

## Analysis of photochemical and dark glyoxal uptake: Implications for SOA formation

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[1] The dependence of glyoxal uptake onto deliquesced ammonium sulfate seed aerosol was studied under photochemical (light + hydroxyl radical (OH)) and dark conditions. In this study, the chemical composition of aerosol formed from glyoxal is identical in the presence or absence of OH. In addition, there was no observed OH dependence on either glyoxal uptake or glyoxal-driven aerosol growth for this study. These findings demonstrate that, for the system used here, glyoxal uptake is not affected by the presence of OH. In combination with previous studies, this shows that the exact nature of the type of seed aerosol, in particular the presence of a coating, has a large influence on fast photochemical uptake of glyoxal. Due to the challenge of relating this seed aerosol dependence to ambient conditions, this work highlights the resulting difficulty in quantitatively including SOA formation from glyoxal in models. **Citation:** Galloway, M. M., C. L. Loza, P. S. Chhabra, A. W. H. Chan, L. D. Yee, J. H. Seinfeld, and F. N. Keutsch (2011), Analysis of photochemical and dark glyoxal uptake: Implications for SOA formation, *Geophys. Res. Lett.*, *38*, L17811, doi:10.1029/2011GL048514.

### 1. Introduction

[2] The formation of secondary organic aerosol (SOA) is traditionally explained via uptake of gas-phase species onto aerosol following vapor pressure and partitioning theory [Pankow, 1994a, 1994b; Odum *et al.*, 1996]. Recent work has shown that chemical reactions occurring within the aerosol can increase SOA yields as well as alter both chemical and optical aerosol properties [Carlton *et al.*, 2007; Ervens *et al.*, 2008; Galloway *et al.*, 2009; Nozière *et al.*, 2009; Shapiro *et al.*, 2009; Bones *et al.*, 2010]. Glyoxal has a high effective Henry's Law coefficient, which results in more efficient uptake onto aqueous aerosol droplets than expected for a small carbonyl [Ip *et al.*, 2009]. In the aerosol, glyoxal can react with other species to form acetal oligomers, imidazoles, other high molecular weight compounds, and be oxidized with OH to carboxylic acids [Carlton *et al.*, 2007; De Haan

*et al.*, 2009b; Galloway *et al.*, 2009; Tan *et al.*, 2009]. Due to this potential contribution to SOA, glyoxal has received increasing attention [Kroll *et al.*, 2005; Liggio *et al.*, 2005; Corrigan *et al.*, 2008; Galloway *et al.*, 2009; Volkamer *et al.*, 2009].

[3] Glyoxal uptake onto liquid (deliquesced) aqueous ammonium sulfate (AS) seed aerosol has been studied under dark [Kroll *et al.*, 2005; Liggio *et al.*, 2005; Galloway *et al.*, 2009] and photochemical conditions [Volkamer *et al.*, 2009]. Photochemical conditions will be defined as UV-irradiation with explicit addition of a source of gas-phase OH radicals. Galloway *et al.* [2009] showed that dark uptake is largely reversible except for minor imidazole formation. However, drying of the aerosol results in glyoxal being retained [De Haan *et al.*, 2009a]. Volkamer *et al.* [2009] studied SOA formation from acetylene (C<sub>2</sub>H<sub>2</sub>) via glyoxal in a photochemical system and dark glyoxal uptake onto different types of seed aerosol. Whereas rapid photochemical uptake was observed for pure AS, pure fulvic acid, and mixed AS/fulvic acid seed, no rapid photochemical uptake was observed in mixed AS/fulvic acid seed that also contained sulfuric or amino acids, highlighting the complex dependence of rapid photochemical uptake on seed composition. SOA yields from the fast photochemical uptake are substantially higher than from slow, dark-type uptake [Ervens and Volkamer, 2010], hence a thorough understanding of the seed dependence of fast photochemical glyoxal uptake and the chemical processes responsible for it are central for models of SOA formation.

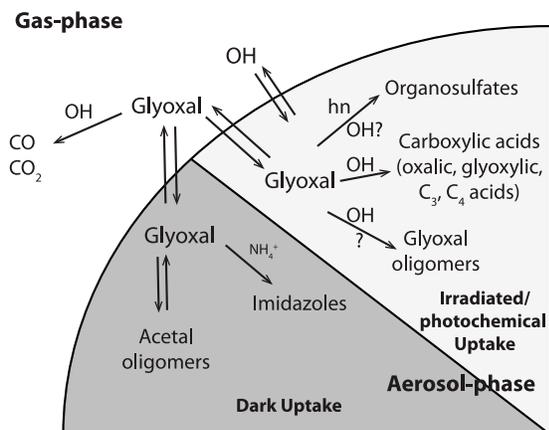
[4] In the gas-phase, OH oxidizes glyoxal to form CO, CO<sub>2</sub>, and other high volatility species that do not contribute to aerosol growth (Figure 1). Hence, the gas-phase reaction of glyoxal with OH should not form aerosol. The observed rapid photochemical glyoxal uptake strongly indicates condensed-phase reactions with OH [Volkamer *et al.*, 2009]. Carlton *et al.* [2007] observed oxalic acid production in laboratory studies of photochemical oxidation of glyoxal in bulk aqueous, cloud-processing-like systems with a source of condensed-phase OH radicals. In a related study, Tan *et al.* [2009] demonstrated that transition from cloud to aerosol-processing conditions leads to increased concentrations of larger (C<sub>3</sub>–C<sub>4</sub>) carboxylic acids. As the condensed-phase glyoxal-OH reaction produces higher molecular weight compounds, specifically carboxylic acids, any observed increase in aerosol from glyoxal and OH should be a result of carboxylic acid formation within the aerosol. The goals of the work presented here were to investigate these processes within aqueous aerosol and the extent to which photochemical glyoxal uptake affects the chemical composition of the resulting aerosol, in particular

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**Figure 1.** Simplified schematic of glyoxal reactions within aqueous AS aerosol. Glyoxal oligomers formed during photochemical uptake refers to any type of higher molecular weight compound. Whereas dark-type reaction products and kinetics have been extensively studied, photochemical reaction products have only been studied in detail for laboratory bulk samples more similar to cloud processing conditions. These studies show that condensed-phase reactions of glyoxal with OH produce carboxylic acids, leading to oxidized organic aerosol.

the presence of carboxylic acids and higher molecular weight compounds.

## 2. Experimental Methods

### 2.1. Preparation and Instrumentation

[5] Experiments were carried out in the Caltech dual 28 m<sup>3</sup> Teflon chambers, described in detail elsewhere [Cocker *et al.*, 2001; Keywood *et al.*, 2004]. The chambers were flushed with clean, humidified air for over 40 hrs before each experiment. AS seed particles (~60–80 nm diameter) were generated by atomization of 0.015 M aqueous AS using a constant rate atomizer. Methyl nitrite (CH<sub>3</sub>ONO) was used as the OH source, and was prepared following the method described by Chan *et al.* [2010], stored at liquid nitrogen temperatures, and allowed to vaporize into a 500 mL glass bulb before injection into the chamber by a dry air stream. The mixing ratio of injected CH<sub>3</sub>ONO was 1 ppm and the initial OH concentration was  $\sim 7 \times 10^7$  molec cm<sup>-3</sup>. Gas-phase glyoxal was prepared from glyoxal trimer dihydrate as described by Galloway *et al.* [2009], vaporized into a 2 L glass bulb, and injected using a dry air stream. Temperature, relative humidity (RH), O<sub>3</sub>, and NO<sub>x</sub> were continuously monitored. Aerosol size distribution, number and volume concentrations were monitored using a differential mobility analyzer (TSI 3081) coupled with a condensation particle counter (TSI 3760). All aerosol volume data are corrected for wall loss, as described by Ng *et al.* [2007]. CH<sub>3</sub>ONO was monitored via a gas chromatograph with flame ionization detector (Agilent 6890N). The Madison Laser-Induced-Phosphorescence instrument monitored gas-phase glyoxal [Huisman *et al.*, 2008].

[6] An Aerodyne HR-ToF-AMS operating in “V-mode” continuously collected real-time particle mass spectra [DeCarlo *et al.*, 2006; Canagaratna *et al.*, 2007]. Data were analyzed using a fragmentation table to separate out sulfate,

ammonium, and organic spectra and to allow for monitoring of specific mass-to-charge ratios (see auxiliary material) [Allan *et al.*, 2004].<sup>1</sup> AMS mass fragments  $m/z$  58 (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub><sup>+</sup>) and  $m/z$  105 (C<sub>3</sub>H<sub>5</sub>O<sub>4</sub><sup>+</sup>) are tracers for glyoxal and its oligomers, respectively, and have been used to monitor non-oxidative glyoxal uptake [Galloway *et al.*, 2009]. Their magnitude is only ~10% of the total organic uptake from glyoxal, but these fragments are useful as tracers of glyoxal uptake into aerosol and oligomer formation. The  $m/z$  44 fragment (CO<sub>2</sub><sup>+</sup>) is typically used as a tracer for oxidized organics in aerosol, especially carboxylic acids [Canagaratna *et al.*, 2007], the glyoxal condensed-phase oxidation products. During these and previous dark (non-oxidative) glyoxal uptake experiments [Galloway *et al.*, 2009], the magnitude of  $m/z$  44 was 8% of  $m/z$  58. In the absence of oxidants, this signal cannot be due to OH-driven oxidation and must be directly from glyoxal. To correct for this contribution, 8% of the  $m/z$  58 signal was subtracted from the  $m/z$  44 signal. The resulting signal corresponds to highly oxidized organics (other than glyoxal but including glyoxal oxidation products, e.g., oxalic acid) and will be referred to as “corrected  $m/z$  44” and used as a tracer of condensed-phase reaction products of glyoxal with OH. All AMS data are normalized to sulfate in order to account for aerosol wall loss and changes in collection efficiency (bounce).

### 2.2. Experimental Procedures

[7] Experimental conditions are summarized in Table 1. AS seed aerosol was injected into the humid chamber and allowed to mix and equilibrate. Then, chamber blacklights were turned on for 2 min to quantify aerosol growth from residual chamber organics without an OH source (1st irradiated period). After this, CH<sub>3</sub>ONO and (usually) NO were added (see Table 1), and blacklights were turned on again to quantify aerosol growth from residual chamber organics with an OH source (2nd irradiated period). After ~15 min, the total and oxidized organic signals on the AMS started to plateau although less than 15% of initial CH<sub>3</sub>ONO had reacted and glyoxal was then injected. After 1 hr, the lights were turned off to allow dark uptake of glyoxal. Blank experiments were run with the same procedures without addition of glyoxal.

## 3. Results

[8] In all experiments, the 1st irradiated period produced no aerosol volume growth and no increase in the total organic or carboxylic acid tracer fraction (corr.  $m/z$  44 to sulfate ratio). At the beginning of the 2nd irradiated period,  $t = 0$  in Figure 2, after CH<sub>3</sub>ONO but before glyoxal injection, a rapid increase in the carboxylic acid tracer (Figure 2c) and aerosol volume were observed at high RH, but not at low RH. This shows that rapid photochemical growth from residual organics can occur under humid conditions, even after extensive cleaning of the chamber. This chamber-background aerosol (OA) was highly oxidized (O/C ratio of 0.95), typical for water-soluble organic carbon (WSOC), high CCN activity, and aqueous processing [Turpin and Lim, 2001; Massoli *et al.*, 2010]. Figures 2a and 2b show that upon injection of gas-phase glyoxal, the aerosol glyoxal-tracer and total OA fractions increased

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2011GL048514.

**Table 1.** Experimental Conditions<sup>a</sup>

Experiment	Initial Glyoxal (ppb)	Initial Seed ( $\mu\text{m}^3 \text{cm}^{-3}$ )	$\Delta$ Seed ( $\mu\text{m}^3 \text{cm}^{-3}$ )	NO (ppb)	RH (%)	T (K)	Lights	OH Precursor
1	None	20	5	625	66	293	5%	CH <sub>3</sub> ONO
2	38	37	N/A <sup>b</sup>	768	54	294	50%	CH <sub>3</sub> ONO
3	None	31	-4	278	82	293	50%	CH <sub>3</sub> ONO
4	131	29	33	1	60	293	10%	None
5	38	19	5	93	76	292	10%	CH <sub>3</sub> ONO
6	59	18	5	860	76	291	10%	CH <sub>3</sub> ONO
7	253	19	96	116	67	292	10%	CH <sub>3</sub> ONO

<sup>a</sup> $\Delta$  seed volume is calculated at lights off.

<sup>b</sup>Glyoxal was allowed to equilibrate with the walls before seed injection.

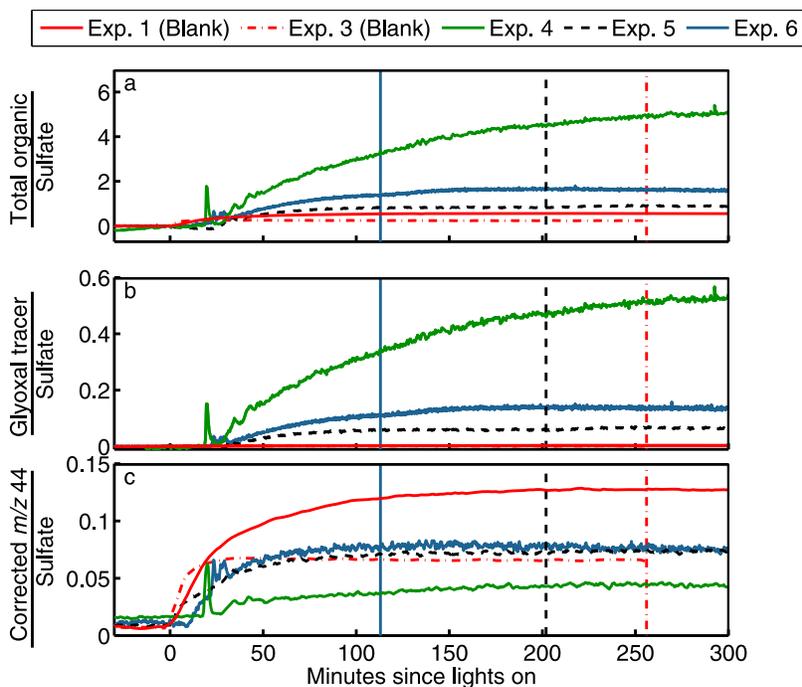
rapidly, whereas the carboxylic acid tracer (corr.  $m/z$  44) was not affected and closely resembled the blanks, demonstrating that formation of carboxylic acids from glyoxal, the expected OH-driven aerosol-processing products, is not observed under our photochemical uptake conditions. In summary, Figure 2 highlights that photochemical aerosol-phase reaction/oxidation products are independent of glyoxal, whereas total organic growth during the photochemical experiments clearly depends on glyoxal but this glyoxal-dependent growth in our photochemical experiments closely resembles that of slow, dark-type uptake.

[9] Figure 3 depicts the change in carboxylic acid, glyoxal, and total OA fractions during the photochemical processing period ( $t = 0$  up to vertical lines shown in Figure 2) as a function of gas-phase glyoxal. The glyoxal tracer and the total OA fraction depend on glyoxal, corr.  $m/z$  44 to sulfate ratio is statistically independent of glyoxal concentrations from 0 to 260 ppb. The experimental variability, most readily observed in the difference between the blank experiments

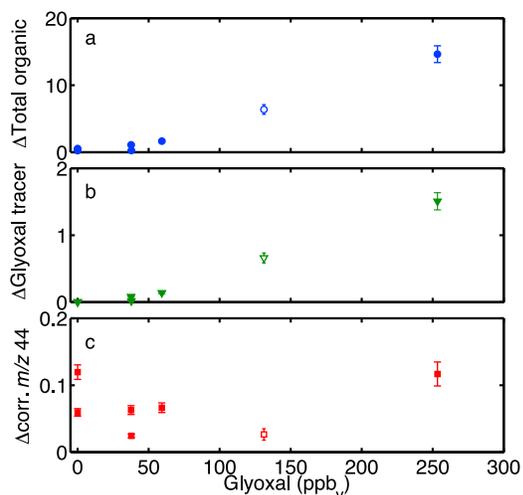
(Figure 3c), does not allow us to fully rule out a small dependence of the carboxylic acid tracer (corr.  $m/z$  44 to sulfate) on glyoxal. However, this contribution must be very small compared to that of the slow, dark-type glyoxal uptake. The fact that no such contribution is observed demonstrates that virtually all uptake from glyoxal can be explained by non-oxidative (dark-type) uptake. Once the blacklights are turned off, OH is quickly depleted. If OH is responsible for an increased glyoxal uptake, the growth in glyoxal and total organic to sulfate ratios should slow down or level off at lights off. This is not the case (Figures 2a and 2b), and glyoxal uptake increases slightly when the blacklights are turned off, likely as a result of the drop in temperature and rise in RH.

#### 4. Discussion

[10] Under all conditions studied here, the observed aerosol growth can be fully explained by slow, dark-type



**Figure 2.** (a) Total organic tracer, (b)  $m/z$  58 and (c) carboxylic acid (corr.  $m/z$  44) tracers, all normalized to sulfate. For experiments with gas-phase glyoxal, glyoxal injections occurred at  $\sim 15$  minutes after lights were turned on. Vertical lines indicate when lights were turned off for each experiment to observe glyoxal uptake in the absence of light and OH. After this time, a slight increase in glyoxal and organic tracer can be seen, while there is no increase in oxidized organic tracer. The growth rate of the oxidized organic fraction does not increase upon addition of glyoxal. After initial fluctuations from glyoxal mixing in the chamber, glyoxal uptake rates are very similar for all experiments.



**Figure 3.** Change in (a) total organic fraction, (b) glyoxal-tracer fraction ( $m/z$  58), and (c) the oxidized fraction (corr.  $m/z$  44) of aerosol during time of OH exposure for all experiments. These data are normalized to sulfate. Solid points indicate experiments with OH source present, open points indicate an irradiated experiment with no OH source present. Error bars reflect precision.  $\Delta$ organic and  $\Delta$ glyoxal-tracer increase with increasing glyoxal concentration. The variability in blanks shows that environmental factors and not precision dominate the variability of the corr.  $m/z$  44 to sulfate ratio but not the total organic to sulfate ratio. The trend in oxidized organic with gas-phase glyoxal is statistically not significant, indicating that the contribution to aerosol as a result of oxidized glyoxal uptake is very small.

glyoxal uptake and fast photochemical uptake that results only from residual organics in the chamber. The oxidized OA fraction (carboxylic acids) was not attributable to glyoxal (Figure 3c) in our uptake experiments with glyoxal and a gas-phase OH source. This is in contrast to the laboratory studies of bulk aqueous oxidation of glyoxal by OH with a condensed-phase OH source, which saw photochemical products, specifically carboxylic acids [Carlton *et al.*, 2007; Tan *et al.*, 2009]. The corrected  $m/z$  44 (carboxylic acid) signal indicates the presence of oxidation products, but blank experiments show that this is not a result of glyoxal uptake but from residual chamber organics. With the exception of the oxidized aerosol fraction, which exhibits no dependence on glyoxal, the glyoxal-dependent growth rate and composition of the aerosol as judged by the AMS are identical in the presence and absence of OH. Although the AMS fragments both oligomers and other higher molecular weight compounds, previous experiments have clearly shown that glyoxal oligomers can be detected [Galloway *et al.*, 2009; Liggio *et al.*, 2005]. If OH affected the oxidation or oligomerization chemistry in the aerosol, a shift to higher masses would be evident in the overall AMS mass spectra when compared to dark uptake conditions. Analysis of the  $m/z$  105 to  $m/z$  58 ratio rules out that OH influences the formation of glyoxal (acetal) oligomers. Our analysis also shows that the overall mass spectra of photochemical glyoxal uptake are not shifted to higher molecular weights or do not indicate other changes compared to dark uptake. In addition, analysis with particle-into-liquid-samplers

and analysis of filter extracts of aerosol did not show any higher molecular weight compounds, such as organosulfates or carboxylic acids (see auxiliary material).

[11] The observation of only slow, dark-type uptake in our experiments matches the results for mixed AS/fulvic/amino/sulfuric acid seed particles of Volkamer *et al.* [2009] but disagrees with their AS results that show fast photochemical uptake. This merits further discussion, specifically in the context of the exact nature of the seed, its influence on uptake, and resulting atmospheric implications. The seed introduced into the chamber consisted of pure AS seed aerosol, for which Volkamer *et al.* [2009] saw fast photochemical uptake. However, the seed to which glyoxal was exposed in our study was not pure as it had experienced a small amount of growth from chamber background aerosol, which was unavoidable under humid conditions even after extensive chamber cleaning.

[12] The key question is if and how this small amount of background aerosol or differences in experimental procedure resulted in a barrier for photochemical glyoxal uptake but not dark-type uptake. It was not known if a coating was present on the aerosol, and it is possible that, despite its high O/C ratio, expected high CCN activity, and WSOC-like properties, the chamber-background aerosol formed a coating. This coating may have prevented fast photochemical uptake but not slower dark-type uptake of glyoxal. This could result if dark-type uptake is rate-limited by a bulk-process whereas fast photochemical uptake is rate-limited by surface reactions. It is also possible that direct injection of glyoxal rather than photochemical generation from  $C_2H_2$  could explain the different results. Glyoxal oligomers may have formed in the gas-phase as a result of the high concentrations at the injection port, although it is unclear whether this is a gas-phase or wall/surface process. These oligomers have much lower vapor pressures than glyoxal and should rapidly partition to surfaces, including aerosol, potentially forming a coating. We also conducted experiments in which glyoxal was injected and allowed to equilibrate to the walls before seed was injected and photochemistry initiated (Exp. 2) in which case one might expect the oligomers to rapidly partition to the chamber walls before the seed was present. No fast photochemical uptake was observed, but it is possible that chamber background-aerosol rapidly coated the seed. A coating on our seed from chamber background or glyoxal/glyoxal oligomers could reconcile our results with those of Volkamer *et al.* [2009] if such coatings were not present for the latter experiments.

[13] The atmospheric implications of this work are less dependent on the differences than the similarities between our experimental results for AS and those of Volkamer *et al.* [2009]. Both studies show that fast photochemical uptake does not occur for all types of seed aerosol. The critical question is which type of seed is closest to atmospheric conditions. If the lack of fast photochemical uptake is caused by a coating on the seed, it is important to determine the necessary conditions and types of coatings that are common in the atmosphere to determine when and where ambient aerosol will show fast glyoxal uptake. Answering these questions about ambient aerosol and further elucidating conditions of fast photochemical uptake is required to determine the role of glyoxal in SOA formation from uptake on aerosol. At present, this is unclear and this work high-

lights the difficulty in both quantitatively and accurately including SOA formation from glyoxal in models.

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