for this reaction in the literature.

In conclusion, N-containing products or any other unaccounted products were very unlikely to affect the kinetic analyses in our work. We would probably not provide as much detail as above in the manuscript, but we can mention the main points of this discussion to justify the validity of our analyses.

Other questions

- given the many examples of aldol condensation and acetal formation presented in our previous papers, we were hoping to skip it this time.

- p 3, li 21-22: these are final concentrations. Text will be changed.

- section 2.1: epsilon is the absorption coefficient. We will change the mention of 'absorbance'. Yes, the concentration is included in epsilon in the equations. This was also explained in more detail in Noziere and Cordova, JPC A, 2008.

- p. 6: The '2008' in the text has to be corrected by a '2009' now that this paper is published.

- p11: 'Apparent' Henry's law coefficient is also used, as in the reference 'Apparent partition coefficient of 15 carbonyls compounds between air and seawater', X. Zhou and K. Mopper, Environ. Sci. Technol., 24, 1864, 1990, for instance.

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