Reactive uptake of glyoxal by particulate matter

John Liggio
Centre for Atmospheric Chemistry and Chemistry Department, York University, Toronto, Ontario, Canada

Shao-Meng Li
Meteorological Service of Canada, Toronto, Ontario, Canada

Robert McLaren
Centre for Atmospheric Chemistry and Chemistry Department, York University, Toronto, Ontario, Canada

Received 9 June 2004; revised 30 September 2004; accepted 17 December 2004; published 19 May 2005.

[1] The uptake of gaseous glyoxal onto particulate matter has been studied in laboratory experiments under conditions relevant to the ambient atmosphere using an aerosol mass spectrometer. The growth rates and reactive uptake coefficients, γ, were derived by fitting a model of particle growth to the experimental data. Organic growth rates varied from 1.05 × 10⁻¹¹ to 23.1 × 10⁻¹¹ μg particle⁻¹ min⁻¹ in the presence of ~5 ppb glyoxal. Uptake coefficients (γ) of glyoxal varied from 8.0 × 10⁻⁴ to 7.3 × 10⁻³ with a median γ = 2.9 × 10⁻³, observed for (NH₄)₂SO₄ seed aerosols at 55% relative humidity. Increased γ values were related to increased particle acidity, indicating that acid catalysis played a role in the heterogeneous mechanism. Experiments conducted at very low relative humidity, with the potential to be highly acidic, resulted in very low reactive uptake. These uptake coefficients indicated that the heterogeneous loss of glyoxal in the atmosphere is at least as important as gas phase loss mechanisms, including photolysis and reaction with hydroxyl radicals. Glyoxal lifetime due to heterogeneous reactions under typical ambient conditions was estimated to be τ_{het} = 5–287 min. In rural and remote areas the glyoxal uptake can lead to 5–257 ng m⁻³ of secondary organic aerosols in 8 hours, consistent with recent ambient measurements.


1. Introduction

[2] Secondary organic aerosol (SOA) formation via gas-particle partitioning processes is an area of increased study. An understanding of these processes is important because aerosols play a role in climate change [Pilinis et al., 1995; Twomey, 1991], visibility [Elderling and Cass, 1996; Elderling et al., 1993; Yuan et al., 2000], and adverse health effects [Dockery et al., 1993; Schwartz and Dockery, 1992]. Significant progress has been made with respect to particulate organic product identification [Bowman et al., 1997; Pankow, 1994a, 1994b]; however much of the studies has focused on low-volatility products, which are expected to easily partition into the particle phase on the basis of gas-particle partitioning theory. Recently studies have shown that volatile compounds can also be taken up by aerosols, particularly carbonyls known to be capable of heterogeneous reactions [Jang et al., 2002, 2003; Jang and Kamens, 2001a; Kalberer et al., 2004; Noziere and Riemer, 2003; Olson and Hoffmann, 1989; Tobias and Ziemann, 2000]. Although the role of gas phase carbonyls as a source of radicals [Seinfeld and Pandis, 1998] and organic nitrates [Grosjean et al., 1996] has been studied extensively, little is known regarding their contribution to SOA by means of heterogeneous reactions. Potential mechanisms for this include hydration of the carbonyl followed by acid catalyzed polymerization or acetal/hemiacetal formation in the presence of alcohols [Jang et al., 2002, 2003; Jang and Kamens, 2001a], aldol condensation reactions [Noziere and Riemer, 2003] as well as other reactions known to occur in bulk solution [Olson and Hoffmann, 1989; Tobias and Ziemann, 2000]. Evidence of the formation of organic sulfate compounds as a means of carbonyl uptake has also recently been presented [Liggio et al., 2005]. Heterogeneous reactions of these types imply that SOA yields may be significantly larger than those predicted by partitioning theory, which is especially relevant given that most organic photo-oxidation products contain carbonyl functionality.

[3] Glyoxal is one of most prevalent dicarbonyls in the ambient atmosphere. It is primarily formed from the photodissociation of aromatic hydrocarbons [Jang and Kamens, 2001b; Yu et al., 1997], and is also a minor oxidation product of isoprene [Carter and Atkinson, 1996; Yu et al., 1995], and other biogenic species [Fick et al., 2003]. The often high concentrations of aromatic and biogenic species in ambient air imply that partitioning of glyoxal could be a
significant contributor to SOA. In fact, glyoxal has been found to produce significant aerosol yields, attributed to hydration and polymerization [Jang and Kamens, 2001a]. Although the body of qualitative structural evidence is increasing for the formation of low-volatility products, a quantitative understanding of the significance of these reactions to the ambient atmosphere is lacking. Typically laboratory studies of these processes that have identified product compounds are performed under conditions significantly different than those of the ambient atmosphere. The elevated gas phase and particle concentrations associated with such experiments make a simple extrapolation to the ambient conditions difficult. More rigorous kinetic experiments have also been performed, primarily involving the reactive uptake of carbonyl species such as formaldehyde and acetone on aqueous droplets, sulfuric acid films or bulk solution [Duncan et al., 1999; Iraci and Tolbert, 1997; Jayne et al., 1996; Tolbert et al., 1993]. The kinetics for the reactive uptake of glyoxal onto particles more closely simulating ambient material would be a useful tool in an assessment of the atmospheric importance of this process. In a previous paper [Liggio et al., 2005] a heterogeneous mechanism for this uptake as well as mass spectral evidence for the formation of glyoxal-acetals and sulfates has been presented.

[4] In the present work, a simple uptake model is fit to the experimental data obtained during the study on reactive uptake of glyoxal [Liggio et al., 2005] to determine the reactive uptake coefficient (γ). This coefficient is defined as the probability that a collision between a gas molecule and the particle surface will result in uptake, considering all aspects of the uptake process including diffusion, mass accommodation, solubility and reactivity. Data were obtained by exposing seed aerosols to gas phase glyoxal within a chamber while an aerosol mass spectrometer (AMS) was used to probe the chemical composition of the growing particles and quantify the total organic content. Particle mass spectra were obtained on line during reactive uptake. The effect of seed composition, in particular particle acidity and relative humidity, on the observed uptake coefficients and growth rates will be presented. The atmospheric implications of this uptake will also be discussed.

2. Experimental Description

[5] The entire apparatus utilized in these experiments is given schematically in Figure 1. A detailed description of this system has been reported previously [Liggio et al., 2005]. Briefly, studies were conducted in a 2 m³ Teflon...
were obtained with the AMS to provide the structural and
introduced into the bag with pre-existing gaseous glyoxal.
Particles of known inorganic composition were
bag (Whelch Flurocarbon Inc.) enclosed in an aluminum
support. Particles of known inorganic composition were
introduced into the bag with pre-existing gaseous glyoxal.

**Table 1. Summary of the Initial Conditions and Particle Growth During Uptake Experiments**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Nebulizer Solution, M</th>
<th>RH, %</th>
<th>Gaseous Glyoxal, ppb</th>
<th>Initial Diameter, nm</th>
<th>Final Diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SO₄²⁻ = 0.024 NH₄⁺ = 0.048 H₂O⁻ = 5 × 10⁻⁶</td>
<td>49</td>
<td>5.1</td>
<td>127.8</td>
<td>339.1</td>
</tr>
<tr>
<td>2</td>
<td>SO₄²⁻ = 0.024 NH₄⁺ = 0.048 H₂O⁻ = 5 × 10⁻⁶</td>
<td>98</td>
<td>4.9</td>
<td>201.7</td>
<td>409.1</td>
</tr>
<tr>
<td>3</td>
<td>HSO₄ = 0.033 SO₄²⁻ = 0.029 H₂O⁻ = 0.042 NH₄⁺ = 0.048</td>
<td>55</td>
<td>4.8</td>
<td>248.1</td>
<td>507.5</td>
</tr>
<tr>
<td>4</td>
<td>HSO₄ = 0.033 SO₄²⁻ = 0.029 H₂O⁻ = 0.042 NH₄⁺ = 0.048</td>
<td>98</td>
<td>3.6</td>
<td>258.1</td>
<td>478.1</td>
</tr>
<tr>
<td>5</td>
<td>HSO₄ = 0.033 SO₄²⁻ = 0.029 H₂O⁻ = 0.042 NH₄⁺ = 0.048</td>
<td>11</td>
<td>4.9</td>
<td>223.7</td>
<td>222.7</td>
</tr>
<tr>
<td>6</td>
<td>HSO₄ = 0.096 SO₂ = 0.042 H₂O⁻ = 0.130 NH₄⁺ = 0.050</td>
<td>50</td>
<td>4.5</td>
<td>289.4</td>
<td>522.6</td>
</tr>
<tr>
<td>7</td>
<td>HSO₄ = 0.096 SO₂ = 0.042 H₂O⁻ = 0.130 NH₄⁺ = 0.050</td>
<td>88</td>
<td>5.3</td>
<td>231.7</td>
<td>440.1</td>
</tr>
<tr>
<td>8</td>
<td>NaCl = 4.63 × 10⁻³ KCl = 1.14 × 10⁻³ MgCl₂ = 7.5 × 10⁻³ CaCl₂ = 1.1 × 10⁻³</td>
<td>70</td>
<td>4.9</td>
<td>248.1</td>
<td>478.1</td>
</tr>
<tr>
<td>9</td>
<td>NaN₂ = 0.038</td>
<td>60</td>
<td>5.4</td>
<td>271.4</td>
<td>426.4</td>
</tr>
<tr>
<td>10</td>
<td>NO₃⁻ = 0.060 Na⁺ = 0.038 H₂O⁻ = 0.022</td>
<td>65</td>
<td>5.1</td>
<td>272.4</td>
<td>414.4</td>
</tr>
</tbody>
</table>

Equilibrium concentrations are presented. Experiments 1 and 2 particles are produced from (NH₄)₂SO₄ solution, experiments 3–7 from (NH₄)₂SO₄ acidified with varying amounts of H₂SO₄, and experiment 10 from NaN₂ solution acidified with HNO₃.

**Initial diameter refers to the aerodynamic diameter after initial hygroscopic growth, if any, measured by the AMS.**

3. Results and Discussion

[5] A summary of the extent of particle growth for all experiments is given in Table 1. Generally particle growth was significant for most experiments regardless of the seed particle composition. Various inorganic particles were utilized, including ammonium sulfate (experiments 1 and 2), ammonium sulfate acidified with sulfuric acid to varying degrees (experiments 3–7), sea salt (experiment 8), sodium nitrate (experiment 9) and sodium nitrate acidified with nitric acid (experiment 10). In most cases, particles approximately doubled in diameter during the course of each experiment except experiment 5, which was conducted at very low relative humidity. The net organic mass uptake by the particles varied from 4.8 to 46 μg m⁻³. The net increases are significantly more than can be accounted for by glyoxal solubility based solely on Henry’s law. The concentration of a species in the aqueous fraction of particles based on Henry’s law can be given as

\[ C_p = HC_p(MW)W(1 \times 10^{-3}) \]

where \( C_p \) is the particulate phase concentration of the species of interest (μg m⁻³), \( H \) the effective Henry’s law constant (M atm⁻¹), \( C_g \) the gas phase concentration (atm), \( MW \) the molecular weight (g mol⁻¹) and \( W \) the available particle water content (μg m⁻³). If the Kelvin effect of the particle curvature is considered, \( C_p \) will be reduced from that predicted by equation (1). For a typical example relevant to this study, \( W \) was estimated at 5 μg m⁻³ or approximately 20% of a total particle mass of 25 μg m⁻³.

Substitution of this and other known parameters (\( C_g = 5 \) ppb, \( MW = 58 \) g mol⁻¹, \( H = 3.6 \times 10^{10} \) M atm⁻¹) into equation (1) results in a \( C_p \) of approximately 5.3 × 10⁻⁴ μg m⁻³. Thus, although the effective Henry’s law constant for glyoxal is rather large [Zhou and Mopper, 1990a], only a minor fraction would be present in the aqueous phase based solely on hydration.

[16] As the calculated value based on hydration is several orders of magnitude smaller than what is observed experimentally, further reaction of the hydrated glyoxal must have taken place. A mechanism for this reaction is presented
in Figure 2, which has been postulated in a previous paper [Liggio et al., 2005], involving hydration and subsequent cyclic acetal formation of compounds containing up to 3 monomer units. Larger oligomers may arise over a longer period of time. These acetal ring structures have been identified in the AMS mass spectra for the particles [Liggio et al., 2005]. However, a quantitative assessment of the relative importance of each oligomer, from the overall particle mass spectra, is not possible. This is primarily because many fragments can arise from several or all observed products, and reference spectra for these compounds are unavailable.

A common difficulty associated with chamber experiments is the particle wall losses. Because of the losses, decreases in the measured organic mass over time are not necessarily indicative of reductions in the reactive uptake. To remove the effect of particle wall losses on the observed organic growth, the ratio of organic mass to sulfate mass in the particles was determined and is given in Figure 3. This ratio is proportional to the organic mass on a per particle basis since the mass of SO$_4^{2-}$ per particle does not change over time. Particle SO$_4^{2-}$ was measured on the AMS simultaneously with the organic mass, among others, and in fact this is one of the intrinsic advantages of using the AMS for this study.

Although a doubling of diameter (Table 1) indicated that particles took up significant amounts of organic material, the full extent of glyoxal reactive uptake is only observed in Figure 3. After 1 hour, the ratio of organic to sulfate mass was approximately 2 for many experiments,
but after 4 hours the ratio increased to greater than 10 for several experiments, indicating that the particles became primarily organic in nature. Also, the growth curves presented in Figure 3 tend to show an accelerated growth at longer times as indicated by the slightly positive curvatures. These growth rates on a per particle basis are given in Table 2. The organic mass per particle is determined by multiplying the ratio in Figure 3 by the constant $SO_4^{2-}$ per particle which is derived from the AMS sulfate mass and the particle number distributions. The growth rate per particle at any given time is the slope of the curve at that time, or the numerical derivative of a fit to the uptake model described below. Accordingly the organic growth rates varied by experiment between $1.0 \times 10^{-11}$ and $2.7 \times 10^{-10}$ $\mu g$ particle$^{-1}$ min$^{-1}$, and during the course of a single experiment were accelerated by up to 54%. The observed acceleration in the rate of uptake is likely a result of the increasing surface area available as the particles grow, as discussed further below. Also shown in Table 2 are the average growth rates in the geometric diameter of the particles determined from the DMA data (nm min$^{-1}$). Growth rates of the particles determined from the DMA

Figure 3. Ratio of organic mass to sulfate mass as a function of time for selected experiments, as determined by the AMS.
reaction can then be expressed as

$$k = \frac{a g}{C_{eq} N_p}$$

where $a$ is the particle radius, $g$ is the gas phase concentration far away, and $C_{eq}$ is the gas phase concentration at equilibrium.

The overall second-order rate of reaction can then be expressed as $k_{net}$ multiplied by the particle number density ($N_p$) or

$$\frac{dC_{org}}{dt} = \gamma a^2 \langle c \rangle C_g N_p = k_b C_g N_p,$$  

where the rate of gas phase loss is equal to the rate of change of the particulate organic concentration ($C_{org}$). $C_g$ is the gas phase concentration derived by assuming that $C_{eq} \ll C_{eq}$. The rate of change of organic mass on a per particle basis, $m_{org}$, is obtained by dividing equation (3) by $N_p$ and incorporating a heterogeneous mass factor, $F_h$, that accounts for the increase in organic mass as it reacts heterogeneously from the reactant (glyoxal) to form particulate phase organic material. The nature of this mass factor will be discussed later. Hence

$$\frac{dm_{org}}{dt} = \gamma a^2 \langle c \rangle C_g F_h,$$  

where $\gamma$ is the uptake coefficient, a measure of the reactive uptake of glyoxal including all inherent chemical reactions as a whole can be determined in the form of an uptake coefficient ($\gamma$). On the basis of kinetic theory of gasses, the net rate of transfer ($F_{net}$) of gas molecules in and out of a given particle can be derived by considering the gas collision rate with a stationary surface, and the particle surface area. It can be expressed as

$$\Phi_{net} = \Phi_{in} - \Phi_{out} = \gamma \pi a^2 \langle c \rangle (C_{eq} - C_g),$$  

where $\gamma$ is the uptake coefficient, $a$ the particle radius and $\langle c \rangle$ the mean molecular speed of the gas given by $\frac{\sqrt{8RT}}{\pi MW}$, $C_g$, and $C_{eq}$ represent the gas phase concentration far away, and in equilibrium with the particle surface, respectively. The overall second-order rate of reaction can then be expressed as $k_{net}$ multiplied by the particle number density ($N_p$) or

$$\frac{dC_{org}}{dt} = \gamma a^2 \langle c \rangle C_g N_p = k_b C_g N_p,$$  

where the rate of gas phase loss is equal to the rate of change of the particulate organic concentration ($C_{org}$). $C_g$ is the gas phase concentration derived by assuming that $C_{eq} \ll C_{eq}$. The rate of change of organic mass on a per particle basis, $m_{org}$, is obtained by dividing equation (3) by $N_p$ and incorporating a heterogeneous mass factor, $F_h$, that accounts for the increase in organic mass as it reacts heterogeneously from the reactant (glyoxal) to form particulate phase organic material. The nature of this mass factor will be discussed later. Hence

$$\frac{dm_{org}}{dt} = \gamma a^2 \langle c \rangle C_g F_h.$$  

In these experiments the organic mass loading ($\mu g_{org} m^{-3}$) is measured as a function of time with the AMS, from which the organic mass per particle is calculated. The uptake coefficient is determined by fitting the experimental data to a theoretical model, also describing the increase in organic mass per particle ($m_{org}$). In the current simple model a spherical inorganic particle with initial radius $a_o$ and volume $V_o$ is exposed to gas phase glyoxal and grows to a radius of $a$ and volume $V$ (Figure 4). For this analysis it is assumed that the uptake is irreversible and that the aerosol is monodisperse. The difference in volume (growth) can be related to the additional organic mass added, through the density of the organic mass by

$$a = \left( \frac{3 m_{org} + a_o}{4 \pi \rho} \right)^{1/3},$$  

which is substituted into equation (4) to yield a differential equation where only $m_{org}$ is time dependent,

$$\int_{m_o}^{m} \left( \frac{m_{org} + d}{m_{org}} \right)^{2/3} dm_{org} = \int_t^t k dt.$$

Figure 4. Schematic of the uptake model.

Table 2. Total Organic Growth Rates and Uptake Coefficients

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Seed Type</th>
<th>RH, %</th>
<th>Particle pH</th>
<th>Mean Diameter Growth Rate, $\mu m$ min$^{-1}$</th>
<th>Mass Growth Rate Range, $\mu g$ particle$^{-1}$ $\times 10^{11}$</th>
<th>Mean Mass Growth Rate, $\mu g$ particle$^{-1}$ $\times 10^{11}$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>49</td>
<td>&lt;6</td>
<td>0.37</td>
<td>5.3–6.8</td>
<td>6.0</td>
<td>2.6 $\times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>98</td>
<td>6</td>
<td>0.37</td>
<td>4.3–5.7</td>
<td>5.0</td>
<td>2.2 $\times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>(NH$_4$)$_2$SO$_4$/H$_2$SO$_4$</td>
<td>55</td>
<td>-0.73</td>
<td>0.33</td>
<td>11.3–15.0</td>
<td>13.1</td>
<td>2.9 $\times 10^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>(NH$_4$)$_2$SO$_4$/H$_2$SO$_4$</td>
<td>98</td>
<td>-0.48</td>
<td>0.90</td>
<td>13.4–20.7</td>
<td>16.9</td>
<td>7.3 $\times 10^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>(NH$_4$)$_2$SO$_4$/H$_2$SO$_4$</td>
<td>11</td>
<td>-1.3</td>
<td>0.10</td>
<td>1.03–1.1</td>
<td>1.05</td>
<td>8.0 $\times 10^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>(NH$_4$)$_2$SO$_4$/H$_2$SO$_4$</td>
<td>50</td>
<td>-0.91</td>
<td>0.63</td>
<td>17.3–22.4</td>
<td>19.8</td>
<td>5.0 $\times 10^{-3}$</td>
</tr>
<tr>
<td>7</td>
<td>(NH$_4$)$_2$SO$_4$/H$_2$SO$_4$</td>
<td>88</td>
<td>-0.44</td>
<td>0.83</td>
<td>20.3–26.1</td>
<td>23.1</td>
<td>4.8 $\times 10^{-3}$</td>
</tr>
<tr>
<td>8</td>
<td>NaN$_2$</td>
<td>60</td>
<td>7</td>
<td>1.3</td>
<td>8.1–8.8</td>
<td>8.5</td>
<td>2.3 $\times 10^{-3}$</td>
</tr>
<tr>
<td>9</td>
<td>NaN$_2$/HNO$_3$</td>
<td>65</td>
<td>-0.71</td>
<td>1.0</td>
<td>19.1–26.1</td>
<td>22.5</td>
<td>6.6 $\times 10^{-3}$</td>
</tr>
</tbody>
</table>

$^a$Growth rates and uptake coefficients for experiment 8 are indeterminable because of the inability of the AMS to quantify the seed mass (~NaCl) under the current experimental conditions.

$^b$Particle pH is approximate value calculated with the Aerosol Inorganic model (AIM). Particle pH for experiment 1 could not be calculated with the AIM model because of formation of solids in the model. Assuming that a very small fraction of water exists, the pH of this fraction is likely less than that of experiment 2.

$^c$Numbers are determined from DMA data, using mean initial and final geometric diameters.

$^d$Numbers are determined from AMS data, using mean of the dynamic growth rates.

geometric diameters, and assuming a density of 1.3 g cm$^{-3}$, compare favorably to the organic growth rates determined from the AMS data.

3.1. Uptake Model

[13] A measure of the reactive uptake of glyoxal including all inherent chemical reactions as a whole can be determined in the form of an uptake coefficient ($\gamma$). On the basis of kinetic theory of gasses, the net rate of transfer ($F_{net}$) of gas molecules in and out of a given particle can be derived by considering the gas collision rate with a stationary surface, and the particle surface area. It can be expressed as

$$\Phi_{net} = \Phi_{in} - \Phi_{out} = \gamma \pi a^2 \langle c \rangle (C_{eq} - C_g),$$  

where $\gamma$ is the uptake coefficient, $a$ the particle radius and $\langle c \rangle$ the mean molecular speed of the gas given by $\frac{\sqrt{8RT}}{\pi MW}$, $C_g$, and $C_{eq}$ represent the gas phase concentration far away, and in equilibrium with the particle surface, respectively. The overall second-order rate of reaction can then be expressed as $k_{net}$ multiplied by the particle number density ($N_p$) or

$$\frac{dC_{org}}{dt} = \gamma \pi a^2 \langle c \rangle C_g N_p = k_b C_g N_p,$$  

where the rate of gas phase loss is equal to the rate of change of the particulate organic concentration ($C_{org}$). $C_g$ is the gas phase concentration derived by assuming that $C_{eq} \ll C_{eq}$. The rate of change of organic mass on a per particle basis, $m_{org}$, is obtained by dividing equation (3) by $N_p$ and incorporating a heterogeneous mass factor, $F_h$, that accounts for the increase in organic mass as it reacts heterogeneously from the reactant (glyoxal) to form particulate phase organic material. The nature of this mass factor will be discussed later. Hence

$$\frac{dm_{org}}{dt} = \gamma \pi a^2 \langle c \rangle C_g F_h.$$  

In these experiments the organic mass loading ($\mu g_{org} m^{-3}$) is measured as a function of time with the AMS, from which the organic mass per particle is calculated. The uptake coefficient is determined by fitting the experimental data to a theoretical model, also describing the increase in organic mass per particle ($m_{org}$). In the current simple model a spherical inorganic particle with initial radius $a_o$ and volume $V_o$ is exposed to gas phase glyoxal and grows to a radius of $a$ and volume $V$ (Figure 4). For this analysis it is assumed that the uptake is irreversible and that the aerosol is monodisperse. The difference in volume (growth) can be related to the additional organic mass added, through the density of the organic mass by

$$\int \frac{\left( \frac{4\pi a^3 - 4\pi a_o^3}{3} \right) \rho}{m_{org}} = \int_k dt,$$  

where $\rho$ is the density of the organic mass. Rearrangement of equation (5) gives a relationship between the radius of the particle and the added organic mass given by

$$a = \left( \frac{3m_{org} + a_o}{4 \pi \rho} \right)^{1/3},$$  

which is substituted into equation (4) to yield a differential equation where only $m_{org}$ is time dependent,

$$\int_{m_o}^{m} \left( \frac{m_{org} + d}{m_{org}} \right)^{2/3} dm_{org} = \int_t^t k dt.$$  

Figure 4. Schematic of the uptake model.
where

\[ k = \gamma \pi C_g \langle c \rangle F_h \]

\[ b = \frac{3}{4\pi \rho} \quad d = a_0^3 \]

Since particles were introduced into the chamber over a prolonged period of time, some particles must have experienced more growth than others during the filling process. Consequently the limits of integration were chosen so as to only include data collected after the particle filling period was complete. Therefore the left side of equation (7) was integrated from the mass at the end of filling \((m_0)\) to mass \(m\), and the right side integrated from the end of the filling period \((t_0)\) to some time \(t\). The constants \(m_0\) and \(t_0\) were taken directly from the experimental data. Integration of equation (7) with the above limits yields a relation for the organic mass as a function of time,

\[ m_{\text{org}} = \left( \frac{bk(t - t_0) + 3(bm_0 + d)^{1/3}}{3b^{1/3}} \right) - \frac{d}{b} \]  \( (8) \)

### 3.2. Determination of \( \gamma \)

[14] A plot of \( m_{\text{org}} \) as a function of time for selected experiments is presented in Figure 5. Equation (8) is fit to this experimental data and is also presented in Figure 5. The uptake coefficients are obtained from the parameter \( k \) where \( C_g \) and \( \langle c \rangle \) are known. The heterogeneous mass factor, \( F_h \), was chosen using the following reasoning. A change in mass occurs for the specific case of a heterogeneous reaction of glyoxal, by incorporation of 2 water molecules into the molecular formula of the final organic product through the hydration reactions (Figure 2). The organic mass measured by the AMS includes the additional mass of these water molecules. In this case \( F_h \) is larger than 1.0 and can be obtained by taking the ratio of the molecular weight of the final product \((C_2H_2O_2)_n(H_2O)_2\) \( n = 1, 2, 3 \); to the molecular weight of \( n \) units of glyoxal monomer: \( n(C_2H_2O_2) \) \( n = 1, 2, 3 \). The corresponding values of the heterogeneous correction factors, \( F_h \) \( (n) \) would be: 1.62 \( (n = 1) \), 1.31 \( (n = 2) \) and 1.21 \( (n = 3) \). The value \( n = 1 \) corresponds to the formation of the gemdiol in solution (B in Figure 2), which has previously been argued to be a minor component of the mix, as is likely the case for product C. In this study, since we cannot determine the relative proportions of the different products (B, C, D, E, F), we have used a value of \( F_h = 1.26 \) (product D) and \( n = 3 \) (product E), for the determination of the reactive uptake coefficients. The formation of higher oligomers \((n > 3)\) is possible, although the value of \( F_h \) only drops to 1.10 \( (n = 6) \). The best fit for these experiments was obtained by fixing the constants \( b \) and \( d \), with the density of the organic mass estimated as 1.3 g cm\(^{-3}\) and the initial seed radius \( (a_0) \) determined experimentally from the mean of the size distribution. The error associated with the correction factor is expected to be considerably smaller than the uncertainties related to the organic mass determination via the AMS. These include uncertainties with respect to the particle focusing efficiency of the AMS for ammonium sulfate, and the ionization efficiency of the organic mass in the absence of an authentic reference standard. These uncertainties are likely significantly larger than the uncertainty in the chosen value of \( F_h \) which is expected to be less than 10%. The relative uncertainty in the \( k \) parameter derived from the fitting procedure (from which \( \gamma \) is calculated) ranged from 1.8 to 10%. The gas phase glyoxal measurement has an estimated
accuracy of 20%, which likely contributes most significantly to the overall uncertainty of the uptake coefficients. A conservative estimate of the overall uncertainty in the calculated uptake coefficients is approximately 40%. Uptake coefficients derived in this manner including the above corrections are presented in Table 2.

[15] An alternative approach in calculating the uptake coefficients is to fit the experimental data to equation (8), substitute the fit parameters back into this equation, and numerically differentiate the result. The result is the analytical expression

$$\frac{dm_{org}}{dt} = 3bk \left( \frac{b(t - t_0) + 3(bm_0 + d)^{1/3}}{3b^{1/3}} \right)^2.$$  (9)

The numerical value for this relation at a given time is set equal to equation (4), from which substitution of the experimental particle radius at each time step, and other constants from equation (4) gives the uptake coefficient as a function of time. The results of this approach are presented in Figure 6 for several experiments and verify that the uptake coefficient is roughly constant over time. The uptake coefficient calculated by this approach and averaged over time, is in good agreement with those calculated directly from the fit. The relative standard deviation between the calculation methods ranged from 0.83 to 8.1%.

[16] A slight decrease in $\gamma$ over time can be observed for some experiments. This decrease is statistically significant in some cases, and is in the range of $-10\%$ to $-15\%$ per hour. One might expect a decrease in $\gamma$ over time since the particles transform from primarily inorganic to organic composition over the course of the experiment. The relatively small change in $\gamma$ during this transformation likely indicates that the uptake is largely determined by the presence of water. This argument would be consistent with the proposed first step of the heterogeneous reaction, solvation. The similarity of the absolute values of $\gamma$, and those measured in water (37), also supports this argument.

[17] Calculated uptake coefficients (Table 2) varied from $8.0 \times 10^{-4}$ to $7.3 \times 10^{-3}$, and are in general agreement with uptake coefficients determined for glyoxal on aqueous droplets ($\gamma \sim 10^{-3}$) using a droplet train technique [Schweitzer et al., 1998]. No other data are available regarding the uptake of glyoxal. However, the range of observed $\gamma$ is also consistent with those for other carbonyl compounds reported in literature, on a variety of substrates. The formaldehyde/sulfuric acid system has been the most common system studied to date, with uptake coefficients measured on sulfuric acid films ($\gamma \sim 2 \times 10^{-3}$) [Iraci and Tolbert, 1997], droplets ($\gamma = 2.7 \times 10^{-3} - 2.7 \times 10^{-2}$) [Jayne et al., 1996], and bulk solution ($\gamma = 1 \times 10^{-2} - 8 \times 10^{-3}$) [Tolbert et al., 1993]. Uptake coefficients for other carbonyls including acetaldehyde, acetone and propionaldehyde, on mineral oxide particles have also been reported ($\gamma \sim 10^{-4} - 10^{-6}$) [Li et al., 2001] and are significantly lower. Not only are uptake coefficients in this work in reasonable agreement with $\gamma$ of similar systems, but also consistent with the presumption in the literature that heterogeneous reactions must occur to result in the observed uptake parameters.

3.3. Effect of Acidity and Humidity

[18] The approximate pH of the particles has been calculated using an aerosol inorganic model (AIM) [Clegg et al., 1998]. Given that initial molar ratios and RH conditions were used as input into the model, the resultant pH values likely only represent particles at the beginning of experiments, and do not take into account changes in the hygroscopicity or organic content as the particles grow. However, modeled pH values do serve as a relative measure of the acidity of particles between experiments. The results of the present work indicate that the reactive uptake of glyoxal may be acid catalyzed in some instances. In general, $\gamma$ increased by a factor of $\sim 2-3$ when an
acidiﬁed seed was used compared to nonacidiﬁed seeds under similar conditions (Table 2: experiments 1 versus 6, experiments 2 versus 4 or 7, and experiments 9 versus 10). This implies that the nature of the acid is likely unimportant as only acidic protons are necessary, consistent with the proposed heterogeneous reaction mechanism. The effect of particle acidity is also evident in the particle growth rates presented in Table 2 and the organic to seed ratios in Figure 3. Experiments using non acidiﬁed (NH₄)₂SO₄ particles (experiments 1 and 2) exhibited growth rates of 5 × 6 × 10⁻¹¹ μg particle⁻¹ min⁻¹ compared to 13.1 – 23.1 × 10⁻¹¹ μg particle⁻¹ min⁻¹ for acidiﬁed seed particles. A similar effect is observed for acidiﬁed and nonacidiﬁed NaNO₃ particles (8.5 × 10⁻¹¹ and 22.5 × 10⁻¹¹ μg particle⁻¹ min⁻¹, respectively). Recent publications have also suggested that reactive uptake of carbonyls is likely acid catalyzed [Jang et al., 2003; Jang and Kamens, 2001a].

[19] Although the presence of acid increases the rate of heterogeneous reaction, acidic aerosols were not necessary for the uptake to occur, and even with a decrease of 8 pH units, uptake coefﬁcients and growth rates increased at most by a factor of only 3. Significant growth was observed on nonacidiﬁed (NH₄)₂SO₄, NaCl and NaNO₃ particles (experiments 1, 2, and 9) with reasonably high growth rates and uptake coefﬁcients. This is consistent with uptake efﬁciencies for glyoxal on aqueous droplets, which have been shown to have negligible pH dependence at temperatures approaching room temperature [Schweitzer et al., 1998] and with recent studies which found that polymerization in aerosols does not require acid catalysis [Kalberer et al., 2004].

[20] Other deviations from an acid catalyzed model have also been noted in this study. Growth rates and uptake coefﬁcients for experiments 4 and 7 (pH = –0.48 and –0.44) are unexpectedly larger or similar to those for experiments 3 and 6 (pH = –0.73 and –0.91) even though less acidic particles were utilized. This may be a result of potentially unstable reaction products under highly acidic conditions, whose decomposition may compete with formation reactions. Studies of the depolymerization of glyoxal dimers has shown that a reverse process is in fact acid catalyzed with a rate constant that increases substantially in solutions with a pH below 2 [Fratzke and Reilly, 1986]. Slightly less acidic particles may also promote the formation of some more prevalent oligomers while reducing the rate of formation for others.

[21] Experiments at low relative humidities are expected to produce particles with low pH, and thus potentially result in signiﬁcant reactive uptake in an acid catalyzed model. However the reactive uptake of glyoxal for such an experiment (RH 11%, experiment 5) was signiﬁcantly less than all other experiments resulting in no signiﬁcant increase in particle diameter. The resultant uptake coefﬁcient (8.0 × 10⁻⁵) and growth rate (1.05 × 10⁻¹¹ μg particle⁻¹ min⁻¹) were also considerably less than all others. In addition, the particles produced during the experiment contained an organic fraction that constituted less than 10% of the total particle mass. This may be explained by noting that at very low RH, sufﬁciently below the deliquescent point, the aqueous content of the particles as well as the amount of hydrated glyoxal is likely very small. As a result, fast heterogeneous reactions can potentially deplete the available aqueous layer and completely consume the gem-diol precursors. Without the necessary precursors, further reactive uptake of glyoxal is halted as observed in Figure 3. Re-establishment of an aqueous equilibrium with the particles would result in the additional uptake of water and glyoxal, which in turn would allow the heterogeneous reactions to continue. However, it is likely that the initial reactive uptake producing a somewhat hydrophobic mass signiﬁcantly changed the hygroscopic nature of the particles, thus preventing further water uptake from occurring. This may have implications for reactive uptake of glyoxal on ambient urban particles that are primarily hydrophobic.

[22] The effect of particle acidity is also evident in the time evolution of many of the mass fragments observed in particle mass spectra. The evolution of several of these ions normalized to a SO₄²⁻ fragment ion (m/z 48) is given in Figure 7. Normalization removes the effect of particle wall losses and results in a signal that is proportional to the concentration of the species associated with a given fragment on a per particle basis. With the exception of experiment 5, the evolution of fragments (m/z 117 and 135) known to arise predominantly from glyoxal oligomers [Liggio et al., 2005], was slowed upon RH increases and hence pH. This effect in Figure 7 is most prevalent, when comparing sets of experiments with the same initial particle composition but conducted at different RH (experiments 1 versus 2, experiments 3 versus 4, and experiments 6 versus 7). Since the time evolution of oligomer fragments is proportional to the oligomerization rate, a delay in this rate may also be an indication of acid catalysis given that dilution at higher RH reduces the particle acidity. Conversely, dilution may reduce the concentration of the gem-diol precursor, and hence also slow the rate of oligomerization. This is only possible where gas phase diffusion of glyoxal to the particle surface is a rate-limiting step in the overall process, since gas-particle equilibrium would require the hydrated glyoxal concentration to remain constant.

[23] Which of the above scenarios is operating depends upon the likelihood that gas phase diffusion of glyoxal is rate limiting. This can be evaluated by determining whether these experiments were performed in the diffusion or gas kinetic limit. According to the add-as resistance model [Molina et al., 1996], the condition for a diffusion limited process is that 3a/λ ≥ 4/α, where a represents the particle radius, λ the gas mean free path and α the mass accommodation coefﬁcient. The mean free path (λ) is given by 3Dg/(c) where Dg is the diffusion constant for glyoxal in air, estimated as 0.3 cm² s⁻¹, intermediate to Dg in H₂O(8) and He which have been calculated elsewhere [Schweitzer et al., 1998]. The mean free path is calculated to be approximately 2.73 × 10⁻⁷ m and an accommodation coefficient (c) of 0.023 for glyoxal on aqueous droplets [Schweitzer et al., 1998] is assumed to be similar to that in the present experiments. Substitution of these parameters as well as a typical particle radius of 230 nm into the above inequality results in 3a/λ = 2.5 and 4/α = 173.9. Consequently, the process occurring here is likely not diffusion limited, as extremely large particles are required in this system to satisfy the above inequality. Therefore it is more likely that a reduction in particle acidity caused by an increase in the
RH produced the observed decline of the fragment evolution and oligomerization rate.

However, an acid catalysis effect in Figure 7 (experiment 1 versus experiment 2, experiment 3 versus experiment 4, and experiment 6 versus experiment 7) for a fragment thought to arise primarily from the hydrated glyoxal (m/z 47), is not clear. In this case an increase in RH has either the opposite or no effect on the fragment evolution. This is an indication that the formation of hydrated glyoxal is more dependent on the aqueous content than the particle acidity. In addition, the fragment evolution for masses that can potentially arise from several oligomers or the hydrated monomer (m/z 59 – Figure 7) is not slowed as significantly upon increasing the RH. Consequently, it is likely that several different oligomers are formed, some by reactions that are more subject to acid catalysis than others. As a result, the magnitude of the reactive uptake of glyoxal may not differ tremendously between highly acidic and nonacidic particles, while the relative contribution of each oligomer may differ significantly.

3.4. Atmospheric Implications

Given that several of these experiments were performed under conditions similar to the real atmosphere (a low initial aerosol seed mass loading, 50% relative humidity and ppbv levels of glyoxal), it is reasonable to expect these reactions to occur in ambient aerosols as a means of uptake of glyoxal and other carbonyls. The range of particle acidities utilized in these experiments was also consistent with pH of ambient aerosols, which have been measured as low as −2.4 [Li et al., 1997]. Currently, direct evidence of a polymerization reaction for glyoxal in ambient aerosols has not been confirmed on the basis of structural identification of products. Indirectly, however, extraction and DNPH derivatization of ambient particulate material has revealed such a process likely occurred (J. Liggio and R. McLaren, Observations of volatile secondary organic carbonyls in atmospheric particulates, manuscript in preparation, 2005, hereinafter referred to as Liggio and McLaren, manuscript in preparation, 2005). During the extraction procedure mild heating caused polymeric structures to revert to monomeric starting material (glyoxal). The DNPH derivatization also served to shift equilibrium toward the free form of glyoxal. Detection of this free glyoxal can explain the higher than expected levels found in ambient particulate matter [Liggio and McLaren, 2003]. The extremely slow kinetics associated with the extraction and derivatization of ambient material also indicated that a thermal decomposition of some polymer likely occurred. This is principally because
Table 3. Estimation of Heterogeneous Glyoxal Reaction Rate Constants and Associated Lifetime Compared With Known Gaseous Loss Processes

<table>
<thead>
<tr>
<th>Environment</th>
<th>Surface Area, $a$ $\mu$m² cm⁻¹</th>
<th>Parameter $k$, $b$ s⁻¹</th>
<th>$\tau_{het}$, $c$ min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural</td>
<td>$7.9 \times 10^2$</td>
<td>$1.9 \times 10^{-4}$</td>
<td>89</td>
</tr>
<tr>
<td>Remote</td>
<td>$1.1 \times 10^2$</td>
<td>$2.7 \times 10^{-4}$</td>
<td>61</td>
</tr>
<tr>
<td>Free troposphere</td>
<td>$2.4 \times 10^2$</td>
<td>$5.8 \times 10^{-5}$</td>
<td>287</td>
</tr>
<tr>
<td>Urban</td>
<td>$1.4 \times 10^2$</td>
<td>$3.4 \times 10^{-3}$</td>
<td>5</td>
</tr>
<tr>
<td>Reaction with OH$^d$</td>
<td></td>
<td>$5.5 \times 10^{-5}$</td>
<td>300</td>
</tr>
<tr>
<td>Photolysis$^e$</td>
<td></td>
<td>$7.88 \times 10^{-5}$</td>
<td>211</td>
</tr>
<tr>
<td>Total gas phase loss$^f$</td>
<td></td>
<td>$1.34 \times 10^{-4}$</td>
<td>125</td>
</tr>
</tbody>
</table>

$^a$Area is adapted from typical surface area distributions (18).
$^b$Parameter $k$ is given as pseudo first order.
$^c$Lifetime is given as the inverse of first-order rate constant.
$^d$In this case, it is assumed that [OH] = $5 \times 10^9$ molecules cm⁻³ and $k_{OH} = 1.1 \times 10^{-11}$ cm³ molecules⁻¹ s⁻¹ [Atkinson et al., 1989].
$^e$Numbers are $j$ value for midday maximum [Jenkin et al., 1996].
$^f$Total is the sum of photolysis and OH reaction rate constants.

an extraction time on the order of days had been necessary for ambient aerosol samples, as compared to an hour for the derivatization of aqueous glyoxal in bulk solution or adsorbed to the surface of a sampling filter. Aspects of these experiments are described elsewhere (Liggio and McLaren, manuscript in preparation, 2005).

The derived uptake coefficients can be used to perform simple calculations as an estimate of the significance of glyoxal uptake to ambient particulate matter. The importance of this uptake as a gas phase glyoxal removal process is evaluated against other gas phase loss mechanisms by comparing the associated lifetimes. Results of this analysis are presented in Table 3. Pseudo first-order rate constants for the heterogeneous reaction of glyoxal are determined by substitution of the appropriate parameters into the relation for the rate constant given in equation (3).

Table 4. Estimation of Ambient Organic Mass That Can Be Formed From Reactive Uptake of Glyoxal

<table>
<thead>
<tr>
<th>Environment</th>
<th>Gaseous Glyoxal [ $f$ ] ppb</th>
<th>Organic Mass Formation Rate, $h$ $\mu$g m⁻³ s⁻¹</th>
<th>Potential Organic Mass Produced, $\mu$g m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural</td>
<td>0.02</td>
<td>$8.92 \times 10^{-6}$</td>
<td>0.032, 0.064, 0.257</td>
</tr>
<tr>
<td>Remote</td>
<td>0.01</td>
<td>$6.50 \times 10^{-6}$</td>
<td>0.023, 0.047, 0.187</td>
</tr>
<tr>
<td>Free troposphere</td>
<td>0.01</td>
<td>$1.38 \times 10^{-6}$</td>
<td>0.005, 0.010, 0.040</td>
</tr>
<tr>
<td>Urban</td>
<td>0.1</td>
<td>$7.98 \times 10^{-4}$</td>
<td>2.87, 5.74, 22.97</td>
</tr>
</tbody>
</table>

$^f$Numbers are typical measured values.
$^h$Rate is calculated as $k$ (Figure 5) $\times$ [glyoxal].

estimation of ambient organic mass that can be formed from reactive uptake of glyoxal

However, is significantly shorter than the overall gas phase glyoxal lifetime. These results indicate that even under relatively clean conditions, heterogeneous glyoxal loss rates are comparable to loss rates due to other gas phase processes, and are significantly faster in more polluted regions. If the heterogeneous reactions are irreversible as implied in these experiments, then a net decrease in the production of HOx from glyoxal and potentially many other carbonyl compounds may result. Given that formaldehyde has been estimated to contribute 25–30% of the total radical production at midday [Lee et al., 1998], and glyoxal 10–15% [Aiello, 2003], the heterogeneous loss to particle of these aldehydes implies that this reduction in HOx may be significant.

The uptake of glyoxal may also be a significant source of secondary organic particulate matter. To emphasize this possibility, the rate of formation of particulate organic mass resulting from the reactive uptake of glyoxal was estimated, and is presented in Table 4. The rates were calculated from the pseudo first-order rate constants in Table 3 and typical gas phase glyoxal measurements for those areas [Cerqueira et al., 2003; Destaillats et al., 2002; Grosjean et al., 2002; Grossmann et al., 2003; Kleinman et al., 1994; Lee et al., 1995, 1998; Spaulding et al., 2002, 2003; Zhou and Mopper, 1990b]. The results of the calculations show that formation rates vary appreciably (1.4 $\times$ 10⁻⁶ – 8.0 $\times$ 10⁻⁷ $\mu$g m⁻³ s⁻¹) with location, and that large amounts of organic mass can be produced in a short time. Under rural, remote and free tropospheric conditions 5–250 ng m⁻³ of particulate phase glyoxal can be produced in eight hours, while urban conditions can produce an organic mass that exceeds that in other areas by up to an order of magnitude (2.9–23.0 $\mu$g m⁻³). Such a large organic mass associated with one compound in urban

Table 3. Estimation of Heterogeneous Glyoxal Reaction Rate Constants and Associated Lifetime Compared With Known Gaseous Loss Processes

<table>
<thead>
<tr>
<th>Environment</th>
<th>Surface Area, $a$ $\mu$m² cm⁻¹</th>
<th>Parameter $k$, $b$ s⁻¹</th>
<th>$\tau_{het}$, $c$ min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural</td>
<td>$7.9 \times 10^2$</td>
<td>$1.9 \times 10^{-4}$</td>
<td>89</td>
</tr>
<tr>
<td>Remote</td>
<td>$1.1 \times 10^2$</td>
<td>$2.7 \times 10^{-4}$</td>
<td>61</td>
</tr>
<tr>
<td>Free troposphere</td>
<td>$2.4 \times 10^2$</td>
<td>$5.8 \times 10^{-5}$</td>
<td>287</td>
</tr>
<tr>
<td>Urban</td>
<td>$1.4 \times 10^2$</td>
<td>$3.4 \times 10^{-3}$</td>
<td>5</td>
</tr>
<tr>
<td>Reaction with OH$^d$</td>
<td></td>
<td>$5.5 \times 10^{-5}$</td>
<td>300</td>
</tr>
<tr>
<td>Photolysis$^e$</td>
<td></td>
<td>$7.88 \times 10^{-5}$</td>
<td>211</td>
</tr>
<tr>
<td>Total gas phase loss$^f$</td>
<td></td>
<td>$1.34 \times 10^{-4}$</td>
<td>125</td>
</tr>
</tbody>
</table>

$^a$Area is adapted from typical surface area distributions (18).
$^b$Parameter $k$ is given as pseudo first order.
$^c$Lifetime is given as the inverse of first-order rate constant.
$^d$In this case, it is assumed that [OH] = $5 \times 10^9$ molecules cm⁻³ and $k_{OH} = 1.1 \times 10^{-11}$ cm³ molecules⁻¹ s⁻¹ [Atkinson et al., 1989].
$^e$Numbers are $j$ value for midday maximum [Jenkin et al., 1996].
$^f$Total is the sum of photolysis and OH reaction rate constants.

an extraction time on the order of days had been necessary for ambient aerosol samples, as compared to an hour for the derivatization of aqueous glyoxal in bulk solution or adsorbed to the surface of a sampling filter. Aspects of these experiments are described elsewhere (Liggio and McLaren, manuscript in preparation, 2005).

The derived uptake coefficients can be used to perform simple calculations as an estimate of the significance of glyoxal uptake to ambient particulate matter. The importance of this uptake as a gas phase glyoxal removal process is evaluated against other gas phase loss mechanisms by comparing the associated lifetimes. Results of this analysis are presented in Table 3. Pseudo first-order rate constants for the heterogeneous reaction of glyoxal are determined by substitution of the appropriate parameters into the relation for the rate constant given in equation (3).

Table 4. Estimation of Ambient Organic Mass That Can Be Formed From Reactive Uptake of Glyoxal

<table>
<thead>
<tr>
<th>Environment</th>
<th>Gaseous Glyoxal [ $f$ ] ppb</th>
<th>Organic Mass Formation Rate, $h$ $\mu$g m⁻³ s⁻¹</th>
<th>Potential Organic Mass Produced, $\mu$g m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural</td>
<td>0.02</td>
<td>$8.92 \times 10^{-6}$</td>
<td>0.032, 0.064, 0.257</td>
</tr>
<tr>
<td>Remote</td>
<td>0.01</td>
<td>$6.50 \times 10^{-6}$</td>
<td>0.023, 0.047, 0.187</td>
</tr>
<tr>
<td>Free troposphere</td>
<td>0.01</td>
<td>$1.38 \times 10^{-6}$</td>
<td>0.005, 0.010, 0.040</td>
</tr>
<tr>
<td>Urban</td>
<td>0.1</td>
<td>$7.98 \times 10^{-4}$</td>
<td>2.87, 5.74, 22.97</td>
</tr>
</tbody>
</table>

$^f$Numbers are typical measured values.
$^h$Rate is calculated as $k$ (Figure 5) $\times$ [glyoxal].
areas is unlikely. However, the true uptake coefficient for urban particles is likely considerably less if a significant fraction of those aerosols contain soot or other nonhygroscopic mass as evidenced by the reduced uptake of experiment 5. In addition, the gas phase glyoxal concentration in an urban plume may decrease dramatically as it is transported away from a source. Hence the rate of glyoxal uptake will also decrease sharply over the same eight hour period, reducing the above urban estimate. Estimates for other atmospheric conditions are not unreasonable for a single compound, and the few measurements of ambient particulate glyoxal that exist are somewhat consistent with the estimates provided here.

[28] Particulate glyoxal has been measured in rural/biogenic areas to be as low as 1–5 ng m\(^{-3}\) [Liggin and McLaren, 2003] and as high as 150 ng m\(^{-3}\) [Matsunaga et al., 2003]. Particulate glyoxal in marine (≈1.8 ng m\(^{-3}\)) and polar environments (0.003–2.29 ng m\(^{-3}\)) has also been measured [Kawamura, 1993; Kawamura et al., 1996]. To date, only a single urban measurement of particulate glyoxal appears in the literature [Kawamura, 1993]. This measurement, from approximately 30 km west of Tokyo, at a level of 46 ng m\(^{-3}\) is significantly less than the above estimates for urban areas. Given the numerous carbonyl species present in the atmosphere and the many possible heterogeneous reactions, uptake of carbonyls to aerosols may be a significant contributor to SOA and demands further study.

[29] Acknowledgments. We would like to acknowledge the National Science and Engineering Research Council and the Meteorological Service of Canada for funding. We thank Kathy Hayden and Richard Leaitch for their technical expertise in operation of the AMS. We thank Michael Mozurkewich and Tak Wai Chan for use of, and technical support with, the DMA/CNC system.

References


Kawamura, K., H. Kasukabe, and L. A. Barrie (1996), Source and reaction pathways of dicarboxylic acids, ketoacids and dicarboxyls in arctic aero-
sols: One year of observations, Atmos. Environ., 30, 1709–1722.

Kleinman, L., et al. (1994), Ozone formation at a rural site in the south-


Noziere, B., and D. D. Riemer (2003), The chemical processing of gas-phase carbonyl compounds by sulfuric acid aerosols: 2,4-pentandione, *Atmos. Environ.*, 37, 841–851.


S.-M. Li, Meteorological Service of Canada, 4905 Dufferin Street, Toronto, ON, Canada M3J 1P3. (rmclaren@yorku.ca)