**Atmospheric
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Discussions**

Common inorganic ions are efficient catalysts for organic reactions in atmospheric aerosols and other natural environments

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Abstract

In this work, inorganic ammonium ions, NH_4^+, and carbonate ions, CO_3^{2-}, are reported for the first time as catalysts for organic reactions in atmospheric aerosols and other natural environments at the Earth's surface. These reactions include the formation of

5   C–C and C–O bonds by aldol condensation and acetal formation, and reveal a new aspect of the interactions between organic and inorganic materials in natural environments. The catalytic properties of inorganic ammonium ions, in particular, were not previously known in chemistry. The reactions were found to be as fast in tropospheric ammonium sulfate composition as in concentrated sulfuric acid. The ubiquitous pres-

10   ence and large concentrations of ammonium ions in tropospheric aerosols would make of ammonium catalysis a main consumption pathway for organic compounds in these aerosols, while acid catalysis would have a minor contribution. In particular, ammonium catalysis would account quantitatively for the aging of carbonyl compounds into secondary "fulvic" compounds in tropospheric aerosols, a transformation affecting the

15   optical properties of these aerosols. In general, ammonium catalysis is likely to be responsible for many observations previously attributed to acid catalysis in the troposphere.

1   Introduction

Until recently organic compounds were thought to react mostly by radical reactions in
20   atmospheric aerosols. Radical reactions usually break down organic compounds into smaller oxidation products, especially in oxygen-rich environments. In contrast, ionic reactions such aldol condensation and acetal formation form new carbon–carbon or carbon–oxygen bonds, respectively. Over the last decade, the possibility of ionic bond-forming reactions in aerosols was investigated (Duncan et al., 1998) and suggested to
25   contribute to the formation of Secondary Organic Aerosols (SOA) (Jang et al., 2002). Their occurrence in real aerosols, in particular for aldol condensation, was supported

by the presence of secondary "fulvic" oligomers, structurally similar to aldol products (Zappoli et al., 1999; Decesari et al., 2001; Kiss et al., 2001; Krivácsy et al., 2001; Kiss et al., 2002; Duarte et al., 2005). More recently, acetal formation in aerosols was proposed as an explanation for the depletion of glyoxal in the atmosphere of Mexico City (Volkamer et al., 2007). Until now, strong acids such as sulfuric acid were thought to be the catalysts responsible for these reactions. But laboratory experiments have established that acid concentrations have to be equivalent to at least 8.5 M of sulfuric acid (50 wt.%) for acid catalysis to be significant in aerosols (Baigrie et al., 1985; Esteve and Nozière, 2005; Casale et al., 2007). While such concentrations are present in stratospheric aerosols (∼15–50 km) they are marginal in tropospheric ones (0 to ∼15 km), implying that acid catalysis should be, too. Our recent works have investigated other catalysts that could trigger bond-forming reactions in tropospheric aerosols and identified amino acids as such catalysts (Nozière et al., 2007; Nozière and Córdova, 2008). The present work brings this exploration one step further by examining the catalytic properties of inorganic ions that are common in tropospheric aerosols and, in general, in natural environments at the Earth's surface.

2 Experimental

The experimental technique used in this study was identical to the one used in our previous studies of amino acid catalysis (Nozière et al., 2007; Nozière and Córdova, 2008). The experiments were performed in glass vials containing 4 mL of salt solution, continuously stirred, and protected from light. Concentrations of 0.1 to 1 M of carbonyl compounds were introduced in these solutions with a syringe. These concentrations are very comparable to those found in aerosols (see for example Maria et al., 2002). The products were identified by Liquid Chromatography – High Resolution Mass Spectrometry (HRMS; Bruker MicrOTOF spectrometer).

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2.1 Kinetic analyses

For the kinetic studies, small samples (<0.3 mL) of the reaction mixtures were placed in a 1-mm quartz cell. Their absorbance, $A_b(\lambda)$, where λ is the wavelength in cm, was measured by a UV-Vis spectrometer (Agilent 8453). This absorbance was converted into an extinction coefficient, ε_λ, by the Beer-Lambert law:

$$A_b(\lambda) = \varepsilon_\lambda \times l \tag{1}$$

where l is the optical pathlength (l=0.1 cm). For a direct comparison with the optical properties of atmospheric aerosols, the extinction coefficients were converted into absorption indices, A_λ (non-dimensional), the imaginary part of the refraction index:

$$A_\lambda = \lambda \times \varepsilon_\lambda / 4\pi \tag{2}$$

The kinetics of the reactions were studied from the real-time formation of the products at 320 nm for acetaldehyde (see Fig. 1, top), at 209 nm for glyoxal, or from the decay of acetone at 270 nm, using a method described in Nozière and Córdova (2008). The reader is referred to this previous work for details. Briefly, the variations of the absorbance, $\varepsilon_\lambda(t)$, were converted into the following expression:

$$\ln(1 - \varepsilon_\lambda/\varepsilon_\infty) = -k^I \times t, \tag{3}$$

where ε_∞ is the absorbance at long reaction time (or high degree of conversion), t, time (in s), and k^I (s^{-1}), the first-order rate constant (Fig. 1, bottom). Obtaining straight lines from Eq. (3) indicated that the reactions were first order in carbonyl concentration. Moreover, the slope of Eq. (3) gave accurate values for k^I, which were independent from the concentrations of carbonyl used in the experiments. Uncertainties on k^I were estimated to about 25%, resulting from 10% of uncertainties on ε_∞, 5% of uncertainties on the absorbance, and to the errors in the linear regressions.

Similarly, reactions were identified as second-order in carbonyl compound when the variations of the absorbance followed a second-order expression equivalent to Eq. (3),

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(Eq. 7 in Nozière and Córdova, 2008). As a detailed study of the second-order reaction of glyoxal is presented elsewhere (Nozière et al., 2008) only first-order rate constants are reported in this work and the reader is referred to our previous work for more detail on the second-order kinetic analysis. The conditions and results for all the kinetic experiments presented in this work are summarized in Table 1.

2.2 Chemicals and general

The solutions were prepared by mixing milliQ water with known quantities of the salts of interest. Ammonium sulfate ($(NH_4)_2SO_4$), Merck, >99.5%; ammonium bisulfate ($(NH_4)HSO_4$), Fluka >99%; ammonium nitrate (NH_4NO_3), Merck >99%; ammonium chloride (NH_4Cl), Merck 99.8%; ammonium bromide (NH_4Br), Aldrich 99.99+%; ammonium fluoride (NH_4F), Acros >98%; sodium carbonate (Na_2CO_3), Sigma >99.0%; ammonium carbonate ($(NH_4)_2CO_3$), Aldrich 99.999%; magnesium carbonate ($MgCO_3$), Sigma; Acetaldehyde (CH_3CHO), Aldrich, >99.5%; Glyoxal (CHOCHO), Aldrich 40% in water (8.8 M); acetone ($CH_3C(O)CH_3$), Aldrich 99.5%; propanal (CH_3CH_2CHO), Aldrich 97%; butanal ($CH_3CH_2CH_2CHO$), Aldrich 99.5%. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian AS 400. Chemical shifts are given in δ relative to tetramethylsilane (TMS), the coupling constants J are given in Hz. The spectra were recorded in $CDCl_3$ as solvent at room temperature, TMS served as internal standard ($\delta = 0$ ppm) for ^{1}H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$ ppm) for ^{13}C NMR.

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3 Results

3.1 Catalysts identification

3.1.1 Ammonium catalysis

The reactivity of acetaldehyde in various aqueous salt solutions was first investigated. A reaction was observed only in solutions containing ammonium ions, NH_4^+, (ammonium sulfate, nitrate, chloride, bromide, fluoride, and bisulfate) but not in those where they were absent (sodium sulfate and sodium chloride), clearly identifying ammonium ions as catalysts. The oligomer products of acetaldehyde, crotonaldehyde (dimer), 2,4-hexadienal (trimer), 2,4,6-octatrienal (tetramer), and 2,4,6,8-decatetraenal (pentamer) were identified by LC- HRMS (Fig. 2A) and ^{1}H NMR, and proved that the reaction was aldol condensation. Similarly, acetone, propanal, and butanal were all found to undergo aldol condensation in ammonium solutions, in particular ammonium sulfate. As in acid catalysis, most of these carbonyl compounds produced linear polyconjugated compounds (i.e. containing alternating single and double bonds) absorbing light over 200–800 nm: acetaldehyde: 226, 272, and 320 nm; propanal: 220, 278, and 318 nm; butanal: 220 and 280 nm (Fig. 3A). Thus, ammonium sulfate aerosols, as well as all ammonium-containing aerosols in the atmosphere, would transform carbonyl compounds into products affecting their absorption index. Glyoxal was also found to react in ammonium-containing solutions. In this case, the reaction proceeded by acetal formation, as shown by the products identified by LC-HRMS, which were generally identical to those obtained in its acid-catalyzed reaction (Liggio et al., 2005). A more complete study of the ammonium-catalyzed reaction of glyoxal and its products is presented elsewhere (Nozière et al., 2008).

Although aldol condensation is a classic reaction in organic chemistry and a plethora of catalysts are already known for it, inorganic ammonium ions, NH_4^+, were not known as catalysts for aldol condensation or acetal formation until now (Nozière and Córdova, 2007). These new catalysts are not only the simplest known so far for these re-

actions but undoubtly the most relevant in natural environments. Ammonium salt solutions are neither strongly acidic nor basic (for ammonium sulfate 20–40 wt.%, pH~5.5), and ammonium-catalyzed reactions do not follow the classical acid- or base-catalysis mechanisms. Their mechanisms are expected to be similar to amino acid catalysis(Nozière and Córdova, 2008) and are currently being investigated.

3.1.2 Carbonate catalysis

Carbonate salts were known to catalyze aldol condensation in organic solvents (Bertini, 1901; Ma et al., 2002) and aqueous solvents at high temperature (Zhang et al., 2003). But to our knowledge this catalytic role has never been reported for environmentally-relevant conditions. The reactions of acetaldehyde, propanal, butanal, acetone, and glyoxal were studied in 5 mM–2 M aqueous solutions of sodium carbonate, Na_2CO_3, magnesium carbonate $MgCO_3$, and ammonium carbonate $(NH_4)_2CO_3$ at 298 and 310 K (for acetone). All these compounds were found to react. HRMS analyses of the products of acetaldehyde identified the usual aldol condensation products and some polyhydroxylated products such as deoxy sugars (Fig. 2B), generally confirming aldol condensation. Acetaldehyde, propanal, and butanal all produced compounds absorbing light between 280 and 400 nm, as previously observed with aldol condensation (Fig. 3B), while glyoxal reacted by acetal formation. Carbonate ions act as strong bases and these reactions thus follow the classical base mechanisms (Zhang et al., 2003). In atmospheric aerosols, carbonate ions are usually associated with crustal material (Krivácsy et al., 1998; Kerminen et al., 2002) and carbonate catalysis could thus take place in primary mineral aerosols. Carbonate catalysis would be more widely relevant at the Earth's surface (e.g. waters, sediments, soils) where these ions are common and mixed with organic material (e.g. Ramseyer et al., 1997). Aldol products are similar to the small fulvic substances found in natural water (Reemtsma and These, 2005 and discussion in Nozière et al., 2007). The carbonate-catalyzed aldol condensation could thus be a pathway for the formation of small colored fulvic substances and, perhaps, the humification of organic matter in alkaline and carbonate-rich environments at the

Earth's surface.

3.2 Reactions within phases and at interfaces

The present work focuses on aqueous salt solutions only to emphasize the importance of these reactions in inorganic aerosols. But all these reactions would also take place in organic solutions. This was already known for carbonate salt catalysis (Bertini, 1901; Ma et al., 2002) and was confirmed in this work for ammonium catalysis by observing the reactions in DMSO using ammonium fluoride (30 mol%) as the catalyst. Furthermore, experiments with butanal in ammonium sulfate 40 wt.% showed that, when the carbonyl compound or its products are not completely soluble in the inorganic phase, the reaction takes place at the inorganic-organic interface, or the products accumulate at this interface. The reactions presented in this work could thus take place inside or at the surface of inorganic aerosols, inside organic aerosols, or at the inorganic-organic interface in mixed-phase particles. Finally, these reactions might also take place at the surface of solid particles, as previously observed for aldol condensation on mineral clays (Li et al., 2001).

3.3 Kinetics

Determining the rate constants for these reactions was essential to estimate their importance in aerosols by comparison with the aerosol residence time in the atmosphere (a few days, in the troposphere). Rate constants were determined for the reactions of acetaldehyde, acetone, and glyoxal, using the method described in the Experimental section. The results are summarized in Table 1 and Fig. 4. For acetaldehyde and acetone the kinetics was first order. The rate constants increased strongly with ion activity. For ammonium ions, these activities were obtained from the AIM model (Clegg et al., 1998), except for ammonium bromide, nitrate, and bisulfate, for which the activity coefficients were taken equal to 0.69. In all carbonate solutions, the activity coefficients of carbonate ions was taken equal to 1. For acetaldehyde at 298 K the rate constant

varied from 2.5×10^{-7} to 6×10^{-7} s^{-1} between ammonium sulfate 20 and 40 wt.% ($\sim$1.6 and 3.6 M, respectively). The latter value is identical to the rate constant of the same reaction in sulfuric acid 13 M (75 wt.%), which clearly demonstrates the importance of ammonium catalysis in tropospheric aerosols. For acetone in ammonium sulfate 40 wt.% (3.6 M), $k=(4.5\pm1.5)\times10^{-6}$ s^{-1} at 308 K. The rate constant also appeared to vary somewhat between different salts. For instance, for acetaldehyde, it was slower in ammonium sulfate than in ammonium fluoride (note that the results for ammonium nitrate, bromide, chloride, and bisulfate on Fig. 4 were measured at 308 K). This effect is currently under investigation but expected to be due to the pK_b or the pH of the solution rather than ionic strength, as recently showed for amino acid catalysis (Nozière and Córdova, 2008) and for the ammonium-catalyzed reaction of glyoxal (Nozire et al., 2008). For glyoxal, the kinetics was first order in ammonium sulfate 20% wt (1.6 M), with $k^I=(1.4\pm0.5)\times10^{-5}$ s^{-1}, but second order for larger concentrations, and would be therefore second order as well in most ammonium sulfate aerosols. A complete kinetic study of glyoxal is presented elsewhere (Nozière et al., 2008) and only limited results are presented here (first-order rate constants).

The rate constants were generally faster with carbonate salts than with ammonium salts. For sodium carbonate 5 mM and ammonium carbonate 1 M (pH=8.9), k(acetaldehyde) $\sim10^{-6}$ s^{-1}, as in sulfuric acid 14 M (78 wt.%). Below 0.1 M of sodium carbonate this rate constant seemed to decrease more markedly, which should be further studied as this is the range the most relevant for natural environments. For acetone in sodium carbonate 1 M, $k=(6.3\pm2.0)\times10^{-7}$ s^{-1}.

4 Environmental implications and conclusion

This work identifies for the first time common environmental ions, inorganic ammonium ions, NH_4^+, and carbonate ions, CO_3^{2-}, as efficient catalysts for the transformations of organic compounds in atmospheric aerosols and natural environments at the Earth's surface and, in particular, for the formation of C-C or C-O bonds. This reveals

a new aspect of the interactions between inorganic and organic material in natural environments. The ammonium-catalyzed reactions would be as fast in tropospheric ammonium sulfate aerosols (20 wt.% to 70 wt.% (supersaturated), for relative humidities RH=40–95%; Xu et al., 1998) as in concentrated sulfuric acid, or even faster. These reactions might also take place at the surface of dry ammonium particles as they do on mineral clays (Li et al., 2001).

The overall consumptions of carbonyl compounds resulting from various catalysts in aerosols are compared in Table 2. This comparison shows that ammonium catalysis should generally be the most important consumption process. Both acid catalysis (in the troposphere) and amino acid catalysis would have small contributions. Carbonate catalysis might be efficient, depending on the concentration of carbonate ions in aerosols, but these ions are much less common in tropospheric aerosols than ammonium ones. Table 2 also shows that, in general, ionic catalysts have to have concentrations of the order of 0.1 M or more to compete with ammonium catalysis in tropospheric aerosols. The probability that other, unknown, catalysts exist at such concentrations in aerosols is very small. Radical reactions could also compete with the ionic reactions, but mostly in daylight while ionic catalysis takes place both in the dark and in the light. This, together with the presence of ammonium ions in virtually all tropospheric aerosols, makes of ammonium catalysis one of the main consumption pathways for organic compounds in tropospheric aerosols, both in term of speed and global occurrence.

The ammonium-catalyzed aldol condensation would thus be a significant "aging" process for primary carbonyl compounds internally mixed with inorganic material in aerosols, such as the organic/inorganic mixtures found in all regions of the atmosphere (Murphy et al., 1998; Cziczo et al., 2004; Kojima, et al., 2004; Takami et al., 2005; Tolocka et al., 2005). As recently discussed (Nozière et al., 2007), aldol condensation would explain the formation and molecular structure of the secondary "fulvic" compounds found in fine aerosols and fog droplets (Zappoli et al., 1999; Decesari et al., 2001; Kiss et al., 2001, 2002; Krivácsy et al., 2001; Duarte et al., 2005; Reemtsma

et al., 2006). These compounds accounted for ~25% of the total organic carbon in these aerosols, and about $0.5\,\mu g\,m^{-3}$ (Zappoli et al., 1999; Krivácsy et al., 2001; Kiss et al., 2002). For the same reasons as discussed above and in Table 2, acid catalysis and amino acid catalysis can not account for such quantities, while ammonium catalysis does: for instance, k(acetaldehyde, $(NH_4)_2SO_4$ 40 wt.%)$=6\times10^{-7}\,s^{-1}$, would correspond to 20% of conversion of the carbonyl compounds in aerosols over 4 days (Table 2). With an initial carbonyl concentrations in aerosol of the order of $0.7\,\mu g\,m^{-3}$ (Maria et al., 2002) this would correspond to $0.2\,\mu g\,m^{-3}$ of "fulvic" compounds.

As these "fulvic" compounds absorb light in the near UV and visible (Nozière et al., 2007) their formation would affect the absorption index of the aerosols, and perhaps their radiative properties, which is one of the main interest of these "aging" processes.

It is however not clear whether ammonium-catalyzed reactions would result in a significant uptake of carbonyl compounds from the gas and the formation of SOA. While their rate constants would be fast enough, the apparent Henry's law constants for the carbonyl compounds in inorganic aerosols might not be large enough. These Henry's Law constants might increase in reactive ammonium-containing media, as as been observed with acid catalysis (see for instance Nozière and Riemer, 2003) but this remains to be investigated. Glyoxal might be the only compound for which the ammonium-catalyzed reaction would result in a significant uptake, because of its exceptionally large Henry's law constant. A complete kinetic study of the ammonium-catalyzed reaction of glyoxal and its possible contribution to the depletion of this compound in Mexico City (Volkamer et al., 2007) is however presented elsewhere (Nozière et al., 2008), and the reader is referred to this manuscript for further discussion.

In conclusion, inorganic ammonium ions and carbonate ions are efficient catalysts for the formation of C-C and C-O bonds in natural environments, including atmospheric aerosols. Ammonium catalysis, in particular, is expected to be an important consumption pathway for carbonyl compounds in tropospheric aerosols, and likely to be responsible for many observations previously attributed to acid catalysis.

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Table 1. Summary of the kinetic experiments presented in this work.

Carbonyl compound	Concentration (M)	Catalyst/salt	Ion activity, a_{NH4+} or a_{CO32-} (M)	First-order rate constant, k (s^{-1})	T (K)
Acetaldehyde	0.1	$(NH_4)_2SO_4$ 40%	3.24	6.7×10^{-7}	298
Acetaldehyde	0.05	$(NH_4)_2SO_4$ 40%	3.24	5.7×10^{-7}	298
Acetaldehyde	0.1	$(NH_4)_2SO_4$ 40%	3.24	5.0×10^{-7}	298
Acetaldehyde	0.5	$(NH_4)_2SO_4$ 30%	2.32	4.4×10^{-7}	298
Acetaldehyde	0.5	$(NH_4)_2SO_4$ 30%	2.32	3.1×10^{-7}	298
Acetaldehyde	0.5	$(NH_4)_2SO_4$ 20%	1.38	2.6×10^{-7}	298
Acetaldehyde	0.5	$(NH_4)_2SO_4$ 20%	1.38	2.5×10^{-7}	298
Acetaldehyde	0.3	NH_4F 2 M	1.2	1.7×10^{-6}	298
Acetaldehyde	0.3	NH_4F 1 M	0.6	1.0×10^{-6}	298
Acetaldehyde	0.3	NH_4F 1 M	0.6	7.9×10^{-7}	298
Acetaldehyde	0.3	NH_4F 1 M	0.6	1.3×10^{-6}	298
Acetaldehyde	0.3	NH_4F 0.5 M	0.3	4.5×10^{-7}	298
Acetaldehyde	0.3	NH_4F 0.5 M	0.3	7.4×10^{-7}	298
Acetaldehyde	0.5	NH_4F 0.5 M	0.3	5.9×10^{-7}	298
Acetaldehyde	0.5	NH_4Cl 4 M	2.56	1.0×10^{-6}	308
Acetaldehyde	1	NH_4Cl 4 M	2.56	1.3×10^{-6}	308
Acetaldehyde	0.5	NH_4Br 2.5 M	1.73	5.4×10^{-7}	308
Acetaldehyde	1	NH_4Br 2.5 M	1.73	7.1×10^{-7}	308
Acetaldehyde	0.5	$NH_4(NO_3)$ 4 M	2.76	9.0×10^{-7}	308
Acetaldehyde	0.5	$NH_4(NO_3)$ 4 M	2.76	5.2×10^{-7}	308
Acetaldehyde	1	$(NH_4)HSO_4$ 30%	2.07	3.9×10^{-7}	308
Acetaldehyde	1	$(NH_4)HSO_4$ 30%	2.07	3.0×10^{-7}	308
Acetaldehyde	0.5	$(NH_4)_2CO_3$ 1 M	1	4.9×10^{-7}	298
Acetaldehyde	1	$(NH_4)_2CO_3$ 1 M	1	4.0×10^{-7}	298
Acetaldehyde	0.5	$(NH_4)_2CO_3$ 0.5 M	0.5	4.3×10^{-7}	298
Acetaldehyde	0.1	Na_2CO_3 1 M	1	9.8×10^{-6}	298
Acetaldehyde	0.1	Na_2CO_3 1 M	1	1.4×10^{-5}	298
Acetaldehyde	0.3	Na_2CO_3 0.5 M	0.5	3.5×10^{-6}	298
Acetaldehyde	0.3	Na_2CO_3 0.5 M	0.5	5.5×10^{-6}	298
Acetaldehyde	0.3	Na_2CO_3 0.1 M	0.1	1.6×10^{-6}	298
Acetaldehyde	0.3	Na_2CO_3 0.1 M	0.1	2.1×10^{-6}	298
Acetaldehyde	0.1	Na_2CO_3 0.1 M	0.1	2.5×10^{-6}	298
Acetaldehyde	0.5	Na_2CO_3 5 mM	0.005	1.1×10^{-6}	298
Acetaldehyde	1	Na_2CO_3 5 mM	0.005	7.2×10^{-7}	298
Acetaldehyde	0.1	$MgCO_3$ 0.55 M	0.55	5.3×10^{-7}	298
Acetaldehyde	0.1	$MgCO_3$ 0.55 M	0.55	5.4×10^{-7}	298
Acetone	0.5	$(NH_4)_2SO_4$ 40%	3.24	4.7×10^{-6}	308
Acetone	0.5	$(NH_4)_2SO_4$ 40%	3.24	4.4×10^{-6}	308
Acetone	0.5	NH_4F 2 M	1.2	3.4×10^{-7}	308
Acetone	0.5	Na_2CO_3 1 M	1	6.3×10^{-7}	308
Glyoxal	0.5	$(NH_4)_2SO_4$ 20%	1.38	5.8×10^{-6}	298
Glyoxal	0.5	$(NH_4)_2SO_4$ 20%	1.38	6.9×10^{-6}	298

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Table 2. Comparison of the overall consumption of acetaldehyde and acetone after 4 days resulting from different catalysts (catalyst solutions are in water).

Catalyst	Acetaldehyde (0.1–0.5 M, 25°C)	Acetone (0.5–1 M, 35°C)
H_2SO_4 8.5 M (50 wt.%) *stratosphere*	50%	<1%
H_2SO_4 1 M (7.5 wt.%, pH=0) *troposphere*	0.1%	≪1%
Na_2CO_3 0.1 M	50%	3%
$(NH_4)_2SO_4$ 3.6 M (40 wt.%)	20%	79%
$(NH_4)F$ 2 M	44%	11%
Glycine 20 mM	7%	Not measured

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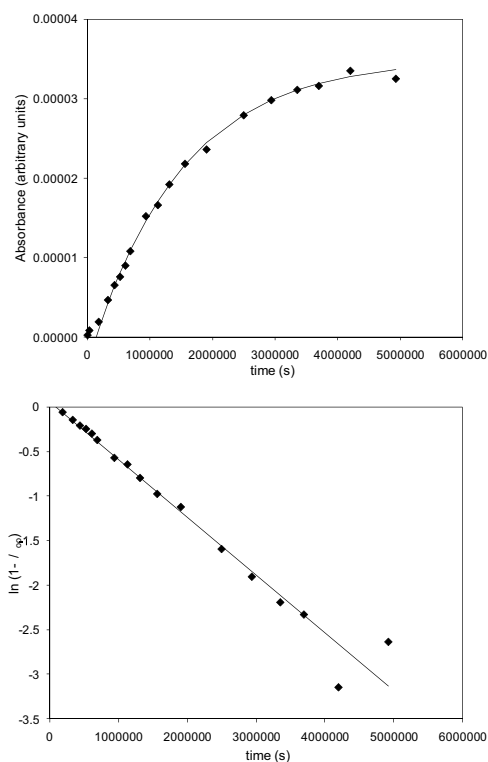
Fig. 1. Top: Real-time formation of the product of acetaldehyde (0.1 M) at 320 nm in ammonium sulfate solutions 40 wt.%, and fit to a first-order function. Bottom: Conversion of the real-time data into Eq. (3) to determine the rate constant, $k^{/}$ (s^{-1}).
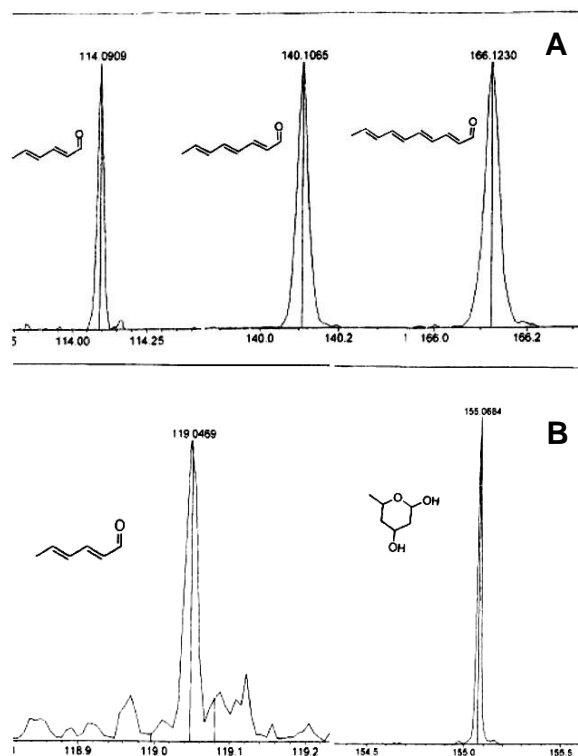
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Fig. 2. HRMS spectra of the aldol products of acetaldehyde and subsequent oligomers $(M+NH_4^+)$ in ammonium sulfate **(A)**, and sodium carbonate $(M+Na^+)$ **(B)**.
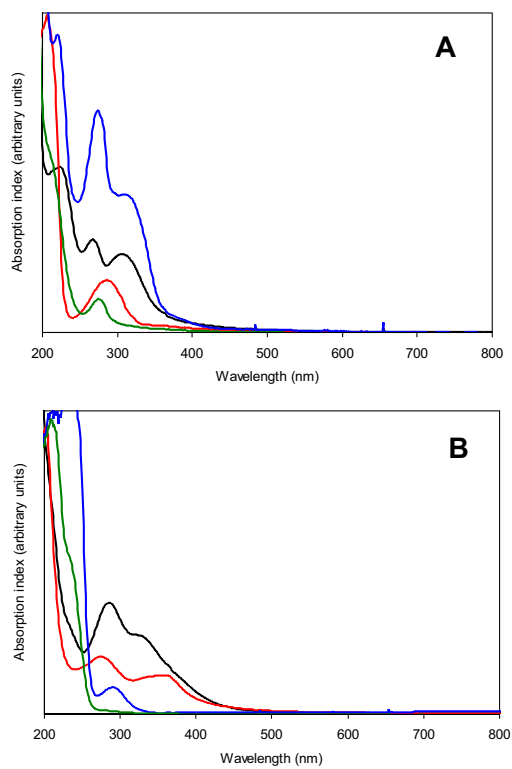
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Fig. 3. Absorption spectra of the products of acetaldehyde (black), glyoxal (red), propanal (blue), and butanal (green) in ammonium sulfate 40 wt.% **(A)**, and sodium carbonate 0.1 M **(B)**.
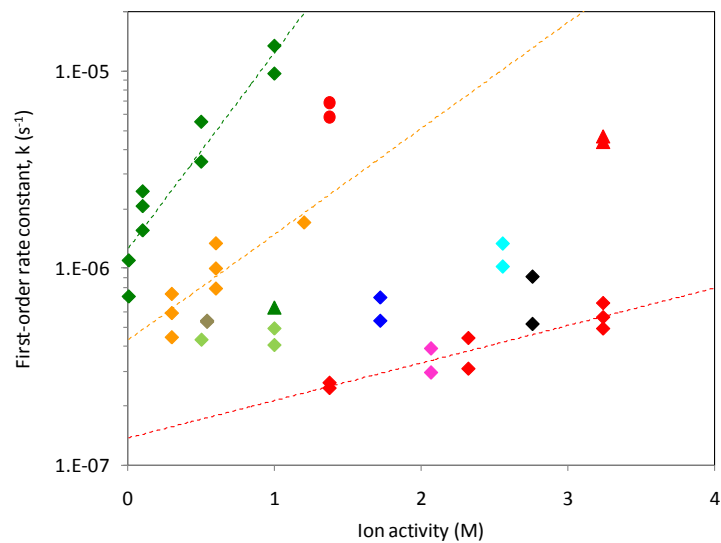
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Fig. 4. First-order rate constants, k (s^{-1}), for the self-condensation of acetaldehyde (diamonds), glyoxal (circles), and acetone (triangles) in ammonium sulfate (red), ammonium fluoride (orange), ammonium nitrate (black), ammonium chloride (clear blue), ammonium bromide (dark blue), ammonium bisulfate (pink), sodium carbonate (dark green), ammonium carbonate (clear green), magnesium carbonate (grey).

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