Kinetics of acid-catalyzed aldol condensation reactions of aliphatic aldehydes

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Abstract

Field observations of atmospheric aerosols have established that organic compounds compose a large fraction of the atmospheric aerosol mass. However, the physical/chemical pathway by which organic compounds are incorporated into atmospheric aerosols remains unclear. The potential role of acid-catalyzed reactions of organic compounds on acidic aerosols has been explored as a possible chemical pathway for the incorporation of organic material into aerosols. In the present study, ultraviolet–visible (UV–vis) spectroscopy was used to monitor the kinetics of formation of the products of the acid-catalyzed aldol condensation reaction of a range of aliphatic aldehydes (C_2–C_8). The experiments were carried out at various sulfuric acid concentrations and a range of temperatures in order to estimate the rate constants of such reactions on sulfuric acid aerosols under tropospheric conditions. The rate constants were generally found to decrease as the chain length of the aliphatic aldehyde increased (except for acetaldehyde, which had an unusually small rate constant), increase as a function of sulfuric acid concentration as predicted by excess acidity theory, and showed normal Arrhenius behavior as a function of temperature. While the kinetic data are generally consistent with previous laboratory reports of aldehyde reactivity in various sulfuric acid media, the aldol condensation reactions involving aliphatic aldehydes do not appear fast enough to be responsible for significant transfer of organic material into atmospheric aerosols.
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1. Introduction

It is now recognized that tropospheric aerosols play an important role in the global climate system. Tropospheric aerosols directly affect climate by scattering and absorbing incoming solar radiation, leading to a net cooling at the surface. Indirectly, aerosols impact climate by serving as cloud condensation nuclei (CCN). The optical and hygroscopic properties, cloud condensation ability and chemical reactivity of aerosols are impacted by heterogeneous reactions, as all of these properties depend on composition. Field measurements indicate that ambient aerosols can be composed of up to 80% by mass organic compounds (Saxena and

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Hildemann, 1996; Middlebrook et al., 1998; Molnar et al., 1999; Turpin et al., 2000).

Organic compounds may be transferred from the vapor phase to the aerosol phase by *physical* processes such as dissolution and condensation. However, it has been difficult to rationalize the high organic content of aerosols by invoking only physical mechanisms. For example, it is clear that many atmospherically abundant organic compounds are not sufficiently soluble to partition significantly into aerosols. Recently, *chemical* mechanisms have been explored as a means by which the transfer of organic compounds from the gas phase to the aerosol phase may be enhanced. In particular, acid-catalyzed reactions of organic compounds on tropospheric aerosols have been investigated in this context, as these reactions are postulated to lead to enhanced uptake of organic compounds by aerosols (Jang et al., 2002; Zhang and Wexler, 2002).

There are several types of acid-catalyzed reactions of carbonyl-containing organic compounds that are well known in bulk solutions (Carey and Sundberg, 1990; Vollhardt and Schore, 1994). For example, the acid-catalyzed aldol condensation reaction of aldehydes results in the conversion of two aldehyde molecules into a single molecule that has a carbon backbone made up of the sum of the carbon atoms in the reactant aldehydes. Barsanti and Pankow (2004) have termed any such carbon backbone building processes (of which the aldol condensation reaction is but one) as accretion reactions, since the end result is the formation of larger molecules from smaller ones. The net result of these types of reactions is the formation of relatively less volatile products (which helps prevent the physical transfer of organic material back into the gas phase), and the dissolution of more reactant to maintain the solubility equilibrium (the "enhanced" solubility effect).

Some field studies have noted that when both SO_2 and volatile organic compound (VOC) concentrations are high, there appears to be additional particle growth, perhaps indicating that acid-catalyzed reactions are causing the accretion of organic compounds into aerosols (Brock et al., 2003; Chu et al., 2004). Brock et al. (2002) found that in power plant plumes where SO_2 concentrations are high and the VOCs concentrations are low, the observed particle growth can be accounted for by SO_2 oxidation alone. However, in a different air parcel where both SO_2 and VOC concentrations were elevated, Brock et al. (2003) found that the particle growth exceeded that which could be explained by SO_2 oxidation alone. However, Zhang and Wexler (2002) found no significant difference in the organic composition of aerosols whether the ambient sulfate aerosols were acidic or neutralized.

Because of the well-known acid-catalyzed aldol condensation reaction for aldehydes, there have been a number of laboratory studies in which the incorporation of gaseous aldehydes into acidic solutions as compared to non-acidic solutions have been investigated (Iraci and Tolbert, 1997; Jang and Kamens, 2001; Jang et al., 2002; M. Jang, et al., 2003; M.S. Jang, et al., 2003; Michelsen et al., 2004; Liggio et al., 2005; Zhao et al., 2005; Surratt et al., 2006). Similar studies have been performed for ketones (M. Jang, et al., 2003; M.S. Jang, et al., 2003; Esteve and Noziere, 2005), acrolein and α-pinene (Czoschke et al., 2003; Iinuma et al., 2004; Tolocka et al., 2004) and isoprene (Limbeck et al., 2003). Many of these studies have concluded that the occurrence of accretion reactions are necessary to explain the uptake of organic material into acidic media (Jang and Kamens, 2001; Jang et al., 2002; Czoschke et al., 2003; M. Jang, et al., 2003; M.S. Jang, et al., 2003; Kalberer et al., 2004; Tolocka et al., 2004; Jang et al., 2005). However, the actual identification of specific molecular products (which are needed to prove which accretion reactions are occurring) has been difficult. Garland et al. (2006) recently used a suite of analytical approaches (aerosol mass spectrometry, FTIR and UV–vis spectroscopy, ^{1}H NMR and GC/MS) to directly show that hexanal undergoes aldol condensation reactions on sulfuric acid aerosols under laboratory conditions. However, high hexanal concentrations were used in the study, and no kinetics data were available to estimate the likelihood of such reactions on tropospheric sulfuric acid aerosols. There have also been several other experiments in which the heterogenous interaction of gaseous aldehydes with sulfuric acid surfaces has been probed. Michelsen et al. (2004) studied the interaction of gaseous acetaldehyde with a film of sulfuric acid using a Knudsen cell apparatus as a function of H_2SO_4 composition and temperature. They found evidence for acetaldehyde reaction in the observation of the apparent enhanced solubility of acetaldehyde under certain conditions. On the other hand, Zhao et al. (2005) found only reversible uptake of octanal on sulfuric acid films, which suggests that aldol condensation reactions for octanal are possibly

quite slow. Noziere and Esteve (2005, 2006) studied the UV–vis spectra of H_2SO_4 solutions exposed to several different carbonyl-containing compounds (including the aldehydes acetaldehyde, propanal and butanal), and concluded that several sequential aldol condensation reactions were occurring. Acetone has also been found to undergo aldol condensation on highly acidic H_2SO_4 surfaces to form mesityl oxide, and ultimately, 1,3,5-trimethyl benzene (Duncan et al., 1999).

In chemical synthesis situations, aldol condensation reactions are widely utilized to build molecules with larger carbon backbones. However, base catalysis is the preferred synthetic route for a variety of reasons (Carey and Sundberg, 1990; Vollhardt and Schore, 1994), and thus the mechanism and kinetics of the acid-catalyzed aldol condensation reaction has received considerably less study. However, it has been established that the mechanism given in Fig. 1 (shown for acetaldehyde, but easily generalized for any aldehyde) is operative in the acid-catalyzed aldol condensation of aldehydes (Noyce and Snyder, 1959). Reactions 1 and 2 are fast, while reaction 3 is slow and known to be the rate-limiting step in the process. Under high acidity conditions, reaction 4 occurs quickly and

irreversibly and an α,β-unsaturated carbonyl compound is formed.

Baigrie et al. (1985) carried out the first extensive kinetics study of the acid-catalyzed aldol reaction for the self-reaction of any aldehyde in their bulk solution study of the acetaldehyde aldol reaction as a function of sulfuric acid concentration at room temperature. They found that crotonaldehyde (the α,β-unsaturated carbonyl compound formed in reaction 4) became the dominant product of the reaction for H_2SO_4 compositions equal to 60 wt% and higher. Under all conditions studied, the kinetics were observed to be second order in acetaldehyde, confirming that reaction 3 is the rate-limiting step in the mechanism. The rate constants were found to increase as a function of acidity, and because of the highly non-ideal nature of the solutions, the kinetics results were interpreted with the aid of excess acidity theory. In a further study of the acetaldehyde aldol self-reaction, Esteve and Noziere (2005) used a rotating wetted-wall reactor to estimate the bulk rate constant for acid-catalyzed reaction of acetaldehyde for two different sulfuric acid compositions. Noziere and Esteve (2005); Noziere et al. (2006) also studied the kinetics of formation of subsequent products (larger than crotonaldehyde) in the acetaldehyde system as a function of acid strength (75–96 wt% H_2SO_4) and temperature (273–314 K). Kinetics measurements have also been carried out for the acid-catalyzed reactions of the following ketones: acetone (Duncan et al., 1999; Esteve and Noziere 2005), 2-butanone, 2,4-pentanedione (Esteve and Noziere, 2005), and methyl vinyl ketone (Noziere et al., 2006).

As discussed above, the kinetics literature for the acid-catalyzed reactions of the aldehydes is primarily focused on the studies of the acetaldehyde system. In particular, studies concerning the effect of the molecularity of the aldehydes on the rate constant and the acid and temperature dependence of the rate constant for aldehydes other than acetaldehyde are lacking. In the present study, UV–vis spectroscopy was used to monitor the kinetics of formation of the products in the bulk phase acid-catalyzed aldol condensation reaction of a range of linear aliphatic aldehydes (C_2–C_8). The experiments were carried out at various sulfuric acid compositions and a range of temperatures in order to estimate the rate constants of such reactions on sulfuric acid aerosols under tropospheric conditions.
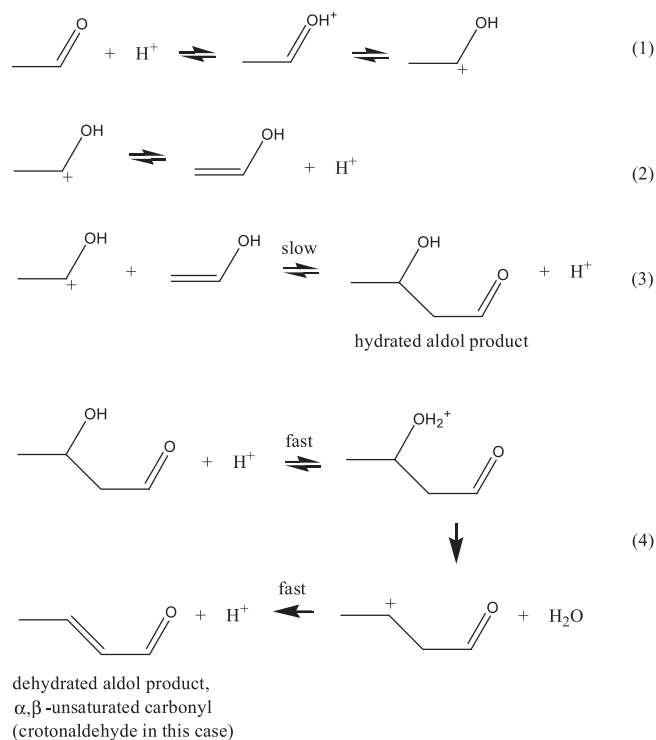

Fig. 1. Acid-catalyzed aldol condensation mechanism for acetaldehyde.

2. Experimental

In concentrated H_2SO_4 (and in H_2O) the strong $\pi \rightarrow \pi^*$ ($\varepsilon \sim 10{,}000\,cm^{-1}\,M^{-1}$) transition arising from the $C = O$ chromophore for aliphatic aldehydes occurs at peak wavelengths less than 200 nm, while the very weak $n \rightarrow \pi^*$ ($\varepsilon \sim 15\,cm^{-1}\,M^{-1}$) transition occurs around 270 nm (Lambert et al., 1987). Therefore, the reactant aldehydes are not easily monitored using standard UV–vis spectroscopy. However, the dehydrated aldol condensation products for the reactions of aliphatic aldehydes are α,β-unsaturated aldehydes (the product of reaction 4 in Fig. 1) which have strong $\pi \rightarrow \pi^*$ ($\varepsilon \sim 10{,}000\,cm^{-1}\,M^{-1}$) transitions at wavelengths of at least 245 nm in concentrated sulfuric acid. According to the Woodward rules (Lambert et al., 1987), the peak wavelengths for hydrated aldol condensation products (the reactant in reaction 4, Fig. 1) are not expected to shift significantly from the parent aldehyde wavelengths. Therefore, the experiments described here specifically concern the kinetics of the formation of the dehydrated aldol condensation product (as opposed to the overall loss of the parent aldehyde or the production of hydrated products). For this reason, it was necessary to perform experiments at sulfuric acid concentrations of 60 wt% and higher to ensure complete dehydration of all aldol reaction products (Baigrie et al., 1985).

The Beer's law molar extinction coefficients—to allow for conversion of the UV–vis absorbance data into absolute production concentrations—were directly determined in 75 wt% H_2SO_4 for crotonaldehyde (the acetaldehyde aldol condensation product) and 2-ethyl-2-hexenal (the butanal aldol condensation product) by preparing dilute solutions in 75 wt% H_2SO_4 and measuring the absorbance at the appropriate peak wavelength. The spectra were collected quickly, to avoid any possible acid-catalyzed reaction.

Aqueous solutions of the aldehydes were prepared by adding pure aldehyde to deionized water and vigorously mixing for several hours to ensure complete dissolution. For the larger aldehydes, the concentrations of these aqueous solutions were determined by their water solubility. The sulfuric acid solutions were prepared by dilution of concentrated (96 wt%) H_2SO_4 with deionized water. The kinetics experiments were typically performed by adding the aqueous solution of the aldehyde (diluted aldehyde solutions were used to avoid transient, locally high concentrations of aldehyde) to the sulfuric acid solution and vigorously mixing for several minutes to ensure solution homogeneity. For example, a typical acetaldehyde experiment involved adding 100 µl of a 1.5 M acetaldehyde solution to 50 ml of 75 wt% sulfuric acid, resulting in a 3×10^{-3} M acetaldehyde in 75 wt% H_2SO_4 solution. A small portion of the reaction mixture was then added to either a 1 mm or 1 cm pathlength quartz cuvette, and the reaction system was continuously monitored in the cuvette by UV–vis spectroscopy. As mentioned above typical initial aldehyde concentrations were on the order of 10^{-3} M, which provided sufficient UV–vis absorbance values and convenient initial rates. For the room temperature experiments, the temperature was 295 ± 1 K. For the temperature dependence experiments, the 50 ml sulfuric acid solution was either precooled or preheated to the appropriate temperature before the addition of the aldehyde solution, and the cuvette was maintained at the desired temperature by the automated temperature control system of the UV–vis spectrometer. The lowest temperature achieved ($-24\,°C$) was dictated by the limited capabilities of the refrigeration system of the temperature control system.

3. Results and discussion

3.1. Identification of reaction products

The aldol condensation reaction products of acetaldehyde (crotonaldehyde) and butanal (2-ethyl-2-hexenal) are commercially available. The spectra of these two products were investigated in concentrated sulfuric acid solutions in order to identify their characteristic peak wavelengths and to determine their Beer's law molar extinction coefficients. In 75 wt% H_2SO_4, crotonaldehyde has a peak absorbance at 245 nm and $\varepsilon = 9280\,cm^{-1}\,M^{-1}$. Similarly, in 75 wt% H_2SO_4, 2-ethyl-2-hexenal has a peak absorbance at 266 nm and $\varepsilon = 11960\,cm^{-1}\,M^{-1}$. While the peak wavelengths shifted as a function of acid strength, the Beer's law molar extinction coefficients varied by less than 10% over the acid and temperature range of the experiments.

Fig. 2 shows several spectra collected as a function of time for an acetaldehyde reaction system in 75 wt% H_2SO_4 at 295 K at a relatively high initial acetaldehyde concentration (6.8×10^{-3} M) carried out in a 1 mm cuvette. At early times, it is readily apparent that crotonaldehyde (with a peak wavelength of
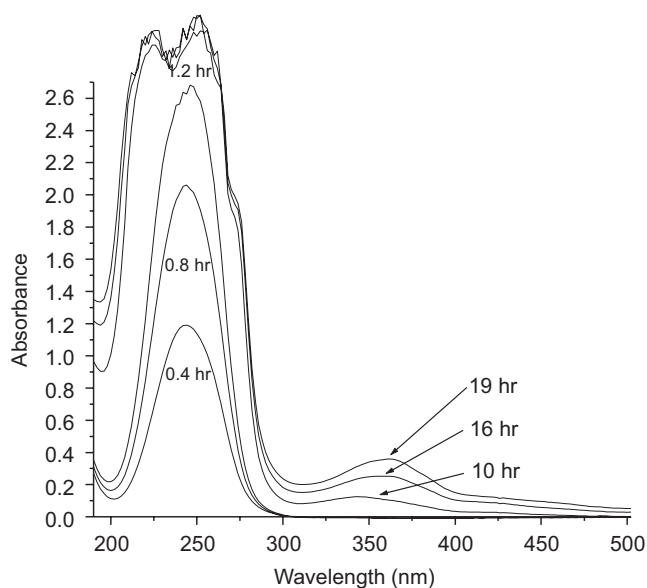
Fig. 2. UV–vis absorption spectra at different reactions times for the acetaldehyde reaction system at $[acetaldehyde]_0 = 6.8 \times 10^{-3}$ M, 75 wt% H_2SO_4 and 295 K.

245 nm) is a major product of the reaction. At later times, the crotonaldehyde peak goes off scale, but a new peak at 364 nm is observed to grow in. According to the Woodward rules for α,β-unsaturated carbonyl compounds (Lambert et al., 1987) the later time product is likely to have either three additional units of conjugation in an aliphatic structure, or two additional units of conjugation as part of a ring structure. The latter possibility has been suggested as a possible product of crotonaldehyde self reaction via a Michael addition mechanism (McIntosh et al., 1980). In our work to determine Beer's law molar extinction coefficients for crotonaldehyde in H_2SO_4 solutions, we noted that these solutions eventually showed small absorptions at 364 nm. Noziere and Esteve have also noted this absorption in their study of acetaldehyde reactions in sulfuric acid (Noziere and Esteve, 2005; Noziere et al., 2006), but have attributed it to additional aldol condensation reactions of products with acetaldehyde. A detailed study of this crotonaldehyde self-reaction is currently under way in our labs.

All other aldehyde reaction systems in this study showed similar product behavior. The peak wavelength for the aldol products for all other systems was 266 nm (the Beer's law molar extinction coefficient was assumed to be the same as for 2-ethyl-2-hexenal for the purposes of the kinetics analysis) and a later time product was also always observed at 364 nm in 75 wt% H_2SO_4. Again, the Woodward rules accurately predict that the in-

creased alkyl chain length will cause a red shift from crotonaldehyde (the acetaldehyde aldol product) to 2-methyl-2-pentenal (the propanal aldol product). However, the additional lengthening of the alkyl chain in the parent aldehydes will not lead to an additional red shift in the dehydrated aldol condensation products (Lambert et al., 1987), as the nature of the alkyl group has a much smaller effect on the peak wavelength (because it is not part of the chromophore electronic system) than does the size of the conjugated system (which is part of the chromophore electronic system).

3.2. Integrated rate law analysis and reaction efficiency

Data were collected at the peak absorption wavelength for each system as a function of time, and the absorption values were converted to absolute aldol product concentration via Beer's Law. Fig. 3 shows such a plot for an acetaldehyde (3×10^{-3} M) kinetics run in 75 wt% H_2SO_4 and 295 K carried out in a 1 mm cuvette. At the lower initial acetaldehyde concentration used in this run (as compared to the data shown in Fig. 2), the 245 nm absorption peak stays on scale ($A_{max} = 1.2$), and the crotonaldehyde concentration can be calculated according to Beer's law at all times. As mentioned above, acetaldehyde does have a weak $n \rightarrow \pi^*$ transition in this range that could potentially complicate the conversion of absorbance data to crotonaldehyde concentration. However, using the initial acetaldehyde concentration of 3×10^{-3} and

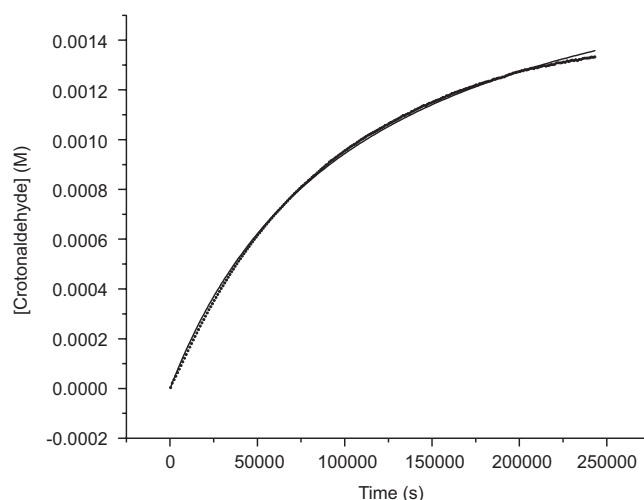

Fig. 3. Experimental data (circles) and second-order kinetics fit (line) of the aldol condensation reaction of acetaldehyde at $[acetaldehyde]_0 = 3 \times 10^{-3}$ M, 75 wt% H_2SO_4 and 295 K.

Beer's law molar extinction coefficient for this transition of $\varepsilon \sim 15\,\mathrm{cm^{-1}\,M^{-1}}$, the maximum absorbance due to acetaldehyde under these conditions is only 0.004, which is insignificant compared to the absorption values ($A_{max} = 1.2$) observed in the experiments.

As will be confirmed in Section 3.3, the reaction is second order in the reactant aldehyde:

$$-\frac{1}{2}\frac{\mathrm{d[aldehyde]}}{\mathrm{d}t} = \frac{\mathrm{d[aldol]}}{\mathrm{d}t} = k[\mathrm{aldehyde}]^2. \qquad (1)$$

The kinetics curve can be directly fit by the integrated second-order product rate law arising from Eq. (1) above (the solid line in Fig. 3):

$$[\mathrm{aldol}]_t = \frac{-1}{(2/[\mathrm{aldehyde}]_0) + 4kt} + \frac{[\mathrm{aldehyde}]_0}{2}. \qquad (2)$$

The fit is shown as the solid line in Fig. 3 and is in excellent agreement with the data, resulting in a bimolecular rate constant of $1.2 \times 10^{-3}\,\mathrm{M^{-1}\,s^{-1}}$. However, this method for determining rate constants was extremely time-consuming (data were collected for 3 days to construct Fig. 3). Section 3.3 describes an alternative initial rates method that was used to more efficiently determine rate constants. However, the data in Fig. 3 provide unique information on the reaction. As the reaction has been followed virtually to completion in Fig. 3, it is possible to estimate the final concentration of the aldol product crotonaldehyde. Therefore, using the stoichiometry of the reaction and the initial concentration of acetaldehyde, it is possible to determine the aldol yield of the reaction. The crotonaldehyde concentration at the longest time is about 0.0013 M, and the initial acetaldehyde concentration was 0.003 M. According to the stoichiometry of the reaction (two acetaldehyde molecules react for every crotonaldehyde molecule formed), a reaction yield of 100% should lead to 0.0015 M crotonaldehyde. Therefore, the observed crotonaldehyde yield of the reaction is greater than 85%.

3.3. Initial rates and aldehyde rate order analysis

In order to expedite the determination of rate constants, an initial rates method was used. In the initial rates method, the kinetics of the reaction are monitored before the reaction has proceeded significantly such that the following approximation holds:

$$\frac{\mathrm{d[aldol]}}{\mathrm{d}t} = k[\mathrm{aldehyde}]^n = k[\mathrm{aldehyde}]_0^n. \qquad (3)$$

In this case, the initial rate of the aldol production is measured as a function of the initial aldehyde concentration. Fig. 4 shows a set of initial rates experiments for the butanal system at 75 wt% H_2SO_4 and 295 K. To linearize the determination of the rate order n, logarithms are taken of both sides of Eq. (3):

$$\log\left(\frac{\mathrm{d[aldol]}}{\mathrm{d}t}\right) = n \log[\mathrm{aldehyde}] + \log k. \qquad (4)$$

Fig. 5 shows the rate order analysis for the data in Fig. 4. From these experiments, a rate order of 1.95 was determined, thus confirming the expected rate order of 2 as given in Eq. (1). Rate constants were calculated via Eq. (3) from measurements of the initial rate and $[\mathrm{aldehyde}]_0$. Typically, at least three kinetics runs (with different initial aldehyde concentrations to confirm the rate order of the process) were carried out for each combination of parent aldehyde, H_2SO_4 concentration and temperature. The statistical error (1σ) for the entire data set of rate constants was 14%. The sources of systematic error in the determination of the rate constants are expected to arise from linearly dependent uncertainties in Beer's law molar extinction coefficients (10%, as discussed above) used to calculate the initial rates, and in the initial concentration of the aldehydes (10%, as estimated from the volumetric precision used in the preparation of the solutions) used to calculate the bimolecular rate constants themselves.
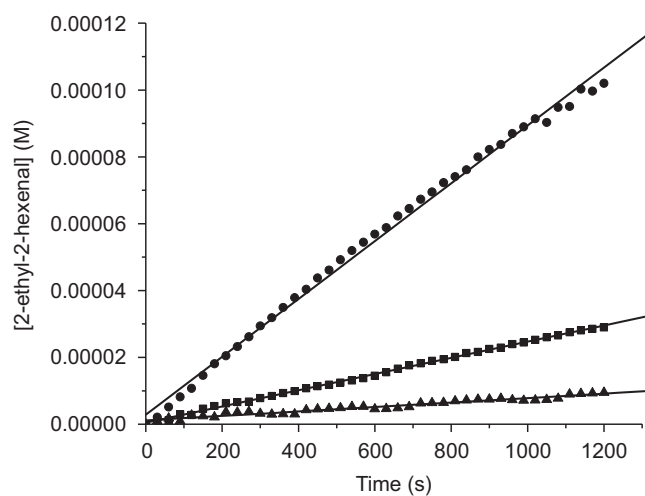

Fig. 4. Initial rates measurements for the aldol condensation reaction of butanal at 75 wt% H_2SO_4 and 295 K. Circles: $[\mathrm{butanal}]_0 = 1.0 \times 10^{-3}\,\mathrm{M}$, squares: $[\mathrm{butanal}]_0 = 5.0 \times 10^{-4}\,\mathrm{M}$, triangles: $[\mathrm{butanal}]_0 = 2.5 \times 10^{-4}\,\mathrm{M}$.
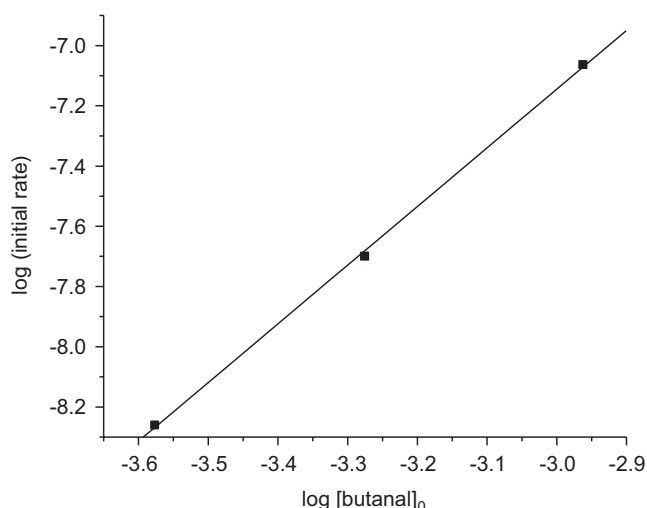
Fig. 5. Rate order determination for the aldol condensation reaction of butanal for data shown in Fig. 4.

3.4. Excess acidity analysis

The acid dependence of the aldol formation rate constants for the acetaldehyde system has been previously investigated and analyzed using the excess acidity formalism (Baigrie et al., 1985). The excess acidity method accounts for the non-ideal behavior of highly acidic solutions and is necessary for the interpretation of acid-catalyzed kinetics results under such conditions. The method has been described in detail previously (Cox and Yates, 1979), and is related to the Hammett acidity function, H_0 (Hammett and Deyrup, 1932). The excess acidity formalism is an attempt to define a linear relationship between the observed rate constant and some acidity function for an acid-catalyzed process, much like a pseudo first-order rate constant can be linearly related to the concentration of the excess reactant. The excess acidity parameter, X, is best thought of as a quantity analogous to pH for concentrated acidic solutions. In their previous study of the acid-catalyzed aldol condensation reaction of acetaldehyde, Baigrie et al. found a linear relationship between ($\log k - \log C_{H+} - \log a_w$) and X, where k is the bimolecular rate constant, C_{H+} is the proton concentration, and a_w is the activity parameter for H_2O, such that the data could be fit to the following expression:

$$(\log k - \log C_{H+} - \log a_w) = mX + b. \qquad (5)$$

As X is analogous to $\log[H^+]$, this analysis is essentially a more sophisticated version of the "log–log" plotting exercise described above to find

the aldehyde rate order but that is instead applied here to find the effective H^+ rate order (the slope, m, in Eq. (5)) for the acid-catalyzed process. The intercept, b, in Eq. (5) represents the value of log k at infinite dilution ($X = 0$). Values for C_{H+} and X for various H_2SO_4 solutions have been compiled (Cox and Yates, 1978), and a parameterized form for a_w has been determined for H_2SO_4 solutions (Shi et al., 2001). For example, in the previous study of the acetaldehyde system, when the data were plotted according to Eq. (5), a slope of 0.95 was obtained, affirming the expectation that the acid catalysis is first order in $[H^+]$ for the aldol condensation mechanism (Baigrie et al., 1985).

Fig. 6 shows the excess acidity plot (carried out as described above) for the acid dependence of the rate constant for aldol condensation for the butanal system at 295 K, from 62.5–88 wt% H_2SO_4. The data are obviously fit well by the excess acidity formalism, and a slope of 0.997 ± 0.015 was determined, again confirming that the acid catalysis is first order in $[H^+]$. Excess acidity analyses were carried out for the 295 K kinetic data for the other aldehyde systems (for acetaldehyde, the present data were combined with the data from the previous investigation (Baigrie et al., 1985)) and the results are given in Table 1. The self-consistency of the analysis method is apparent in that all systems are characterized by a slope of unity (within the 95% confidence interval). As will be subsequently discussed, the parameters from the excess acidity analysis can be used to predict rate constants for
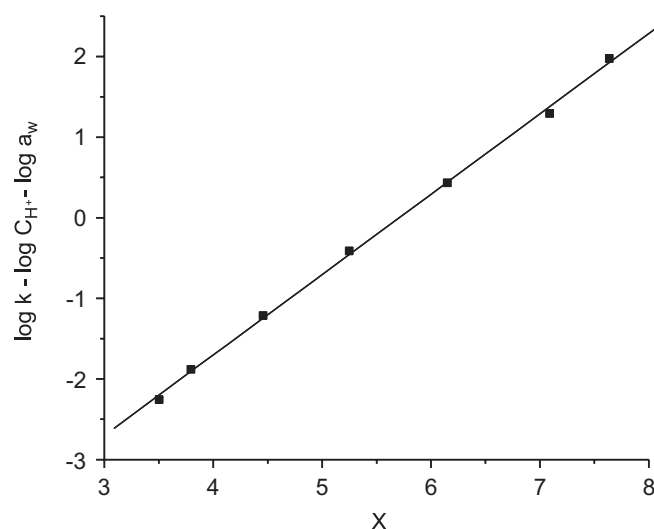

Fig. 6. Excess acidity plot for the aldol condensation reaction of butanal at 295 K. Compositions ranging from 62.5 to 88 wt% H_2SO_4 are represented on this plot.

Table 1
Excess acidity parameters at 295 K

Aldehyde	$m \pm \sigma$ (from Eq. (5))	$b \pm \sigma$ (from Eq. (5))
Acetaldehyde	1.003 ± 0.049	-7.31 ± 0.27
Propanal	0.950 ± 0.031	-5.47 ± 0.17
Butanal	0.997 ± 0.015	-5.691 ± 0.084
Pentanal	0.961 ± 0.020	-5.93 ± 0.11
Hexanal	0.976 ± 0.032	-6.30 ± 0.18
Heptanal	0.99 ± 0.15	-6.31 ± 0.71
Octanal	1.004 ± 0.089	-6.72 ± 0.42

the lower H_2SO_4 concentrations that were not accessible in this study (due to the requirement that the dehydrated aldol product be the dominant form) but that are of interest in assessing the role of aldol condensation reactions in tropospheric aerosols. Because previous kinetic work (Noyce and Snyder, 1959) suggests that the dehydration step (Eq. (4) in Fig. 1) is not rate-limiting, but rather that the rate limiting step is the aldol formation (Eq. (3) in Fig. 1), it should be possible to extrapolate the present data to lower H_2SO_4 concentrations, where the dehydrated aldol product is not formed.

3.5. Aldehyde dependence

This study is the first systematic examination of the dependence of the aldol reaction rate constant for a number of different aldehydes. Fig. 7 shows the 295 K rate constants for each aldehyde system at a number of different H_2SO_4 compositions. As discussed in Section 3.4, the acid dependence of the rate constants can be precisely analyzed through the excess acidity formalism. However, Fig. 7 shows the interesting dependence of the rate constant on the alkyl chain length of the parent aldehyde. In particular, the 75 wt% H_2SO_4 295 K rate constant dramatically increases from acetaldehyde ($1.61 \times 10^{-3} \, M^{-1} \, s^{-1}$) to butanal ($84.9 \times 10^{-3} \, M^{-1} \, s^{-1}$), and then gradually decreases as the alkyl chain lengthens further. The rise in the reactivity from the C_2 to the C_4 aldehyde is probably related to the fact that the β-carbon in acetaldehyde is a primary carbon atom ($-CH_3$), whereas the β-carbon for the other systems is a secondary carbon atom ($-CH_2-$). Presumably, one of the intermediates in the aldol condensation mechanism is destabilized if the reaction occurs at a primary β-carbon. The decrease in reactivity from the C_4 to C_8 aldehyde is not as easily rationalized. In any case, it is important that the present study indicates that acetaldehyde is an unusually unreactive aldehyde, as
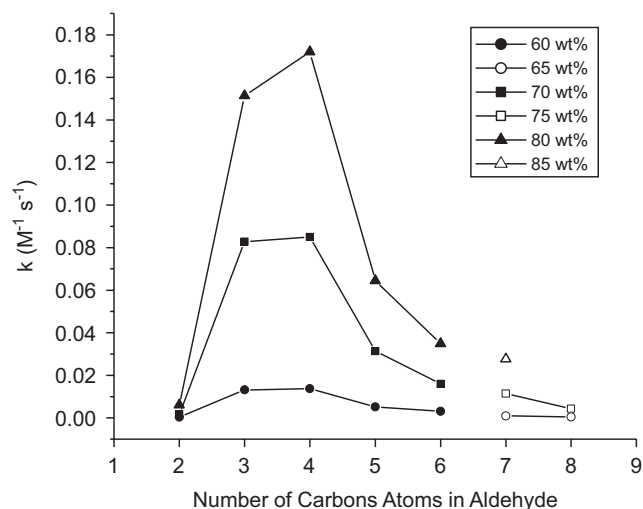

Fig. 7. Dependence of the aldol condensation reaction rate constant on the reactant aldehyde and H_2SO_4 concentration at 295 K.

it is often used in atmospheric studies as the "prototype" aldehyde. From the point of view of aldol reactivity, acetaldehyde is clearly not a representative aldehyde.

3.6. Temperature dependence

Temperature dependence measurements were made for the acetaldehyde, butanal, and hexanal systems at 75 wt% H_2SO_4 to assess whether the temperature dependence of the rate constant varies among the different aldehydes studied. Similar measurements were made for the butanal system at 65 and 85 wt% H_2SO_4 to assess whether the temperature dependence of the rate constant varies among the different H_2SO_4 compositions used. Fig. 8 shows an Arrhenius analysis of the results of the 75 wt% H_2SO_4 experiments. It is clear that normal Arrhenius behavior is observed over the range of temperatures studied (-24 to $42\,^\circ C$). Table 2 contains the Arrhenius parameters determined for all temperature dependence experiments. Within the 95% confidence interval, no difference in the temperature dependence of the rate constant for the different H_2SO_4 compositions was obtained, but a statistically meaningful decrease in the activation energy was determined as the alkyl chain of the parent aldehyde lengthened. Assuming Arrhenius behavior holds, the parameterization of the temperature dependence of the rate constant determined here allows the prediction of rate constants at temperatures below the lowest directly used in the
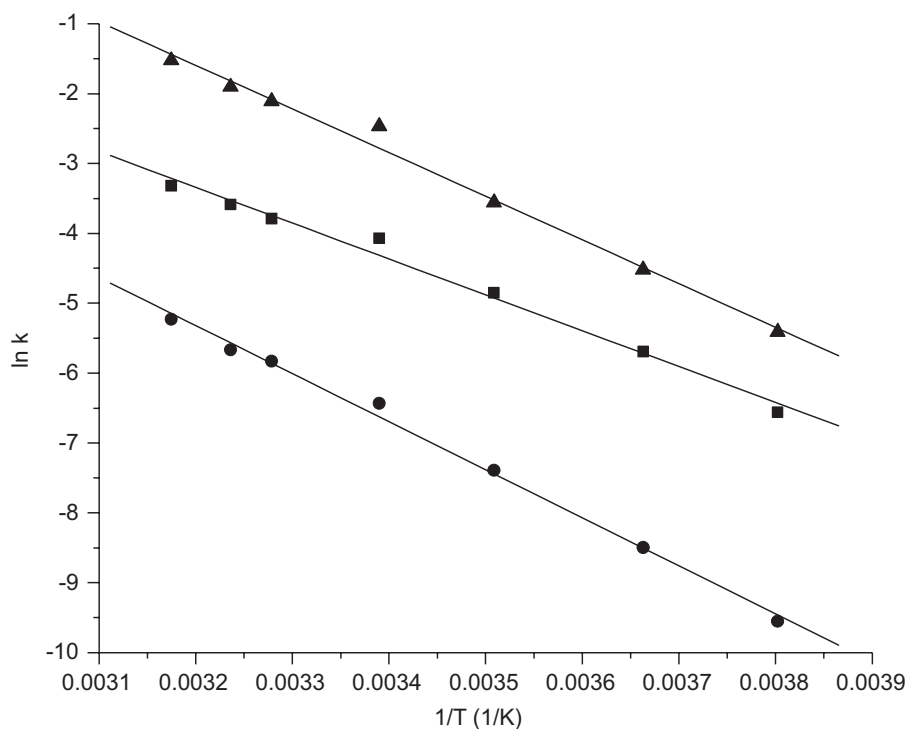
Fig. 8. Arrhenius analysis of the temperature dependence of the aldol condensation reaction rate constant (circles: acetaldehyde; squares: hexanal; triangles: butanal) at 75 wt% H_2SO_4.

Table 2
Arrhenius parameters

Aldehyde	wt% H_2SO_4	$-E_a/R \pm \sigma$ (K)	$\ln A \pm \sigma$
Acetaldehyde	75	-6880 ± 200	16.68 ± 0.69
Butanal	65	-5580 ± 650	14.5 ± 2.2
	75	-6250 ± 270	18.41 ± 0.93
	85	-6470 ± 940	19.7 ± 3.2
Hexanal	75	-5130 ± 250	13.07 ± 0.86

present experiments ($-24\,°C$); such temperatures are often relevant in the upper troposphere.

3.7. Parameterization of kinetic data

In order to improve the utility of the present kinetics data, several parameterizations were determined to allow the calculation of aldol condensation rate constants for any aldehyde, H_2SO_4 composition, and temperature. The excess acidity parameters, log C_{H+} and X were taken from Cox and Yates (1978) and were separately fit to a second-order polynomial expression as a function of wt% H_2SO_4:

$$\log C_{H+} = -2.62 \times 10^{-4} \times (\text{wt\%}H_2SO_4)^2$$
$$+ 3.79 \times 10^{-2} \times (\text{wt\%}H_2SO_4)$$
$$- 2.58 \times 10^{-1}, \qquad (6)$$

$$X = 1.07 \times 10^{-3} \times (\text{wt\%}H_2SO_4)^2 - 1.34 \times 10^{-2}$$
$$\times (\text{wt\%}H_2SO_4) + 3.34 \times 10^{-1}. \qquad (7)$$

The 298 K water activity (a_w) has been previously parameterized as a function of water mole fraction (Y_w) (Shi et al., 2001):

$$Y_w = \frac{(\text{wt\%}H_2SO_4)}{\left[(\text{wt\%}H_2SO_4) + \frac{[100-(\text{wt\%}H_2SO_4)]*M_{H_2SO_4}}{M_{H_2O}} \right]}, \qquad (8)$$

where $M_{H_2SO_4}$ and M_{H_2O} are the molar mass of sulfuric acid and water, respectively.

$$\log a_w = \log\{\exp[0.00305 \times (-69.775 \times Y_w$$
$$- 18253 \times Y_w^2 + 31072.2 \times Y_w^3$$
$$- 25668.8 \times Y_w^4)]\}. \qquad (9)$$

From the excess acidity analysis for each aldehyde (the slope, m, and intercept, b, values given in Table 1 obtained by analysis according to Eq. (5)) and the values of X, $\log C_{H+}$ and $\log a_w$ (parameterized above), the rate constant for each aldol condensation reaction at 295 K for any wt% H_2SO_4 can be calculated:

$$k(295\,K) = 10^{(mX+b+\log C_{H+}+\log a_w)}. \qquad (10)$$

Rate constants at other temperatures can be calculated by using the 295 K rate constant calculated

above (any changes in the apparent rate constant due to the temperature dependence of C_{H+} and a_w are subsumed in the Arrhenius analysis), and the $-E_a/R$ values (given in Table 2) from the appropriate Arrhenius analysis:

$$k(T) = k(295\,\text{K}) \times \exp\left[\frac{-E_a}{R} \times \left(\frac{1}{T} - \frac{1}{295\,\text{K}}\right)\right].$$

(11)

3.8. Comparison to previous work

The present finding that dehydrated aldol products are formed efficiently for a variety of saturated aliphatic aldehydes in concentrated H_2SO_4 solutions is in agreement with earlier studies on acetaldehyde by Baigrie et al. (1985) and Noziere and Esteve (2005) and a study of the interaction of hexanal with actual H_2SO_4 aerosols by Garland et al. (2006). As discussed above, an extensive kinetic data set for acid-catalyzed aldol condensation self-reactions exists only for acetaldehyde (Baigrie et al., 1985; Esteve and Noziere, 2005). The present rate constants for the acetaldehyde self-reaction are about 50% higher than the rate constants determined at 65, 75, and 85 wt% in Baigrie et al., but somewhat lower than the value determined by Esteve and Noziere for 85 wt% H_2SO_4.

Garland et al. (2006) studied the heterogeneous interaction of hexanal vapor with H_2SO_4 aerosols with compositions between 30 and 96 wt% and at 298 K. They report evidence for reaction at all H_2SO_4 compositions, with increasing reaction evident at the highest acidities. Typical reaction conditions were as follows: 7 Torr hexanal, 75 wt% H_2SO_4 and a reaction time of 13 min. In order to calculate the acid phase hexanal concentration, the appropriate Henry's law coefficient is required. Unfortunately, there have been no measurements of this quantity for hexanal in H_2SO_4 solutions. However, if a conservative value of $100\,\text{M}\,\text{atm}^{-1}$ (roughly the value determined by Esteve and Noziere (2005) for acetaldehyde in 70 wt % H_2SO_4 and at 298 K) is assumed, a hexanal concentration of 1.0 M is calculated. Using the present kinetics data (and the parameterizations given above), the bimolecular rate constant is about $1.8 \times 10^{-2}\,\text{M}^{-1}\,\text{s}^{-1}$, and the reaction rate can be calculated: $1.8 \times 10^{-2}\,\text{M}^{-1}\,\text{s}^{-1} \times [1.0\,\text{M}]^2$, which is equal to $1.8 \times 10^{-2}\,\text{M}\,\text{s}^{-1}$. Therefore, for a 780 s experiment, the present kinetics results predict that the reaction will go to completion several times over under these conditions. This result is consistent with

the finding of Garland et al. (2006) that H_2SO_4 aerosols exposed to hexanal under such conditions are composed of as much as 88% organic by mass.

Jang and Kamens (2005) studied the heterogeneous interaction of octanal vapor with various seed aerosols at 298 K with the H_2SO_4 composition controlled by the relative humidity of the smog chamber. Using octanal concentrations of about 260 ppb, the aerosols were observed to increase in volume by as much as factor of 2 over the 1 h timescale of the experiment. Zhao et al. (2005) have measured the Henry's law constant for octanal in 67 wt% H_2SO_4 at 296 K and determined a value of $2300\,\text{M}\,\text{atm}^{-1}$. Assuming a H_2SO_4 composition of 67 wt% for the highest acidity experiments by Jang and Kamens, an octanal aerosol concentration of $6.0 \times 10^{-4}\,\text{M}$ is calculated for these conditions. Using the present kinetics data (and the parameterizations given above), the bimolecular rate constant is about $2.9 \times 10^{-3}\,\text{M}^{-1}\,\text{s}^{-1}$, and the reaction rate can be calculated: $2.9 \times 10^{-3}\,\text{M}^{-1}\,\text{s}^{-1} \times [6.0 \times 10^{-4}\,\text{M}]^2$, which is equal to $1.0 \times 10^{-9}\,\text{M}\,\text{s}^{-1}$. Therefore, for a 1 h experiment, the present kinetics results predict that the reaction has proceeded about only 1% toward completion, and does not appear to provide support for aldol condensation reactions as the explanation for the large growth in organic mass observed in the Jang and Kamens experiments. Similarly, Esteve and Noziere (2005) have used their kinetics data for acetone to show that the acid-catalyzed reactions of acetone are too slow to be responsible for increased organic mass observed in aerosols in smog chamber experiments. Esteve and Noziere also asserted that since atmospheric conditions are much less favorable for such acid-catalyzed reactions than smog chamber conditions, the reactions of ketones with sulfuric acid aerosols are probably not responsible for high organic content of tropospheric aerosols.

3.9. Role of aldehyde aldol condensation reactions on atmospheric sulfuric acid aerosols

While it is clear that acid-catalyzed accretion reactions involving aldehydes have been observed in many laboratory experiments, these experiments typically use higher aldehyde concentrations (most often, much higher) than those observed in the atmosphere in order to drive the reactions to occur on a reasonable time scale. Obviously, kinetic data are needed to extrapolate from such laboratory conditions to those of the atmosphere, particularly as a function of H_2SO_4 composition and temperature.

Similar solubility data (also as a function of H_2SO_4 composition and temperature) is also needed, in order to be able to calculate aerosol phase aldehyde concentrations from the gas phase aldehyde abundance. Interestingly, the fact that the solubility of aldehydes in sulfuric acid is observed to decrease with increasing temperature (the normal situation for all compounds, but confirmed for acetaldehyde by Michelsen et al. (2004)), taken with this study showing that the aldol condensation rate constant increases with increasing temperature (again, the normal situation for most chemical reactions), indicates that the competing temperature effects partially offset each other. In other words, the fact that aerosols are both more acidic and colder at higher altitudes suggests that the aldol condensation reactions under these conditions might actually be similarly efficient compared to the higher temperatures and lower acidity representative of lower altitudes.

It is difficult to perform a representative calculation of the potential role of aldol condensation reactions on atmospheric aerosols because of the many factors that play a role in the efficiency of these reactions, as well as the fact that there will be many different organic compounds simultaneously present on such aerosols. However, we describe a "best case" calculation below that suggests that such reactions are unlikely to be efficient enough to serve as a major mechanism for the transfer of organic compounds into atmospheric sulfuric acid aerosols. While there are several atmospherically abundant aliphatic aldehydes (Kawamura et al., 2000), we use a rough total aldehyde concentration of 10 ppb in our calculations and simply use the present butanal kinetic data in the calculations (this is the fastest reacting aldehyde system in our study). To provide "best case" conditions for aldol condensation reactivity, we use 50 wt% H_2SO_4 composition and 298 K for the aerosol parameters (this is more acidic and warmer than a truly "average" tropospheric H_2SO_4 aerosol). The largest Henry's law coefficient reported for any aldehyde in H_2SO_4 near 298 K is about 2300 M atm^{-1}, reported by Zhao et al. (2005) for octanal in 67 wt% H_2SO_4 at 296 K. Using this Henry's law coefficient and 10 ppb gas phase concentration, an aerosol phase aldehyde concentration of 2.3×10^{-5} M is calculated. This corresponds to only 1.6×10^{-4}% aldehyde by mass; many other studies have pointed out that the simple physical solubility of most organic compounds (aldehydes among them) is much

too small to explain atmospheric aerosols that are 50% organic by mass or more. Under these conditions, the present kinetics data can be used to calculate an aldol condensation rate constant of 1.5×10^{-3} M^{-1} s^{-1}, and the reaction rate can be calculated: 1.5×10^{-3} M^{-1} s^{-1} $\times [2.3 \times 10^{-5}$ M$]^2$, which is equal to 7.9×10^{-13} M s^{-1}. In order to provide some perspective on this rate, it would take approximately 1 year for the aldol condensation reaction to go to completion under these conditions, which would lead to a mere doubling (from 1.6 to 3.2×10^{-4}%) of the organic content of the aerosol. Because the rate depends quadratically on the aerosol phase aldehyde concentration, the solubility of the aldehydes critically controls the efficiency of aldol condensation reactions. Michelsen et al. (2004) measured Henry's law coefficients as high as 145,000 M atm^{-1} for acetaldehyde at 212 K. If this solubility is used in the above calculation, and the rate constant is recalculated for 212 K (but all other parameters are the same), the calculated reaction rate is about the same (6.1×10^{-13} M s^{-1}) as that calculated at 298 K. Therefore, even under the "best case" scenario conditions used in the preceding calculations, it does not appear that aldol condensation reactions involving simple aliphatic aldehydes (up to C_8 in size) are sufficiently fast to play a significant role in the transfer of organic material into atmospheric sulfuric acid aerosols.

4. Conclusions

In summary, UV–vis spectroscopy was used to monitor the kinetics of formation of the products in the bulk phase acid-catalyzed aldol condensation reaction of a range of aliphatic aldehydes (C_2–C_8). The experiments were carried out at various sulfuric acid compositions and a range of temperatures in order to estimate the rate constants of such reactions on sulfuric acid aerosols under tropospheric conditions. While the kinetic data are generally consistent with previous laboratory reports of aldehyde reactivity in various sulfuric acid media, the aldol condensation reactions involving aliphatic aldehydes do not appear fast enough to be responsible for significant transfer of organic material into atmospheric aerosols.

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