# Supplementary Material for "Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets"

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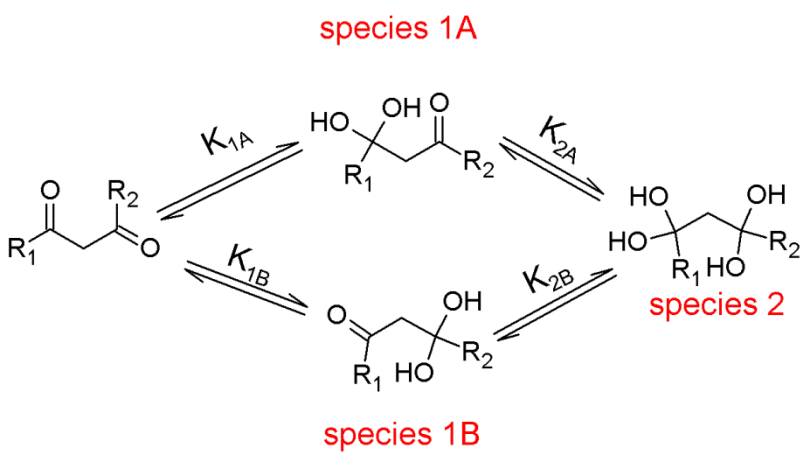
## 1. Hydration of Dicarbonyls

This section describes our approach to account for hydration equilibria in dicarbonyl compounds. Consider an unhydrated and unsymmetrical dicarbonyl with carbonyl groups indentified by the letters "A" and "B" (Scheme S1). In the aqueous phase, hydration can reversibly replace carbonyl "A" with a gem-diol group forming species 1A (equilibrium constant for the hydration process, $K_{hyd} = K_{1A}$) and/or carbonyl "B" with a gem-diol group forming species 1B ($K_{hyd} = K_{1B}$). A certain fraction of the mixture may be double hydrated, with both carbonyl groups converted in the gem-diol form. The corresponding equilibrium constants, $K_{2A}$ and $K_{2B}$ are identified in scheme S1.




Scheme S1: Hydration of a generic dicarbonyl

The molar fraction that is unhydrated, $\alpha_{un}$, fully-hydrated, $\alpha_{fh}$, and partially-hydrated, $\alpha_{ph}$, can be derived from the equilibrium equations (all activity coefficients are set to unity):

$$\alpha_{uh} = (1 + K_{1A} + K_{1B} + K_{1B}K_{2B})^{-1} \tag{1}$$

$$\alpha_{fh} = \left((K_{1B}K_{2B})^{-1} + {K_{2A}}^{-1} + {K_{2B}}^{-1} + 1\right)^{-1} \tag{2}$$

$$\alpha_{ph} = 1 - \left(\alpha_{uh} + \alpha_{fh}\right) \tag{3}$$

Because the gem-diol form is lacking the π*←n transition associated with the carbonyl group, it is appropriate to assume that the rates of photolysis of the singly hydrated dicarbonyl species are approximately one-half of the rate of photolysis of the unhydrated form, resulting in the following expression for *Z*:

$$Z = \frac{\frac{dn_{h\nu}^{gas}}{dt}}{\frac{dn_{h\nu}^{aq}}{dt}} \geq \frac{\alpha_{uh} + 0.5\alpha_{ph}}{\left(R \cdot T \cdot LWC_{v} \cdot k_{H}\right)} \tag{4}$$

## 2. Extinction Coefficients of Aqueous D-Glyceraldehyde and Dihydroxyacetone

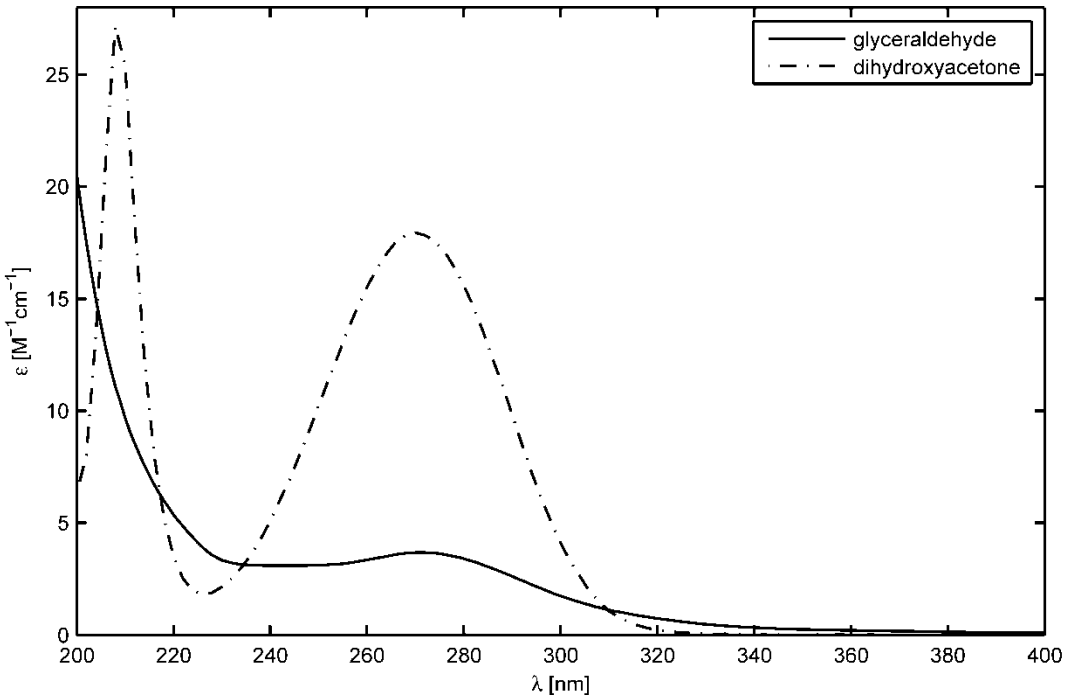



Figure S1: Molar extinction coefficients for D-glyceraldehyde (solid curve) and dihydroxyacetone (dashed curve) at 25$^{o}$C calculated by dividing the absorbance by the total concentration (free + hydrated form). Note the only free from absorbs at 270 nm.

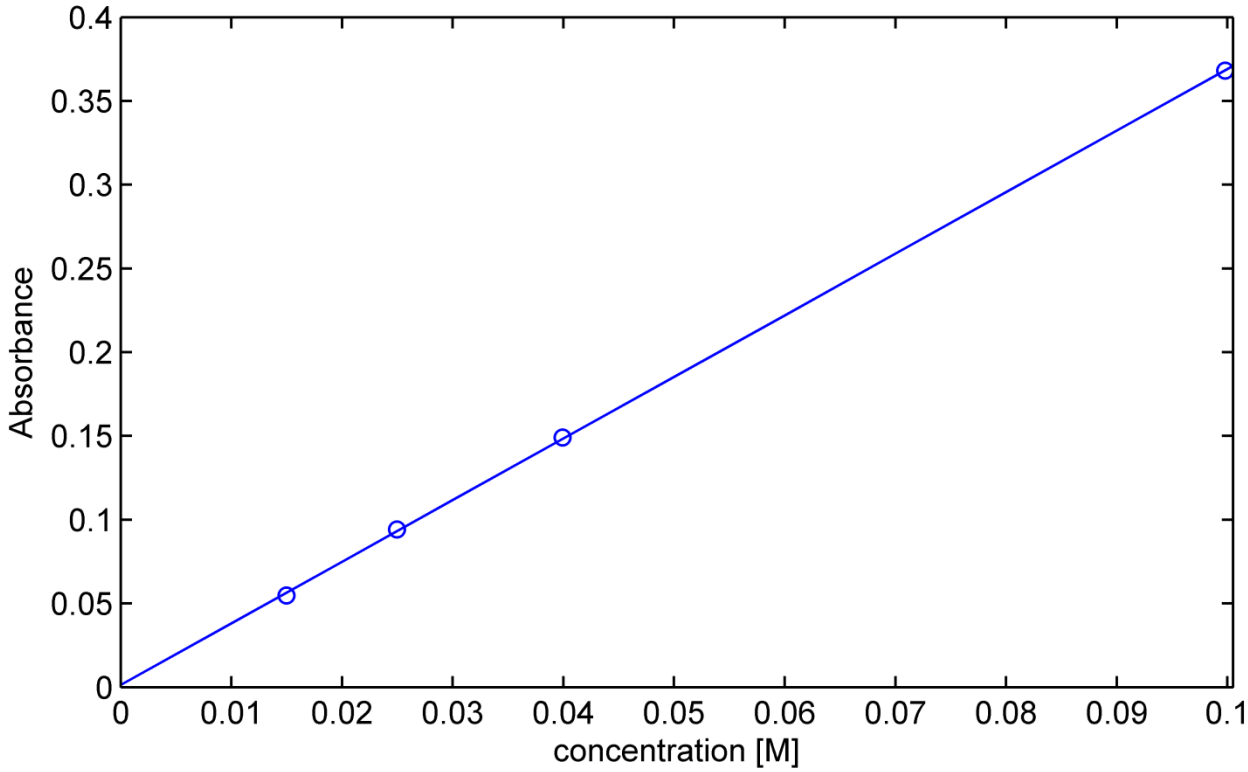



Figure S2: D-glyceraldehyde absorbance at 271 nm as a function of total concentration (free + hydrated form).

Figure S1 shows the molar extinction coefficients for D-glyceraldehyde (solid curve) and dihydroxyacetone (dashed curve) at 25$^{o}$C that were measured in this work. A Beer-Lambert plot of the measurements is shown in Figure S2. Tabulated extinction coefficients are presented in Table S4 and S5. Both glyceraldehyde and dihydroxyacetone exhibit a well defined $\pi^* \leftarrow n$ band that overlaps the solar flux. The $\pi^* \leftarrow n$ band in D-glyceraldehyde is considerably lower in intensity compared to that in dihydroxyacetone because the former is much more prone to hydration than the latter. Specifically, the observed extinction coefficient (the one plotted in Figure S1) is reduced relative to the extinction coefficient of the unhydrated form of the molecule:

$$\varepsilon_{observed} = \frac{\varepsilon_{unhydrated}}{1 + K_{hyd}} \tag{5}$$

For D-glyceraldehyde, this reduction is substantial as $1+K_{hyd}$ = 18.3 (Glushonok et al., 1986), much smaller than the corresponding value for dihydroxyacetone, $1+K_{hyd}$ = 1.77 (Glushonok et al., 2003;Davis, 1973).

### 3. FTIR Spectrum of Gaseous Photolysis Products

Photolysis of aqueous D-Glyceraldehyde produced gas bubbles that formed on the walls of the photolysis cell. The gases produced during photolysis of aqueous D-Glyceraldehyde at 25$^{o}$C were captured and analyzed with a Fourier Transform Infrared (FTIR) spectrometer (Mattson Galaxy Series 5000). A diagram illustrating the FTIR cell is presented in Figure S3.

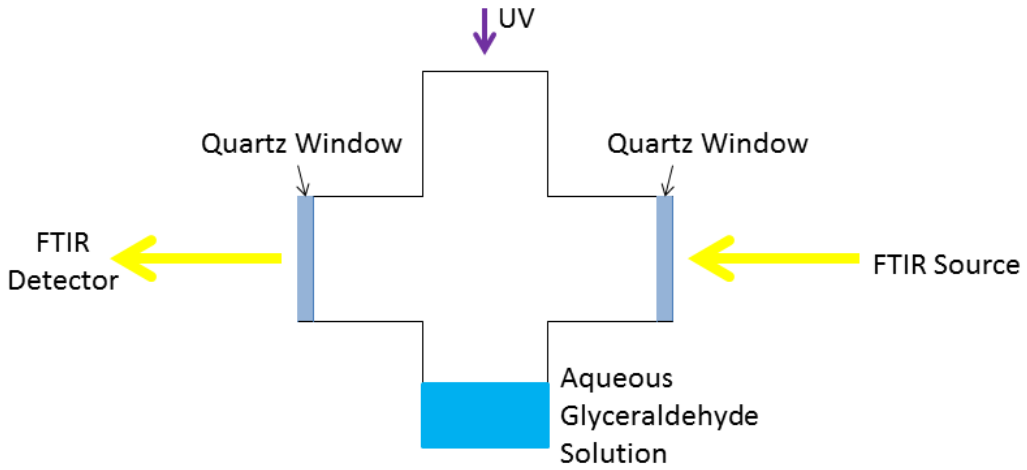



Figure S3: Apparatus used to capture and analyze the gases evolved from photolysis of glyceraldehyde

The FTIR spectrum shown in Figure S4 indicates the presence of carbon monoxide. Carbon monoxide is an expected product of the direct photolysis of D-Glyceraldehyde (see below). We have not attempted to quantify the yield of this product. The FTIR spectrum also indicates the presence of carbon dioxide, a potential product of secondary photolysis. However, we cannot conclude that the carbon dioxide evolved from the photolysis due to the potential presence of $CO_2$ from the ambient air.

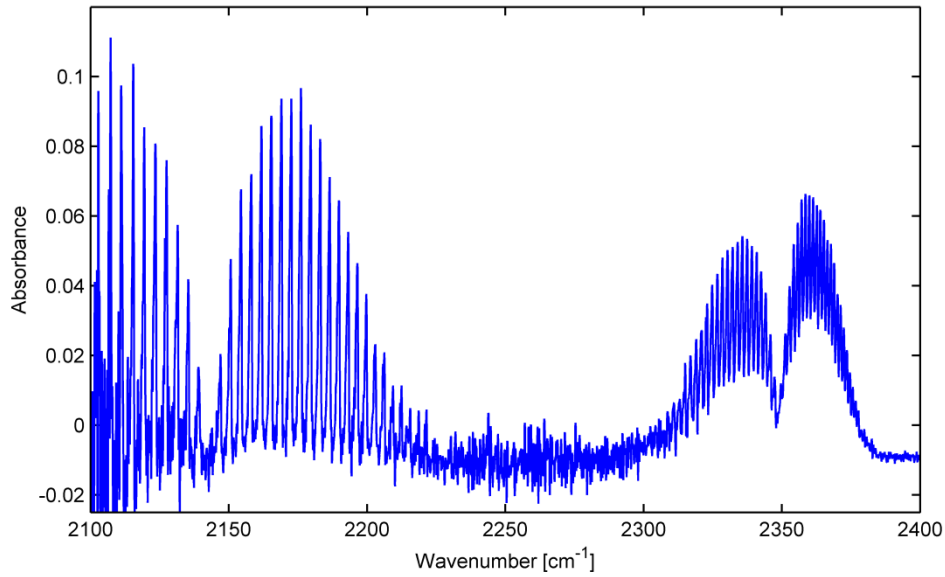



Figure S4: FTIR spectrum of the products of aqueous D-glyceraldehyde photolysis at 25°C. The band centered at 2143 $cm^{-1}$ belongs to carbon monoxide, and the band centered at 2349 $cm^{-1}$ is the asymmetric stretch of $CO_2$.

## 4. Monitoring the Photolysis of Glyceraldehyde Using a UV-Vis Spectrometer

We took UV-Vis spectra measurements during photolysis of 0.1 M aqueous glyceraldehyde solutions at various photolysis times. Figure S5 shows how the absorption of an aqueous glyceraldehyde solution changes when exposed to UV light with a 40 nm bandwidth centered at 300 nm at 25°C.

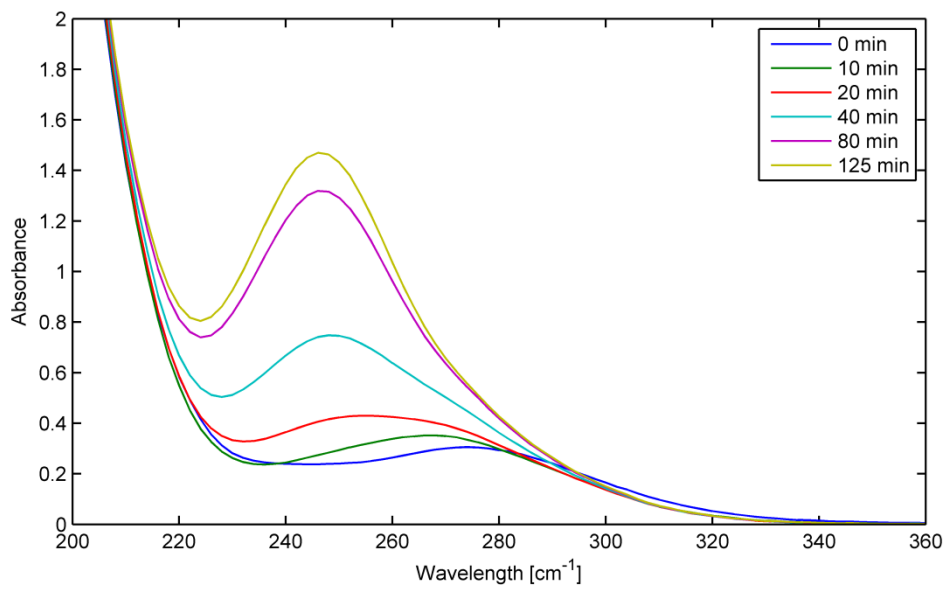



Figure S5: Absorption of glyceraldehyde photolysis solution as a function of time at 25°C

Upon photolysis, the $\pi^* \leftarrow n$ band undergoes a simultaneous hypsochromic and hyperchromic shift. We believe that the band growing at 250 nm belongs to a minor but strongly absorbing photolysis product (which we could not identify because of its small concentration).

## 5. Monitoring the Photolysis of D-Glyceraldehyde with ESI-MS

We calibrated the ESI-MS technique for determining glyceraldehyde solution concentration before each photolysis experiment. Several glyceraldehyde solutions of varying concentrations were derivatized with Girard Reagent T (GT) and analyzed with an ESI-MS instrument. Reaction of carbonyls with the GT ion ($C_5H_{14}N_3O^+$) leads to permanently positively charged adducts according to the reactions below. The first step generates a carbinolamine ion with *m/z* that is 132.1131 higher than the mass of the parent carbonyl molecule. Subsequent dehydration of the carbinolamine intermediate results in the final hydrazone product and an overall shift of 113.0953 between the *m/z* of the observed ion and exact mass. Only hydrozone products were observed in our experiments.

$$>C{=}O \;+\; H_2N\text{-}NH\text{-}C(=O)\text{-}CH_2\text{-}N^+(\text{-}CH_3)_3 \;\rightarrow\; >C(OH)\text{-}NH\text{-}NH\text{-}C(=O)\text{-}CH_2\text{-}N^+(\text{-}CH_3)_3$$

$$>C(OH)\text{-}NH\text{-}NH\text{-}C(=O)\text{-}CH_2\text{-}N^+(\text{-}CH_3)_3 \;\rightarrow\; >C{=}N\text{-}NH\text{-}C(=O)\text{-}CH_2\text{-}N^+(\text{-}CH_3)_3 \;+\; H_2O$$

Tetraethylammonium chloride was added to the GT solution to act as an internal ESI-MS standard (it does not react with carbonyls and is expect to have a similar ionization efficiency to GT and GT+carbonyl adducts). Figure S6 illustrates a typical calibration curve determined with this method. The calibration is approximately linear.

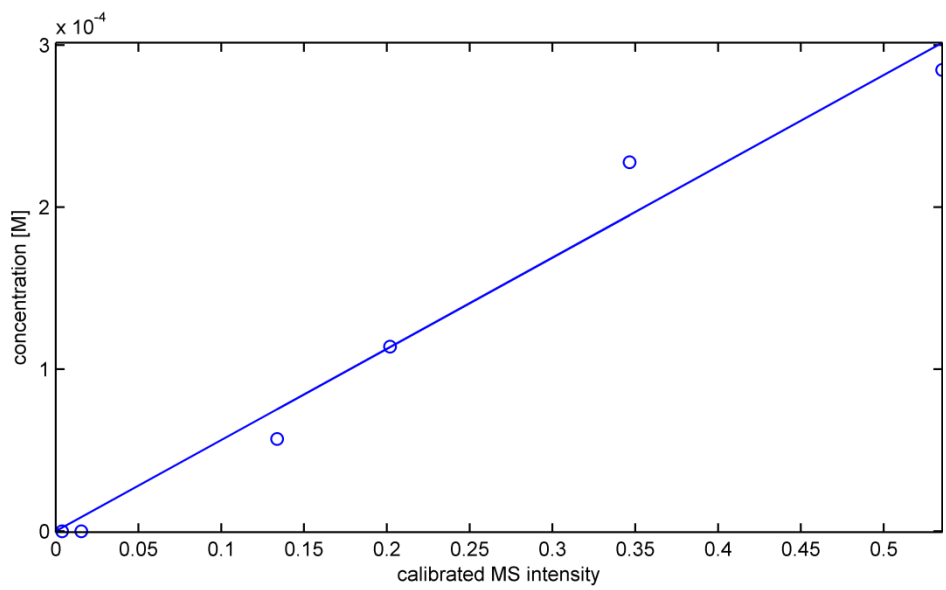



Figure S6: Results of a calibration experiment relating the concentration of glyceraldehyde and the peak intensity of the derivatized glyceraldehyde hydrazone adduct. The ion abundance of the glyceraldehyde-GT peak was normalized by that of the tetraethylammonium internal standard peak.

During a photolysis experiment, 100 μL aliquots of the glyceraldehyde solution were withdrawn from the photolyzed solution periodically and added to 25 mL of a solution containing 0.9 mM GT and 0.05 mM tetraethylammonium chloride. This mixture was allowed to react overnight, forming the GT-glyceraldehyde adduct. The normalized glyceraldehyde-GT adduct peak abundance is shown in Figure S7 as a function of the photolysis time.

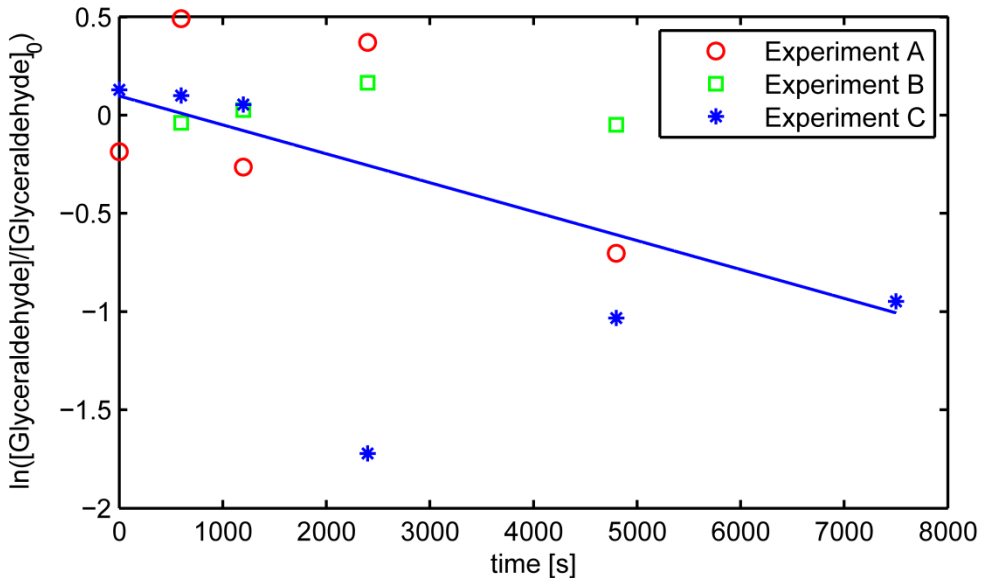



Figure S7: Semi-quantitative measurements of glyceraldehyde concentration as a function of photolysis time at 25°C for three separate experiments.

The observed scatter is due to the difficulties in quantifying the derivatized product with ESI-MS (and possibly due to incomplete GT+carbonyl reactions). The experiment indicated with the blue asterisks has an extreme outlier at 2300 s. However this outlier does not significantly affect the slope of the fitted line as it is close to the center of the x-axis. The slope of the fitted line, along with the known flux from the UV lamp obtained from actinometer measurements, were used to approximate the quantum yield of photolysis.

ESI-MS measurements were also used to identify potential photolysis products. Figure S8 shows an ESI-MS difference spectrum. Positive peak heights indicate that a product was formed while negative peak heights indicate the consumption of a reactant.

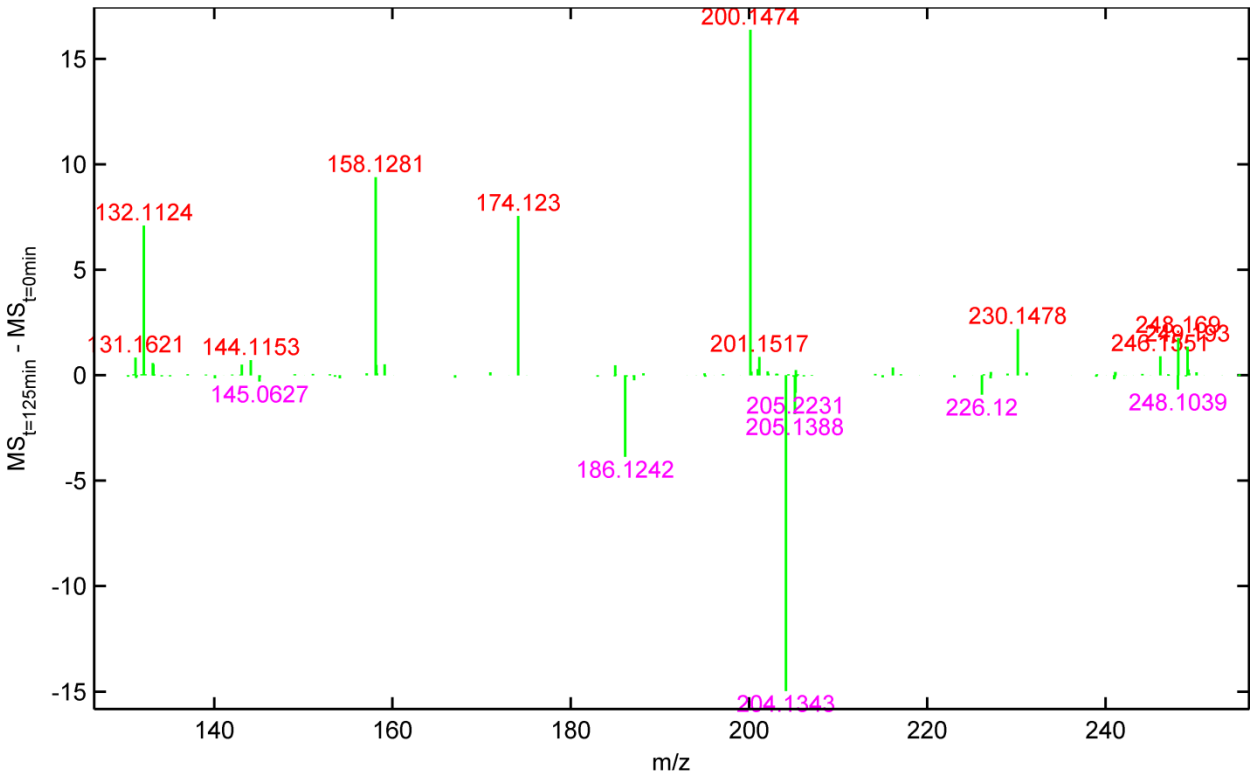



Figure S8: ESI-MS difference spectrum showing the formation of products and the disappearance of reactants from a typical glyceraldehyde photolysis experiment. The solution was photolyzed for 125 minutes.

Peak m/z was calibrated with a two point calibration using tetraethylammonium (observed at *m/z* 130.1590 Da ) and the glyceraldehyde+GT hydrozone adduct (*m/z* 204.1343 Da). Free GT ions appears at *m/z* 132.1124. The product appearing at *m/z* 158.1281 is likely the ethanal+GT hydrozone adduct while the product appearing at *m/z* 174.123 is likely the glycolaldehyde+GT hydrozone adduct. To further confirm the presence of these products, we spiked several solutions with both ethanal and glycolaldehyde. A single hydrozone peak for each adduct was observed. Several other contaminants were consumed and products were formed. However, we were unable to unambiguously assign molecules to these species.

## 6. Reproductions of Figure 6 Under Different Atmospheric Conditions

To test how atmospheric conditions affect the identification of products that may have significant aqueous photolysis rates, four reproductions of Fig. 6 under varying atmospheric conditions are presented in Figures S9-S12. Figure S9 illustrates how solar zenith angle affects the significance of aqueous photolysis. Decreasing the solar zenith angle to its minimum value of zero degrees slightly decreases the Q value for every compound because the maximum rate of aqueous photolysis increases due to increased overlap between the actinic flux and the molar extinction coefficient. However, this decrease in SZA does not affect the conclusions of our analysis (the photolysis is slower than reactions with OH for the majority of compounds). Aqueous photolysis may be important for only two of the compounds studied in the plot: pyruvic acid and acetoacetic acid.

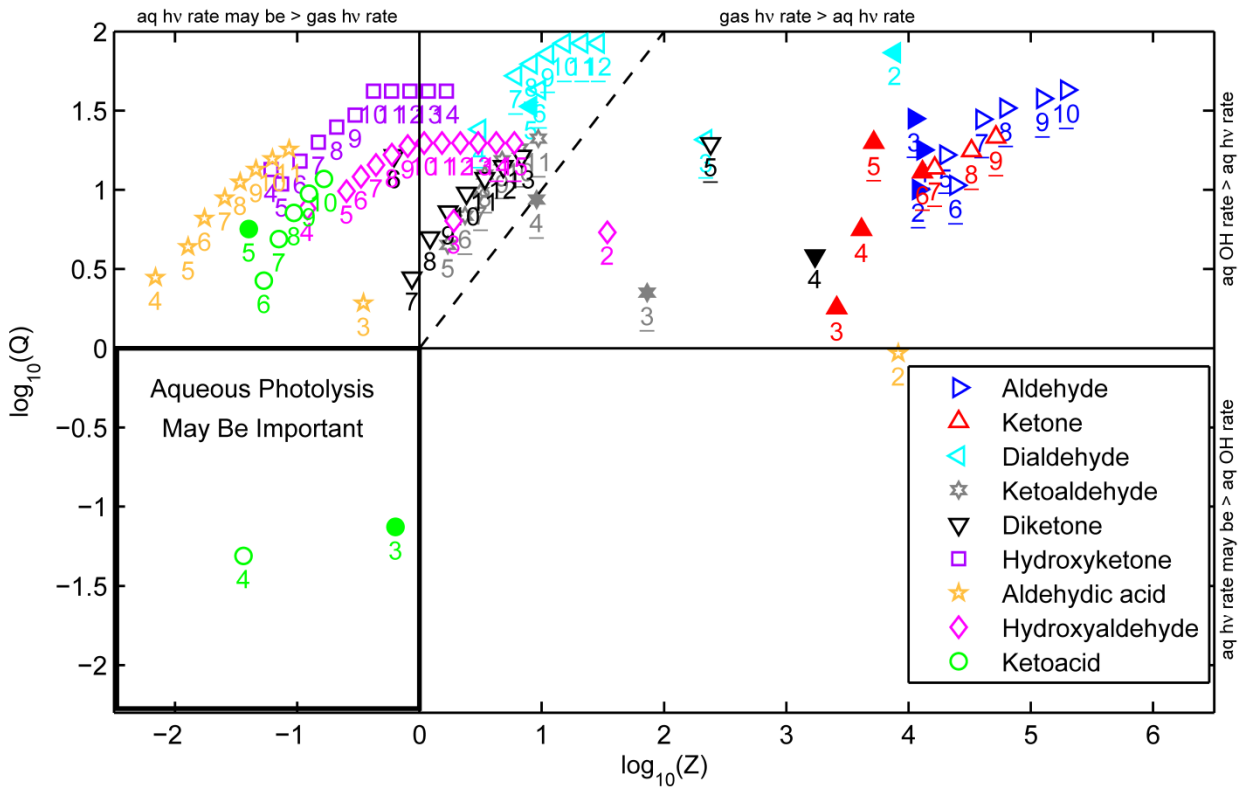



Figure S9: Reproduction of Figure 6 in the manuscript with a SZA of $0^o$. LWC = 0.5 g $m^{-3}$, T = $25^oC$, pH = 2, and $C_{OH} = 10^{-13}$ M.

The effects of decreasing the aqueous hydroxyl radical concentration to a level more commonly seen at night are illustrated in Figure S10. As in Figure S9, decreasing the aqueous OH concentration decreases the value of Q for all compounds. A few additional compounds enter the region where aqueous photolysis may be significant. However, situations where aqueous OH concentrations are $10^{-14}$ M with sunlight at a SZA of $20^o$ are likely uncommon.

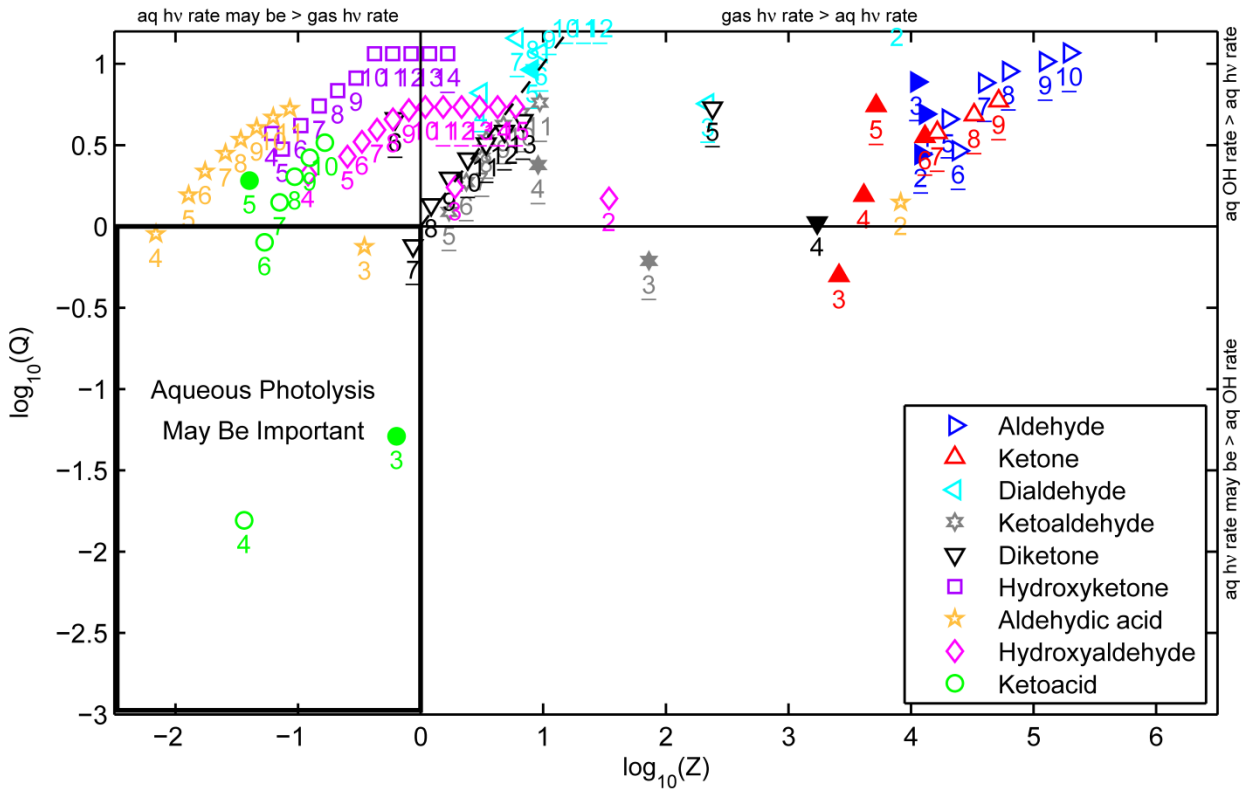



Figure S10: Reproduction of Figure 6 in the manuscript with $C_{OH}$ = 2.5 x $10^{-14}$ M. SZA is 20°, LWC = 0.5 g $m^{-3}$, T = 25°C, and pH = 2.

Figure S11 details the effects of changing the LWC to 0.05 g $m^{-3}$. The lower LWC value increases the significance of the gas-phase processes. Pyruvic acid moves into the region where gaseous photolysis is the most significant sink.

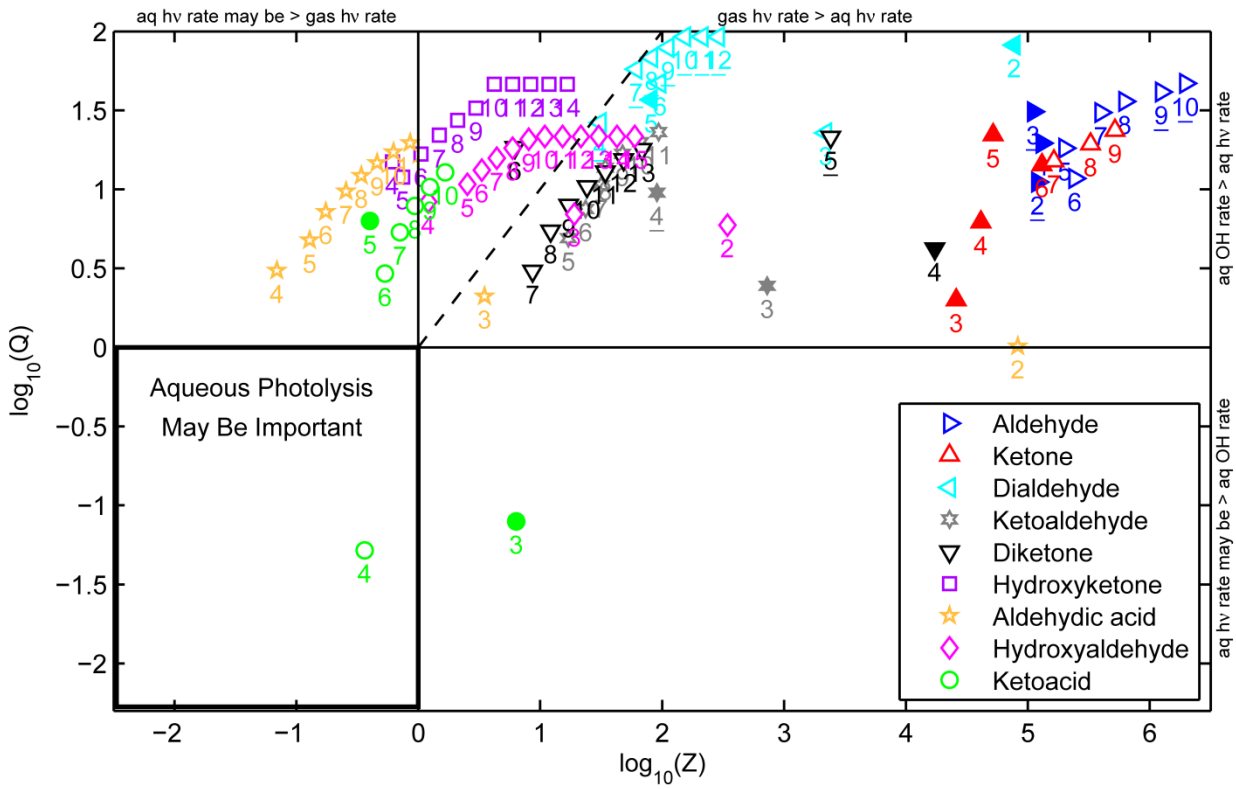



Figure S11: Reproduction of Figure 6 in the manuscript with LWC = 0.05 g $m^{-3}$. SZA is $20^{o}$, T = $25^{o}$C, pH = 2, and $C_{OH} = 10^{-13}$ M.

Figure S12 shows how cloud-water acidity affects the fate of aldehydic acids and ketoacids. Changing the cloud-water acidity from a pH of 2 to a pH of 6 does not significantly change the chemical behavior of the acids investigated.

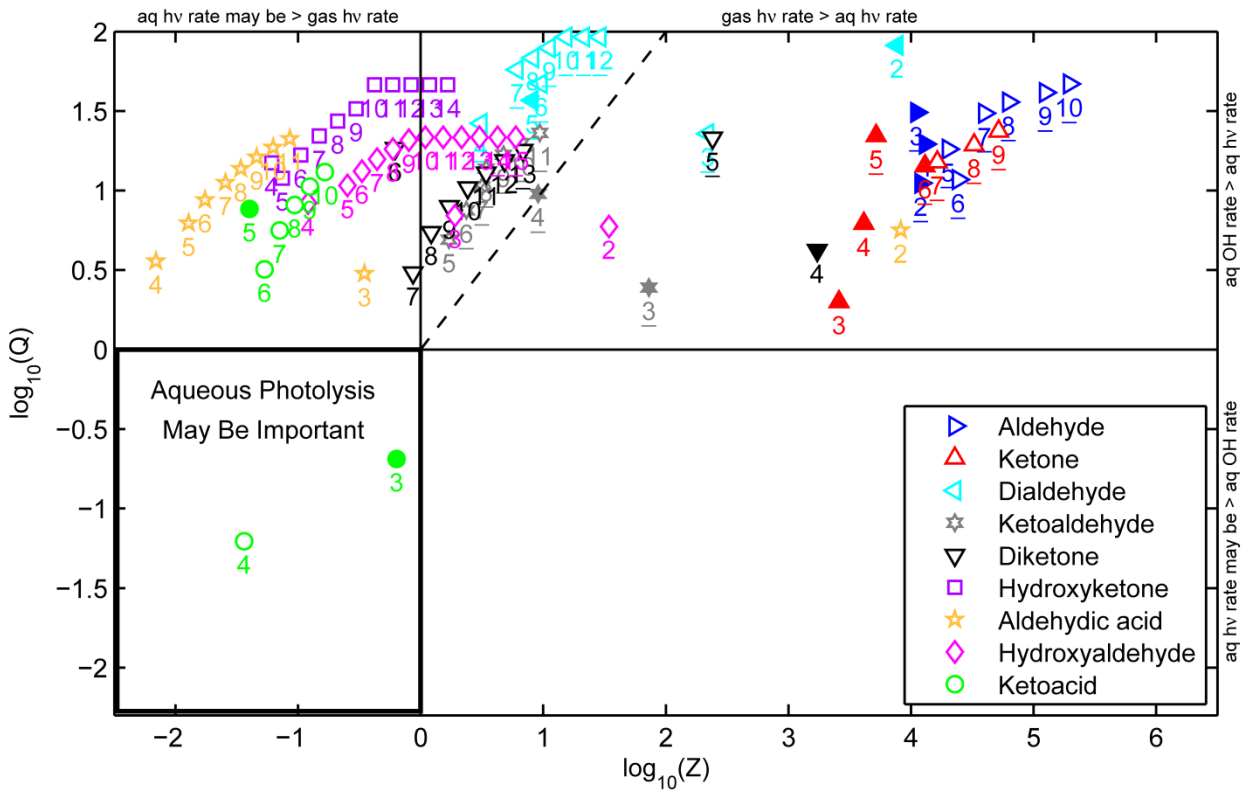



Figure S12: Reproduction of Figure 6 in the manuscript with pH = 6. SZA is 20$^{o}$, LWC = 0.5 g m$^{-3}$, T = 25$^{o}$C, and $C_{OH}$ = $10^{-13}$ M.

We also investigated the uncertainties in Q and Z that arise from using estimates of $K_H$, $K_{hyd}$, $k_{OH}$, and $pK_A$ in the absence of experimental data. Uncertainties in Z are a function of root-mean-square deviations between predicted and experimental $K_{hyd}$ values from (Hilal et al., 2005) and standard deviations from bond and group method $K_H$ predictions (EPA, 2011). Uncertainties in Q are a function of the uncertainties in predicting $k_{OH}$ values from the (Doussin and Monod, 2013) SAR and the prediction uncertainty between photolysis rates calculated with the entire UV-extinction coefficients and photolysis rates calculated with $\lambda_{max}$ and $\varepsilon_{max}$. Photolysis rate prediction uncertainties were obtained from a comparison of rates calculated for eight carbonyl compounds with experimentally determined extinction coefficients from (Xu et al., 1993) and this work: ethanal, propanal, butanal, acetone, butanone, 2-pentanone, dihydroxyacetone, and glyceraldehyde (see Figure S14). For purposes of this analysis, compounds with experimental parameters were assigned an uncertainty of zero. Figure S13 displays uncertainties in Q and Z parameters.

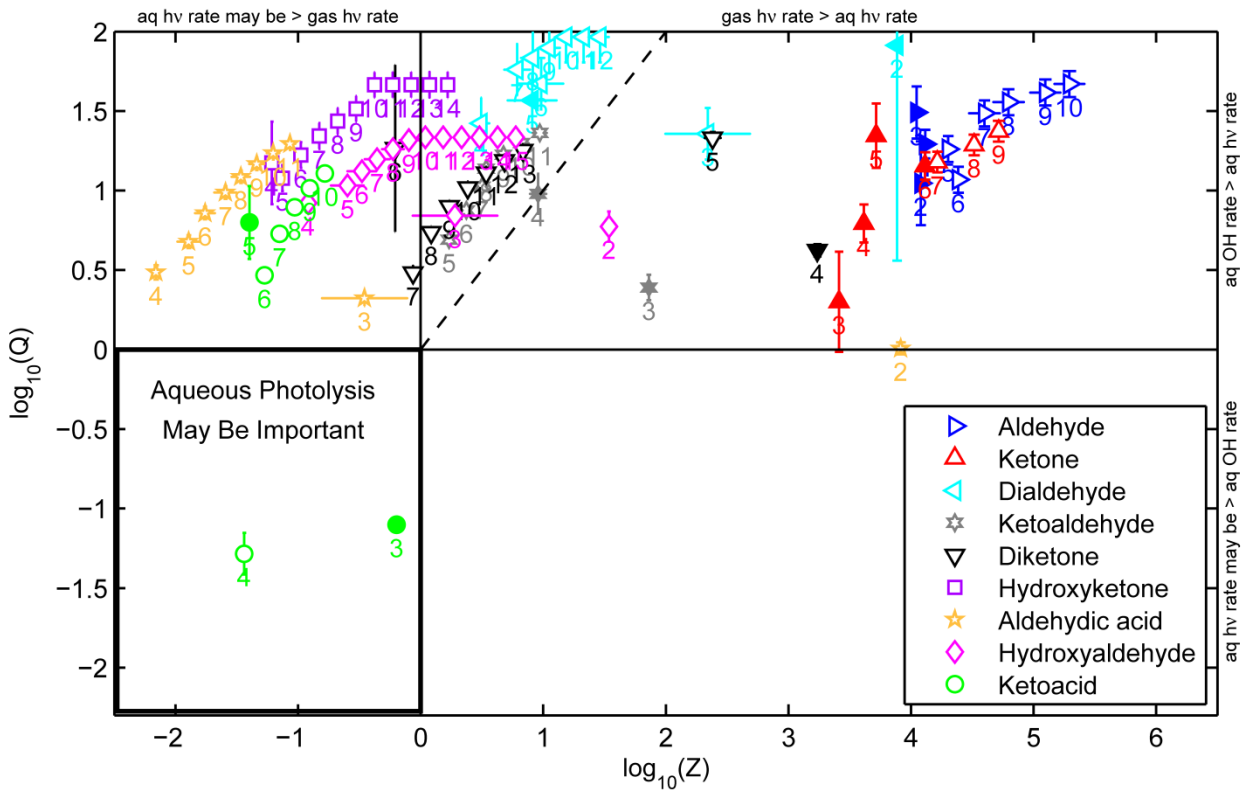



Figure S13: Uncertainty estimates in the parameters Q and Z arising from calculations of model parameters

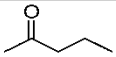
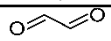
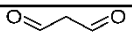
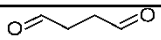
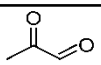
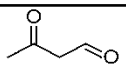
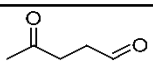
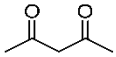
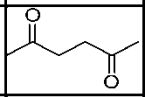
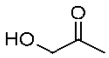
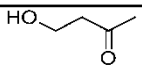
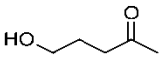
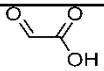
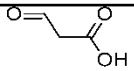
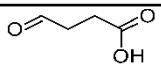
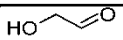
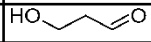
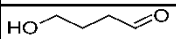
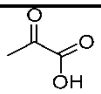
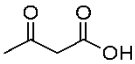
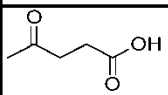
## 7. Literature Values for $\varepsilon_{max}$ and $\lambda_{max}$

The literature values used to generate Figure 6 and Figures S9-S12 are presented in Table S1 below. Structures for the first three molecules in each series are presented in Table S2.

Table S1: $\varepsilon_{max}$ and $\lambda_{max}$ values used to determine aqueous photolysis rates for Figures 6, and S9-S12. The upper row indicates the total number of carbon atoms in a molecule with a functionality specified by the first column. Bold values were obtained from the literature with subscripted reference numbers: Ref 1 (Mackinney and Temmer, 1948); Ref 2 (Xu et al., 1993); Ref 3 (Rice, 1920); Ref 4 (Malik and Joens, 2000); Ref 5 (Schutze and Herrmann, 2004); Ref 6 (Martinez et al., 1975); Ref 7(Gubina et al., 2004); Ref 8 (Steenken et al., 1975); Ref 9 (Maroni, 1957); Ref 10 (Beeby et al., 1987). For compounds without published data, an upper estimate was used based on the properties of molecules with similar functionalities.

| # C atoms | ⇒ | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aldehyde | $\varepsilon_{max}$ | **8.1**$_1$ | **13.1**$_1$ | **13.5**$_1$ | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| | $\lambda_{max}$ | **277.5**$_1$ | **277.5**$_1$ | **282.5**$_1$ | 282.5 | 282.5 | 282.5 | 282.5 | 282.5 | 282.5 | 282.5 | 282.5 | 282.5 | 282.5 | 282.5 |
| Ketone | $\varepsilon_{max}$ | | **17.6**$_2$ | **17.9**$_2$ | **24**$_2$ | **21.2**$_3$ | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| | $\lambda_{max}$ | | **264**$_2$ | **277.5**$_2$ | **271**$_2$ | **279**$_3$ | 280 | 280 | 280 | 280 | 280 | 280 | 280 | 280 | 280 |
| Dialdehyde | $\varepsilon_{max}$ | **5.8**$_1$ | 8 | 8 | **7.9**$_4$ | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| | $\lambda_{max}$ | **267.5**$_1$ | 282 | 282 | **282**$_4$ | 282 | 282 | 282 | 282 | 282 | 282 | 282 | 282 | 282 | 282 |
| Keto-aldehyde | $\varepsilon_{max}$ | | **16**$_5$ | **13**$_6$ | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| | $\lambda_{max}$ | | **284**$_5$ | **280**$_6$ | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 |
| Diketone | $\varepsilon_{max}$ | | | **26.5**$_5$ | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| | $\lambda_{max}$ | | | **284**$_5$ | 285 | **264**$_7$ | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 |
| Hydroxy-ketone | $\varepsilon_{max}$ | | **20**$_8$ | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| | $\lambda_{max}$ | | **267**$_8$ | **270.5**$_9$ | 280 | 280 | 280 | 280 | 280 | 280 | 280 | 280 | 280 | 280 | 280 |
| Acid-aldehyde | $\varepsilon_{max}$ | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| | $\lambda_{max}$ | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 |
| Hydroxy-aldehyde | $\varepsilon_{max}$ | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| | $\lambda_{max}$ | **277**$_{10}$ | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 |
| Ketoacid | $\varepsilon_{max}$ | | **19.5**$_1$ | 25 | **25.1**$_1$ | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| | $\lambda_{max}$ | | **317.5**$_1$ | 317.5 | **270**$_1$ | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 | 285 |

Table S2: Structures corresponding to the molecules listed in Table S1. As described in the text, functional groups occupy the terminal positions in the chain.

| | C# = 1 | C# = 2 | C# = 3 | C# = 4 | C# = 5 | C# = 6 |
|---|---|---|---|---|---|---|
| Aldehyde |  |  |  | | | |
| Ketone | N/A | N/A |  |  |  | |
| Dialdehyde | N/A |  |  |  | | |
| Ketoaldehyde | N/A | N/A |  |  |  | |
| Diketone | N/A | N/A | N/A |  |  |  |
| Hydroxyketone | N/A | N/A |  |  |  | |
| Aldehydic Acid | N/A |  |  |  | | |
| Hydroxyaldehyde | N/A |  |  |  | | |
| Keto Acid | N/A | N/A |  |  |  | |

## 8. Evaluation of the Aqueous Photolysis Rate Constant Parameterization

Figure S14 compares Q-values calculated with published extinction coefficients and Q-values calculated with our $\lambda_{max}$ and $\varepsilon_{max}$ parameterization. The parameterization performs reasonably well for simple carbonyls. Parameterized Q-values have acceptable uncertainties for our order-of-magnitude analysis.

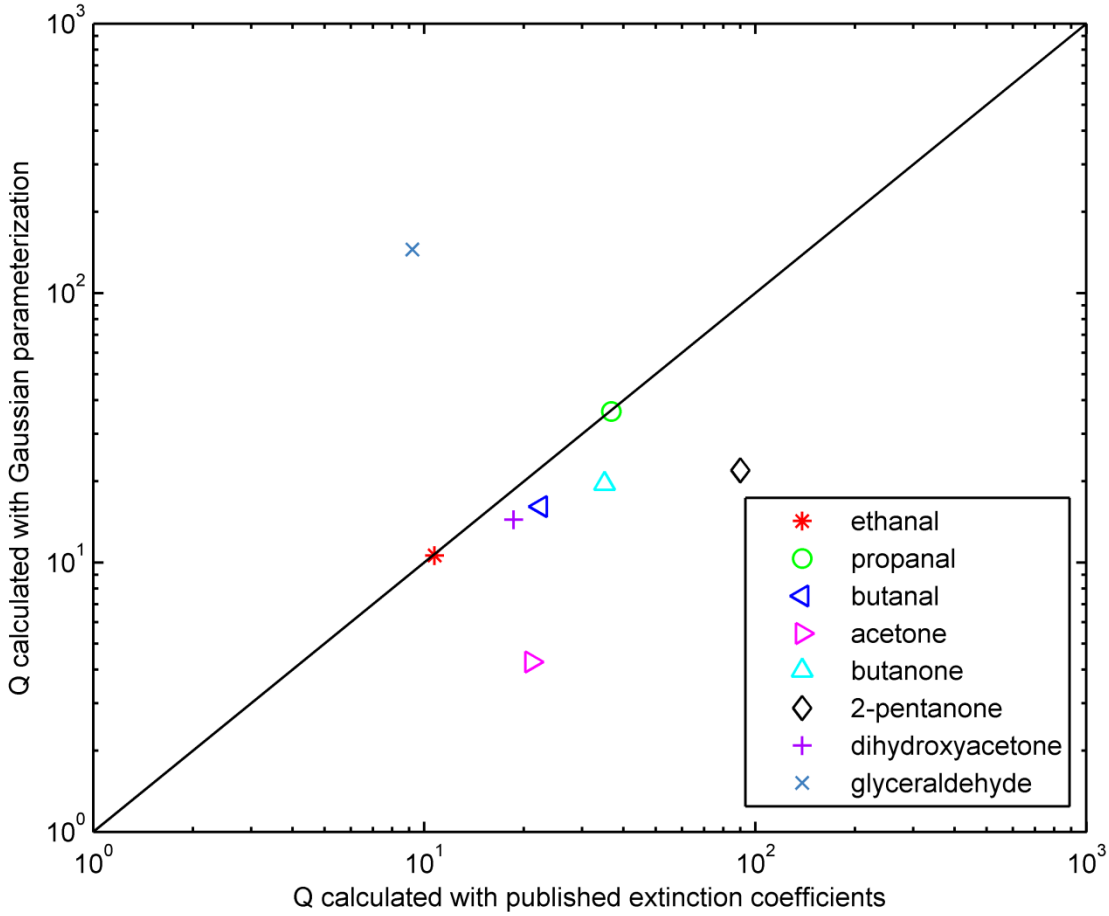



Figure S14: Comparison of Q-values calculated with published extinction coefficients as a function of wavelength and Q-values calculated with our $\lambda_{max}$ and $\varepsilon_{max}$ parameterization

## 9. Comparing Aqueous Photolysis with Aqueous Oxidation by OH at a pH of 6

Figure 5 in the manuscript was reproduced with a pH of 6. Since we do not account for the effects of pH on hydration, only the acids (levulinic acid and pyruvic acid) were affected. A higher pH increased the fraction of anion in solution leading to increased rates of oxidation by OH. However, the increase in the rate of pyruvic acid oxidation is not large enough to exceed the maximum rate of aqueous photolysis.

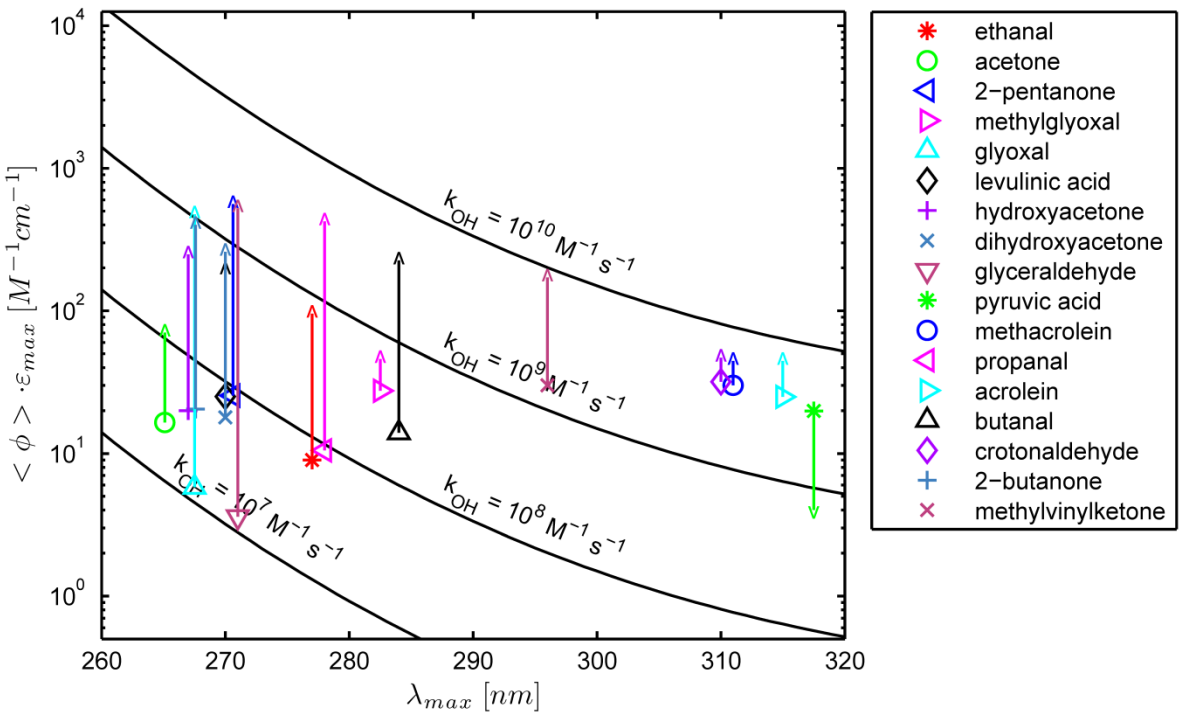



Figure S15: Comparison of aqueous photolysis at a solar zenith angle of 20$^o$ and aqueous oxidation by OH at a typical daytime concentration of $10^{-13}$ M and a pH of 6. Molecules, denoted by the markers in the key, have arrows that point to their corresponding $k_{OH}$. $k_{OH}$ isopleths correspond to $\lambda_{max}$ and $\varepsilon_{max}\cdot<\Phi>$ values where Q = 1. Molecules with values of $\lambda_{max}$ and $\varepsilon_{max}\cdot<\Phi>$ that are below their corresponding $k_{OH}$ value will be preferentially removed with oxidation by OH. Conversely, molecules with values of $\lambda_{max}$ and $\varepsilon_{max}\cdot<\Phi>$ that are above their corresponding $k_{OH}$ value will be preferentially removed by aqueous photolysis.

### 10. Predicted $k_{OH}$ as a Function of Molecular Structure

Figure S16 shows the how SAR-predicted $k_{OH}$ values vary with carbon number for the carbonyls investigated. For purposes of this illustration, all points were calculated with SAR. $k_{OH}$ values increase as carbons with additional abstractable protons are added. Diketones have the lowest rate constants for their corresponding carbon number. This is due to the deactivating ketone functionality. Hydroxyaldehydes have the largest rate constants for their corresponding carbon number due to the activating effects of an alcohol group on adjacent hydrogen atoms and the relative ease of abstracting an aldehydic hydrogen. Rate constants are capped at their diffusion limited value taken as $10^{10}$ L mol$^{-1}$ s$^{-1}$.

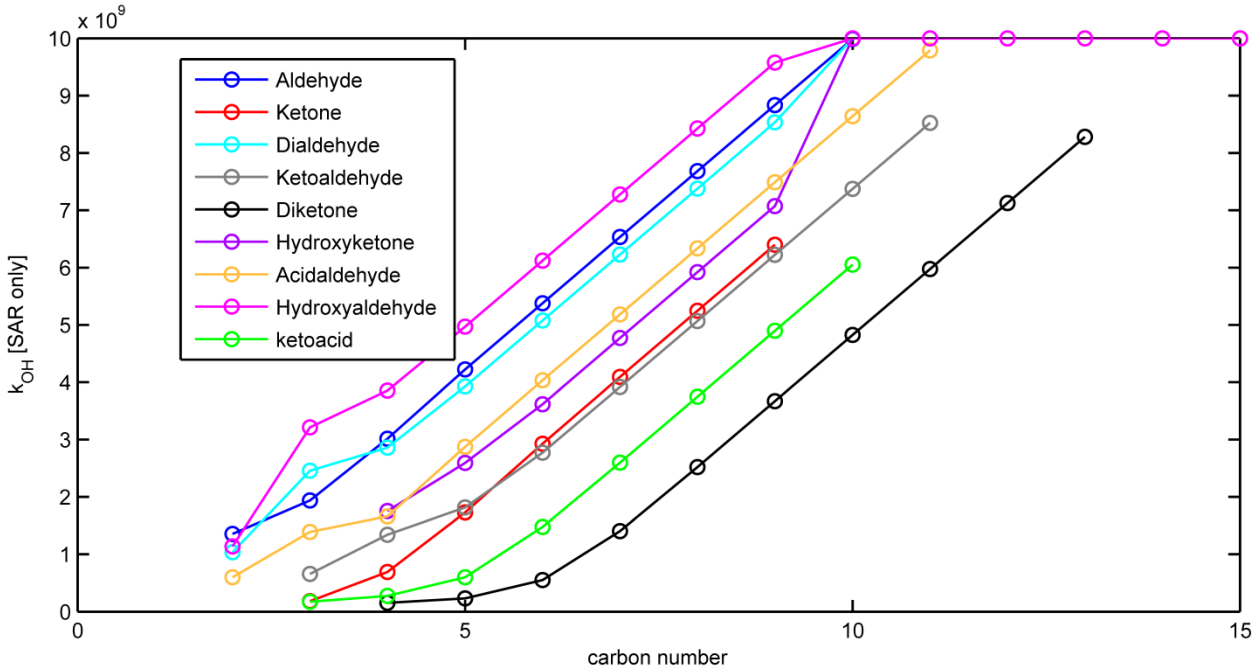



Figure S16: Aqueous rate constants for oxidation by OH as a function of carbon number (in the units of L $mol^{-1}$ $s^{-1}$). All rate constants were predicted with SAR developed by (Doussin and Monod, 2013) and (Monod and Doussin, 2008).

Figure S17 illustrates how the number of hydrogens affects $k_{OH}$ values. As expected, $k_{OH}$ values increase with increasing hydrogen number. The number of hydrogen atoms is a slightly better indicator of the value of $k_{OH}$ as the hydrogen number vs. $k_{OH}$ curves are closer together than the carbon number vs. $k_{OH}$ curves in Figure S16.

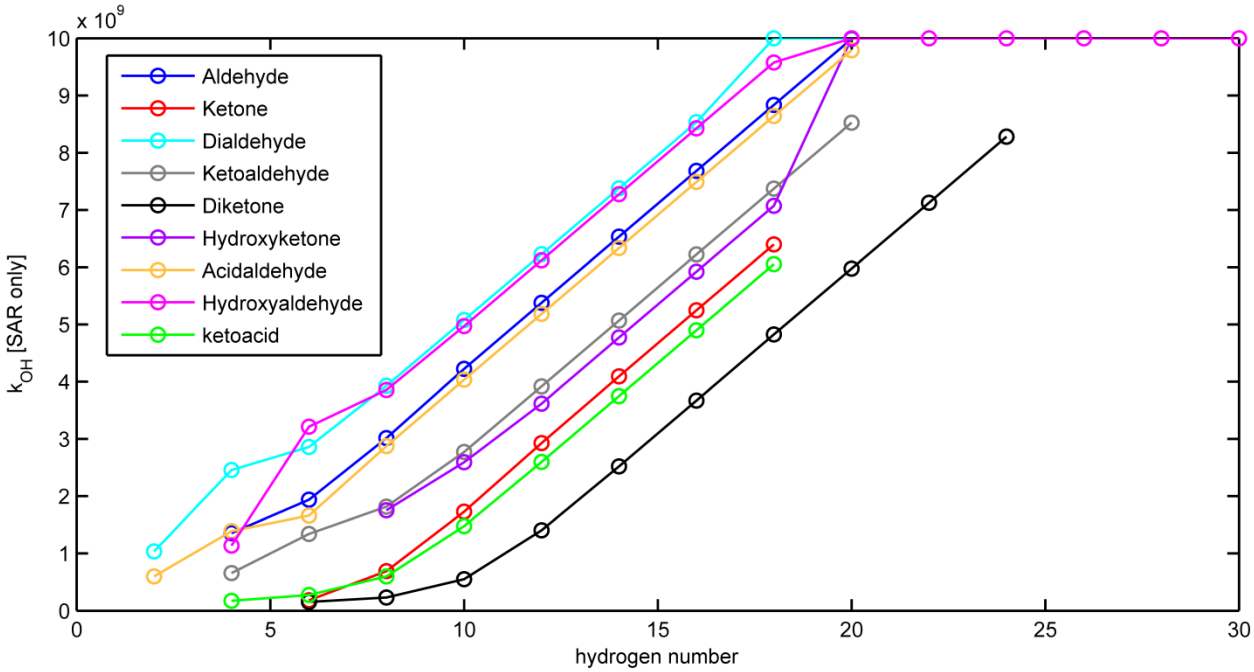
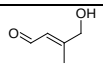
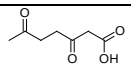
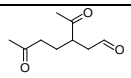
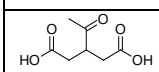



Figure S17: Aqueous rate constants for oxidation by OH as a function of hydrogen number. All rate constants were predicted with SAR developed by (Doussin and Monod, 2013) and (Monod and Doussin, 2008).

## 11. Computational Analysis of Additional Atmospherically Relevant Compounds

We chose four additional compounds to study that were identified in d-limonene (Fang et al., 2012) and isoprene (Jaoui et al., 2006) SOA. The computational methods and results are detailed in the text. Table S3 contains the calculated $\varepsilon_{max}$ and $\lambda_{max}$ values.

Table S3: Calculated $\varepsilon_{max}$ and $\lambda_{max}$ values for compounds found in d-limonene and isoprene SOA. Both 3,6-oxoheptanoic acid and ketolimonaldehyde have two peaks on their calculated spectra.

| Structure | Name | Reference | $\lambda_{max}$ [nm] | $\varepsilon_{max}$[$M^{-1}$ $cm^{-1}$] |
|---|---|---|---|---|
|  | 4-hydroxy-3-methyl-but-2-enal | (Fang et al., 2012) | 276 | 493.4 |
|  | 3,6-oxoheptanoic acid | (Jaoui et al., 2006) | 286/304 | 162.3/5.7 |
|  | ketolimononaldehyde | (Jaoui et al., 2006) | 296/299 | 179.7/192.5 |
|  | ketonorlimonic acid | (Jaoui et al., 2006) | 275 | 88.5 |

## 12. Molecular Dynamics Simulation of Molar Extinction Plots

TDDFT predictions of molar extinction as a function of wavelength for all compounds investigated with computational methods are presented in Figures S18-S27. Lower energy peaks in the visible region are predicted for dicarbonyls with adjacent carbonyl groups (biacetyl and methyl glyoxal). Strong exciton splitting of π*←n excitations result in an additional absorption band. This secondary π*←n band is present in experimental spectra of biacetyl (Cohen et al., 1948) and methyl glyoxal (Staffelbach et al., 1995). Quantum yields are typically significantly lower in the visible range than in the UV, but the enhanced actinic flux may make photolysis in the visible important.

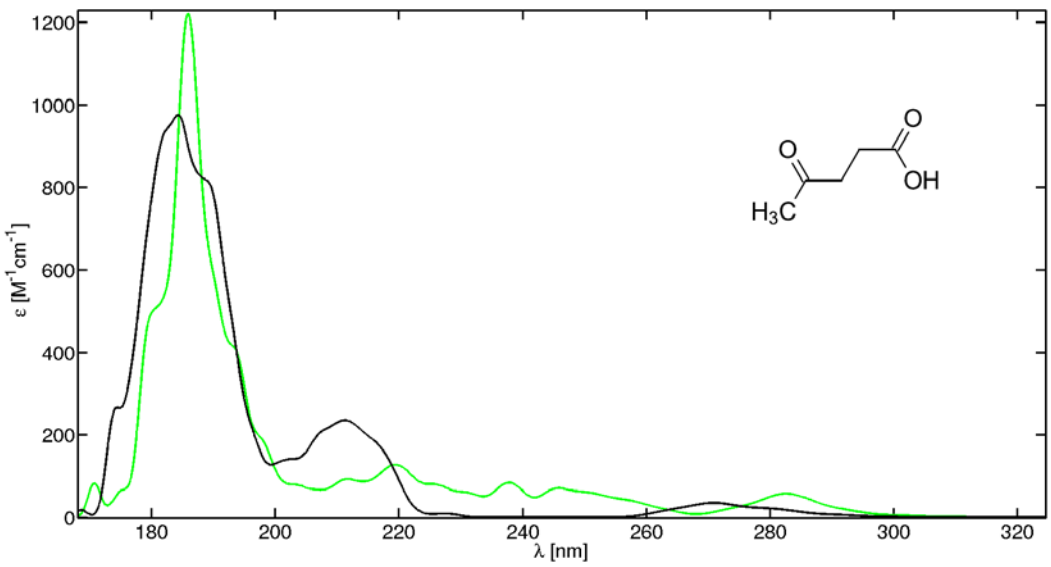



Figure S18: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) levulinic acid [4-oxopentanoic acid].

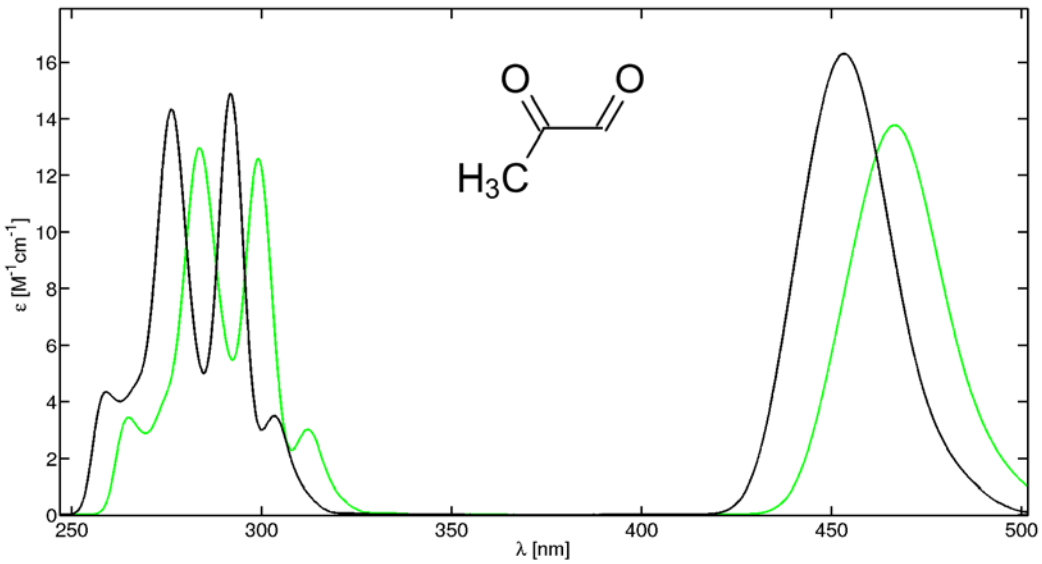



Figure S19: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) methyl glyoxal [2-oxopropanal].

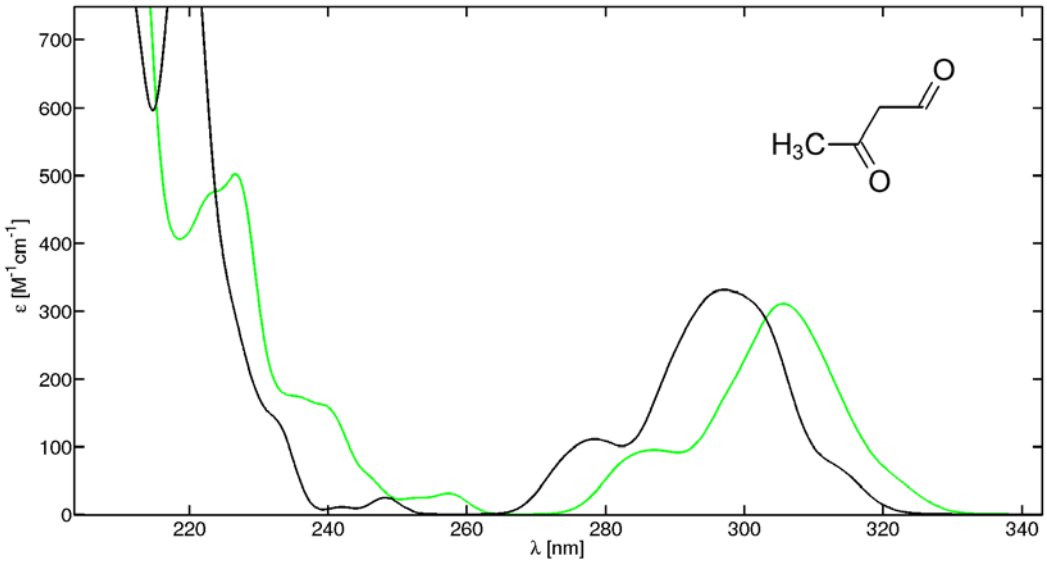



Figure S20: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) 3-oxobutanal.

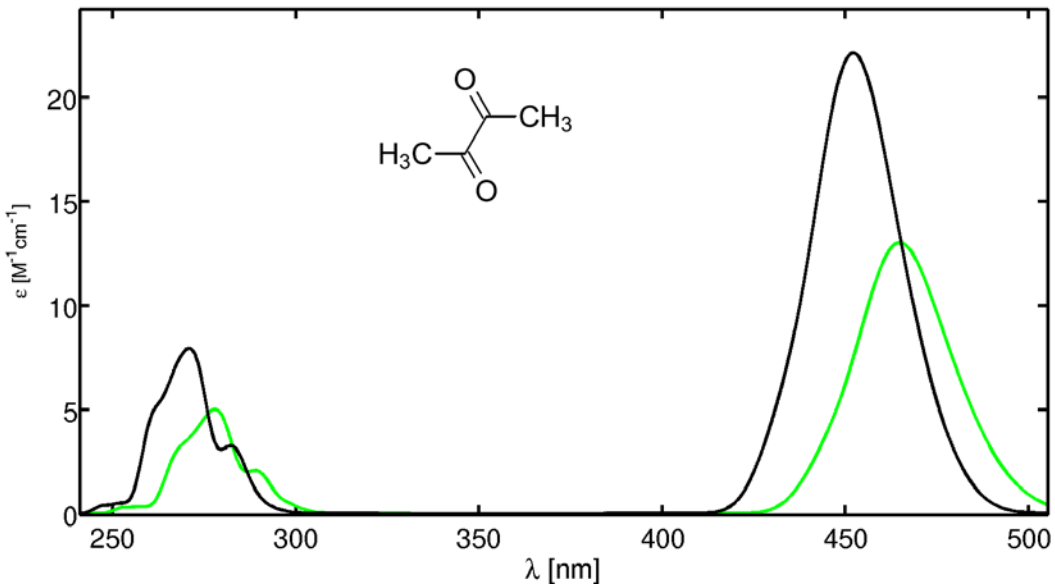



Figure S21: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) biacetyl [2,3-butanedione].

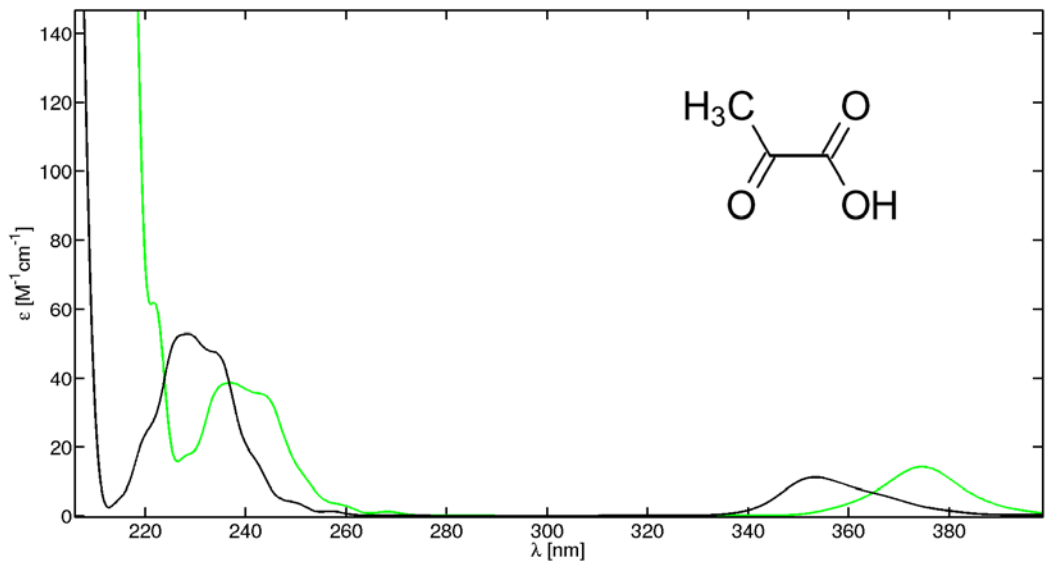



Figure S22: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) pyruvic acid [2-oxopropanoic acid].

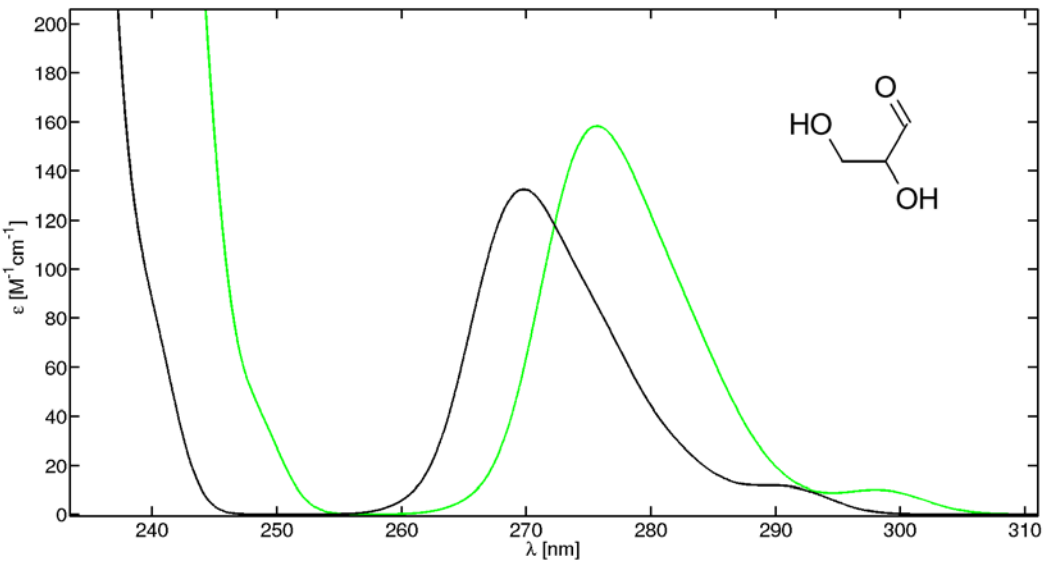



Figure S23: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) glyceraldehyde [2,3-dihydroxypropanal].

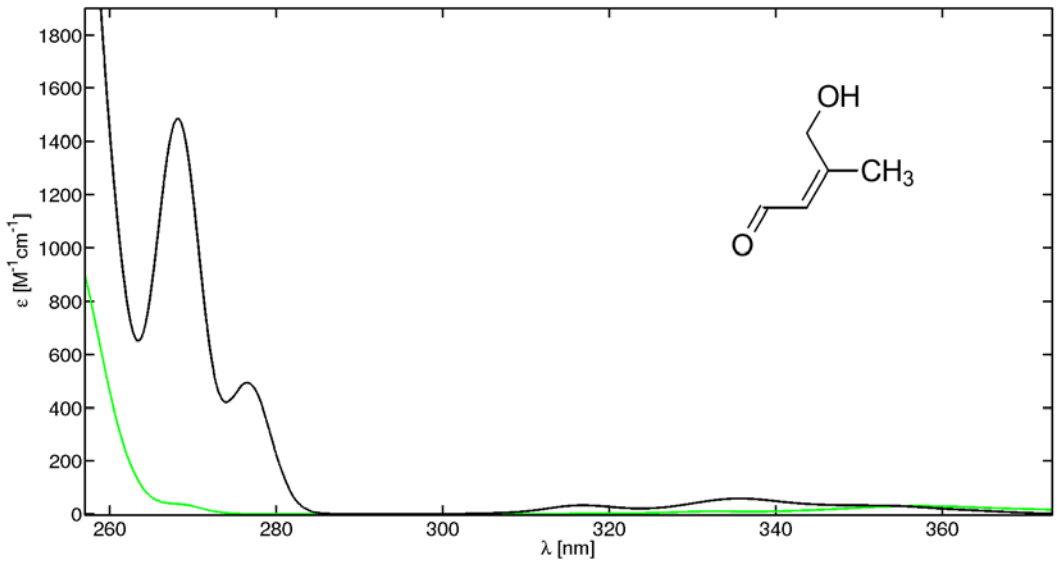



Figure S24: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) 4-hydroxy-3-methyl-but-2-enal.

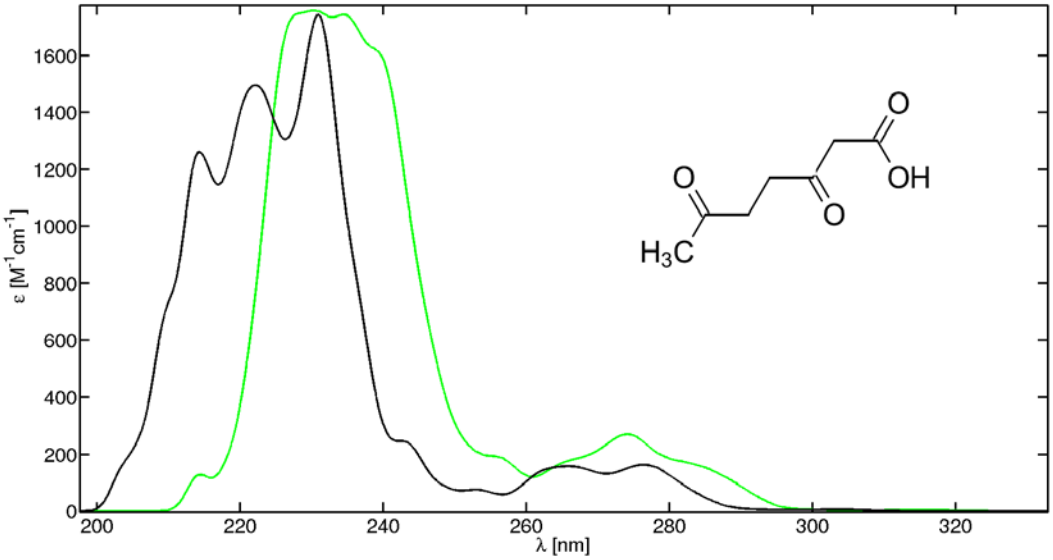



Figure S25: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) 3,6-dioxoheptanoic acid.

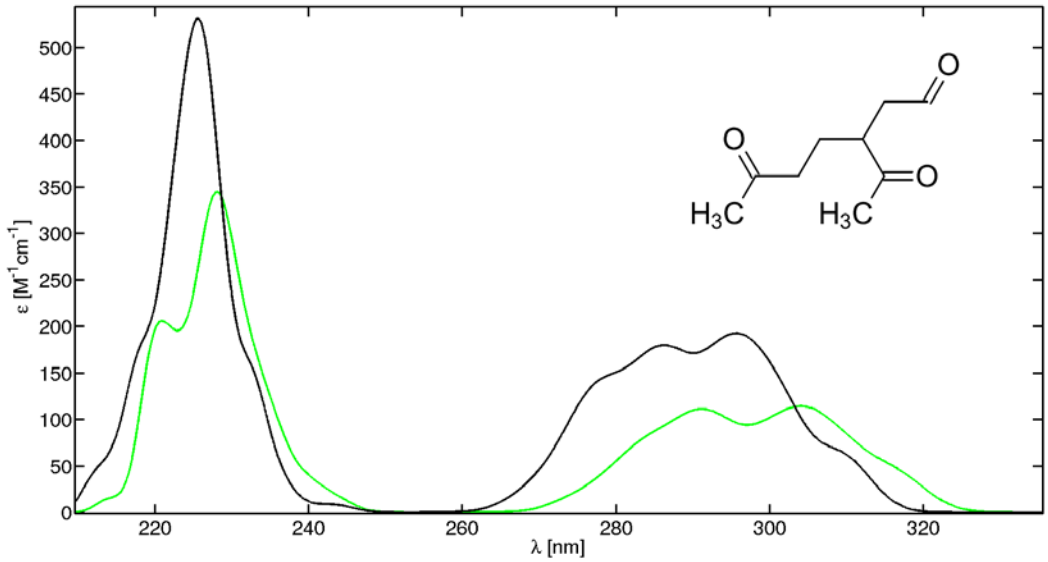



Figure S26: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) ketolimononaldehyde.

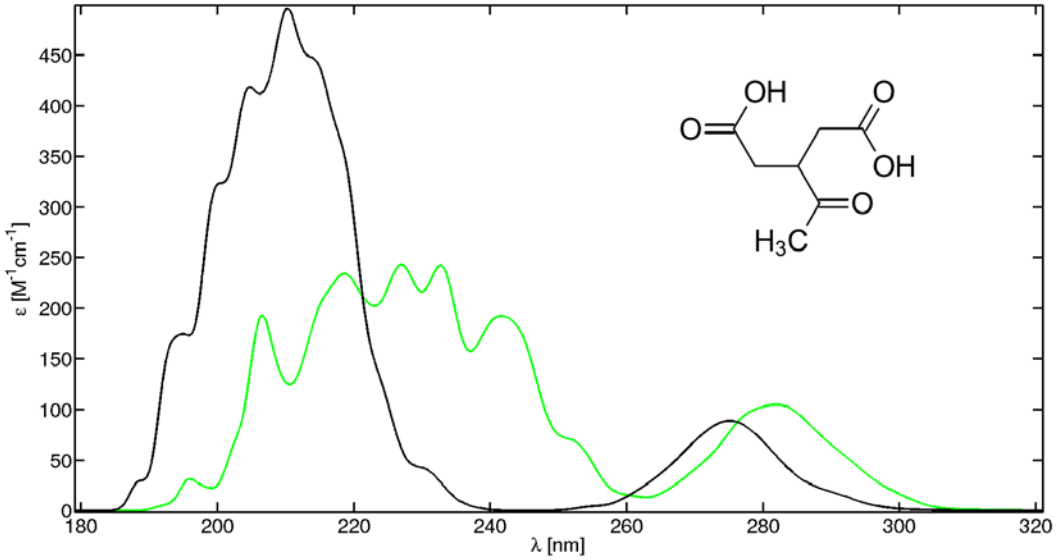



Figure S27: Calculated MD extinction coefficients for gaseous (green) and aqueous (black) ketonorlimonic acid.

## 13. Tabular Extinction Coefficients of Glyceraldehyde and Dihydroxyacetone

Table S4: Measured extinction coefficients of glyceraldehyde in terms of total (free + hydrated) concentration (i.e., decadal absorbance = total concentration × pathlength × extinction coefficient listed in the table). The uncertainties arise from the linear least-squares regression of concentration vs. absorbance when determining the extinction coefficient.

| wavelength (nm) | Extinction (1/M/cm) | uncertainty in Extinction (1/M/cm) | wavelength (nm) | Extinction (1/M/cm) | uncertainty in Extinction (1/M/cm) |
|---|---|---|---|---|---|
| 200 | 20.53 | 0.34 | 241 | 3.08 | 0.02 |
| 201 | 18.95 | 0.31 | 242 | 3.08 | 0.02 |
| 202 | 17.51 | 0.28 | 243 | 3.08 | 0.02 |
| 203 | 16.18 | 0.25 | 244 | 3.08 | 0.02 |
| 204 | 14.95 | 0.23 | 245 | 3.08 | 0.02 |
| 205 | 13.86 | 0.22 | 246 | 3.08 | 0.02 |
| 206 | 12.82 | 0.21 | 247 | 3.09 | 0.02 |
| 207 | 11.92 | 0.20 | 248 | 3.10 | 0.02 |
| 208 | 11.10 | 0.19 | 249 | 3.10 | 0.02 |
| 209 | 10.40 | 0.19 | 250 | 3.10 | 0.02 |
| 210 | 9.69 | 0.18 | 251 | 3.11 | 0.02 |
| 211 | 9.07 | 0.17 | 252 | 3.12 | 0.02 |
| 212 | 8.54 | 0.16 | 253 | 3.14 | 0.01 |
| 213 | 8.04 | 0.15 | 254 | 3.16 | 0.02 |
| 214 | 7.57 | 0.14 | 255 | 3.18 | 0.02 |
| 215 | 7.14 | 0.13 | 256 | 3.20 | 0.02 |
| 216 | 6.71 | 0.12 | 257 | 3.23 | 0.02 |
| 217 | 6.34 | 0.11 | 258 | 3.27 | 0.02 |
| 218 | 5.98 | 0.10 | 259 | 3.30 | 0.02 |
| 219 | 5.67 | 0.09 | 260 | 3.34 | 0.02 |
| 220 | 5.36 | 0.08 | 261 | 3.38 | 0.02 |
| 221 | 5.09 | 0.07 | 262 | 3.42 | 0.02 |
| 222 | 4.84 | 0.06 | 263 | 3.46 | 0.02 |
| 223 | 4.59 | 0.06 | 264 | 3.50 | 0.03 |
| 224 | 4.36 | 0.06 | 265 | 3.54 | 0.02 |
| 225 | 4.12 | 0.05 | 266 | 3.58 | 0.02 |
| 226 | 3.91 | 0.04 | 267 | 3.61 | 0.02 |
| 227 | 3.72 | 0.04 | 268 | 3.64 | 0.02 |
| 228 | 3.56 | 0.04 | 269 | 3.65 | 0.02 |
| 229 | 3.44 | 0.04 | 270 | 3.67 | 0.02 |
| 230 | 3.33 | 0.03 | 271 | 3.68 | 0.02 |
| 231 | 3.27 | 0.03 | 272 | 3.67 | 0.03 |
| 232 | 3.21 | 0.03 | 273 | 3.66 | 0.03 |
| 233 | 3.17 | 0.03 | 274 | 3.65 | 0.03 |
| 234 | 3.15 | 0.03 | 275 | 3.62 | 0.02 |
| 235 | 3.13 | 0.02 | 276 | 3.59 | 0.02 |
| 236 | 3.11 | 0.02 | 277 | 3.55 | 0.02 |
| 237 | 3.10 | 0.02 | 278 | 3.50 | 0.03 |
| 238 | 3.09 | 0.02 | 279 | 3.46 | 0.02 |
| 239 | 3.09 | 0.02 | 280 | 3.40 | 0.02 |
| 240 | 3.08 | 0.02 | 281 | 3.33 | 0.02 |

Table S4: Measured extinction coefficients of glyceraldehyde (continued).

| wavelength (nm) | Extinction (1/M/cm) | uncertainty in Extinction (1/M/cm) | wavelength (nm) | Extinction (1/M/cm) | uncertainty in Extinction (1/M/cm) |
|---|---|---|---|---|---|
| 282 | 3.26 | 0.02 | 324 | 0.63 | 0.00 |
| 283 | 3.19 | 0.02 | 325 | 0.60 | 0.00 |
| 284 | 3.12 | 0.02 | 326 | 0.57 | 0.00 |
| 285 | 3.04 | 0.02 | 327 | 0.55 | 0.00 |
| 286 | 2.96 | 0.02 | 328 | 0.52 | 0.00 |
| 287 | 2.88 | 0.02 | 329 | 0.50 | 0.00 |
| 288 | 2.79 | 0.02 | 330 | 0.48 | 0.00 |
| 289 | 2.70 | 0.02 | 331 | 0.46 | 0.00 |
| 290 | 2.61 | 0.02 | 332 | 0.44 | 0.00 |
| 291 | 2.52 | 0.01 | 333 | 0.42 | 0.00 |
| 292 | 2.43 | 0.01 | 334 | 0.41 | 0.00 |
| 293 | 2.33 | 0.01 | 335 | 0.40 | 0.00 |
| 294 | 2.24 | 0.01 | 336 | 0.38 | 0.00 |
| 295 | 2.16 | 0.01 | 337 | 0.36 | 0.00 |
| 296 | 2.07 | 0.01 | 338 | 0.35 | 0.00 |
| 297 | 1.99 | 0.01 | 339 | 0.34 | 0.01 |
| 298 | 1.90 | 0.01 | 340 | 0.33 | 0.00 |
| 299 | 1.82 | 0.01 | 341 | 0.32 | 0.00 |
| 300 | 1.74 | 0.01 | 342 | 0.31 | 0.00 |
| 301 | 1.67 | 0.01 | 343 | 0.30 | 0.00 |
| 302 | 1.60 | 0.01 | 344 | 0.29 | 0.00 |
| 303 | 1.53 | 0.01 | 345 | 0.28 | 0.00 |
| 304 | 1.46 | 0.01 | 346 | 0.27 | 0.00 |
| 305 | 1.40 | 0.00 | 347 | 0.27 | 0.00 |
| 306 | 1.33 | 0.01 | 348 | 0.26 | 0.00 |
| 307 | 1.27 | 0.00 | 349 | 0.26 | 0.00 |
| 308 | 1.22 | 0.00 | 350 | 0.25 | 0.00 |
| 309 | 1.17 | 0.00 | 351 | 0.24 | 0.00 |
| 310 | 1.12 | 0.00 | 352 | 0.24 | 0.00 |
| 311 | 1.07 | 0.00 | 353 | 0.24 | 0.01 |
| 312 | 1.03 | 0.00 | 354 | 0.23 | 0.00 |
| 313 | 0.99 | 0.01 | 355 | 0.22 | 0.00 |
| 314 | 0.95 | 0.00 | 356 | 0.22 | 0.00 |
| 315 | 0.91 | 0.00 | 357 | 0.22 | 0.01 |
| 316 | 0.87 | 0.00 | 358 | 0.21 | 0.00 |
| 317 | 0.84 | 0.00 | 359 | 0.21 | 0.00 |
| 318 | 0.80 | 0.00 | 360 | 0.20 | 0.00 |
| 319 | 0.77 | 0.00 | 361 | 0.20 | 0.00 |
| 320 | 0.74 | 0.00 | 362 | 0.20 | 0.00 |
| 321 | 0.71 | 0.00 | 363 | 0.19 | 0.01 |
| 322 | 0.68 | 0.00 | 364 | 0.19 | 0.01 |
| 323 | 0.65 | 0.00 | 365 | 0.19 | 0.00 |

Table S4: Measured extinction coefficients of glyceraldehyde (continued).

| wavelength (nm) | Extinction (1/M/cm) | uncertainty in Extinction (1/M/cm) |
|---|---|---|
| 366 | 0.18 | 0.00 |
| 367 | 0.18 | 0.00 |
| 368 | 0.17 | 0.00 |
| 369 | 0.17 | 0.01 |
| 370 | 0.17 | 0.01 |
| 371 | 0.16 | 0.00 |
| 372 | 0.16 | 0.00 |
| 373 | 0.16 | 0.00 |
| 374 | 0.16 | 0.00 |
| 375 | 0.15 | 0.00 |
| 376 | 0.15 | 0.00 |
| 377 | 0.15 | 0.00 |
| 378 | 0.14 | 0.01 |
| 379 | 0.14 | 0.00 |
| 380 | 0.14 | 0.00 |
| 381 | 0.14 | 0.00 |
| 382 | 0.13 | 0.00 |
| 383 | 0.13 | 0.00 |
| 384 | 0.12 | 0.00 |
| 385 | 0.12 | 0.00 |
| 386 | 0.12 | 0.00 |
| 387 | 0.12 | 0.00 |
| 388 | 0.12 | 0.00 |
| 389 | 0.12 | 0.00 |
| 390 | 0.11 | 0.00 |
| 391 | 0.11 | 0.00 |
| 392 | 0.11 | 0.00 |
| 393 | 0.11 | 0.00 |
| 394 | 0.11 | 0.00 |
| 395 | 0.10 | 0.00 |
| 396 | 0.10 | 0.00 |
| 397 | 0.10 | 0.00 |
| 398 | 0.10 | 0.00 |
| 399 | 0.09 | 0.00 |
| 400 | 0.09 | 0.00 |

Table S5: Measured extinction coefficients of dihydroxyacetone in terms of total (free + hydrated) concentration. The uncertainties arise from the linear least-squares regression of concentration vs. absorbance when determining the extinction coefficient.

| wavelength (nm) | Extinction (1/M/cm) | uncertainty in Extinction (1/M/cm) | wavelength (nm) | Extinction (1/M/cm) | uncertainty in Extinction (1/M/cm) |
|---|---|---|---|---|---|
| 200 | 6.32 | 0.20 | 284 | 13.53 | 0.03 |
| 202 | 8.04 | 1.12 | 286 | 12.31 | 0.03 |
| 204 | 13.45 | 4.17 | 288 | 11.11 | 0.04 |
| 206 | 21.12 | 6.43 | 290 | 9.81 | 0.04 |
| 208 | 27.16 | 4.04 | 292 | 8.53 | 0.06 |
| 210 | 25.43 | 0.74 | 294 | 7.27 | 0.02 |
| 212 | 18.37 | 0.14 | 296 | 6.10 | 0.04 |
| 214 | 12.37 | 0.07 | 298 | 5.06 | 0.04 |
| 216 | 8.06 | 0.09 | 300 | 4.10 | 0.03 |
| 218 | 5.24 | 0.06 | 302 | 3.28 | 0.01 |
| 220 | 3.50 | 0.04 | 304 | 2.61 | 0.02 |
| 222 | 2.50 | 0.03 | 306 | 1.94 | 0.01 |
| 224 | 1.98 | 0.03 | 308 | 1.47 | 0.01 |
| 226 | 1.81 | 0.01 | 310 | 1.07 | 0.01 |
| 228 | 1.88 | 0.02 | 312 | 0.81 | 0.01 |
| 230 | 2.14 | 0.01 | 314 | 0.58 | 0.01 |
| 232 | 2.52 | 0.00 | 316 | 0.42 | 0.01 |
| 234 | 2.98 | 0.01 | 318 | 0.30 | 0.02 |
| 236 | 3.55 | 0.01 | 320 | 0.22 | 0.01 |
| 238 | 4.26 | 0.02 | 322 | 0.17 | 0.01 |
| 240 | 5.08 | 0.01 | 324 | 0.12 | 0.00 |
| 242 | 6.00 | 0.03 | 326 | 0.09 | 0.01 |
| 244 | 6.95 | 0.04 | 328 | 0.07 | 0.02 |
| 246 | 8.00 | 0.01 | 330 | 0.06 | 0.01 |
| 248 | 9.07 | 0.02 | 332 | 0.03 | 0.01 |
| 250 | 10.19 | 0.02 | 334 | 0.04 | 0.01 |
| 252 | 11.34 | 0.02 | 336 | 0.02 | 0.01 |
| 254 | 12.45 | 0.03 | 338 | 0.03 | 0.01 |
| 256 | 13.58 | 0.01 | 340 | 0.00 | 0.00 |
| 258 | 14.59 | 0.03 | 342 | 0.02 | 0.01 |
| 260 | 15.51 | 0.04 | 344 | 0.00 | 0.01 |
| 262 | 16.32 | 0.04 | 346 | 0.03 | 0.01 |
| 264 | 17.00 | 0.03 | 348 | 0.01 | 0.01 |
| 266 | 17.54 | 0.01 | 350 | 0.01 | 0.01 |
| 268 | 17.81 | 0.02 | 352 | 0.02 | 0.01 |
| 270 | 17.95 | 0.02 | 354 | 0.02 | 0.01 |
| 272 | 17.83 | 0.02 | 356 | 0.01 | 0.01 |
| 274 | 17.56 | 0.03 | 358 | 0.02 | 0.01 |
| 276 | 17.12 | 0.05 | 360 | 0.02 | 0.02 |
| 278 | 16.43 | 0.04 | 362 | 0.00 | 0.00 |
| 280 | 15.58 | 0.04 | 364 | 0.02 | 0.01 |
| 282 | 14.63 | 0.04 | 366 | 0.00 | 0.01 |

Table S5: Measured extinction coefficients of dihydroxyacetone (continued)

| wavelength (nm) | Extinction (1/M/cm) | uncertainty in Extinction (1/M/cm) |
|---|---|---|
| 368 | 0.02 | 0.01 |
| 370 | 0.00 | 0.00 |
| 372 | 0.01 | 0.01 |
| 374 | 0.00 | 0.00 |
| 376 | 0.00 | 0.00 |
| 378 | 0.00 | 0.00 |
| 380 | 0.00 | 0.00 |
| 382 | 0.01 | 0.01 |
| 384 | 0.00 | 0.01 |
| 386 | 0.00 | 0.00 |
| 388 | 0.00 | 0.00 |
| 390 | 0.00 | 0.00 |
| 392 | 0.00 | 0.00 |
| 394 | 0.00 | 0.00 |
| 396 | 0.00 | 0.00 |
| 398 | 0.00 | 0.00 |
| 400 | 0.00 | 0.00 |

## 14. Expected Chemical Mechanism of Glyceraldehyde Photolysis

Figure S28 illustrates all of the expected primary and secondary channels of glyceraldehyde photolysis. Note the presence of the glyceraldehyde structural isomer upon reaction between glycolaldehyde and formaldehyde. Significant production of this isomer could lead to underestimations in the photolysis quantum yield of glyceraldehyde with the ESI-MS method described above.

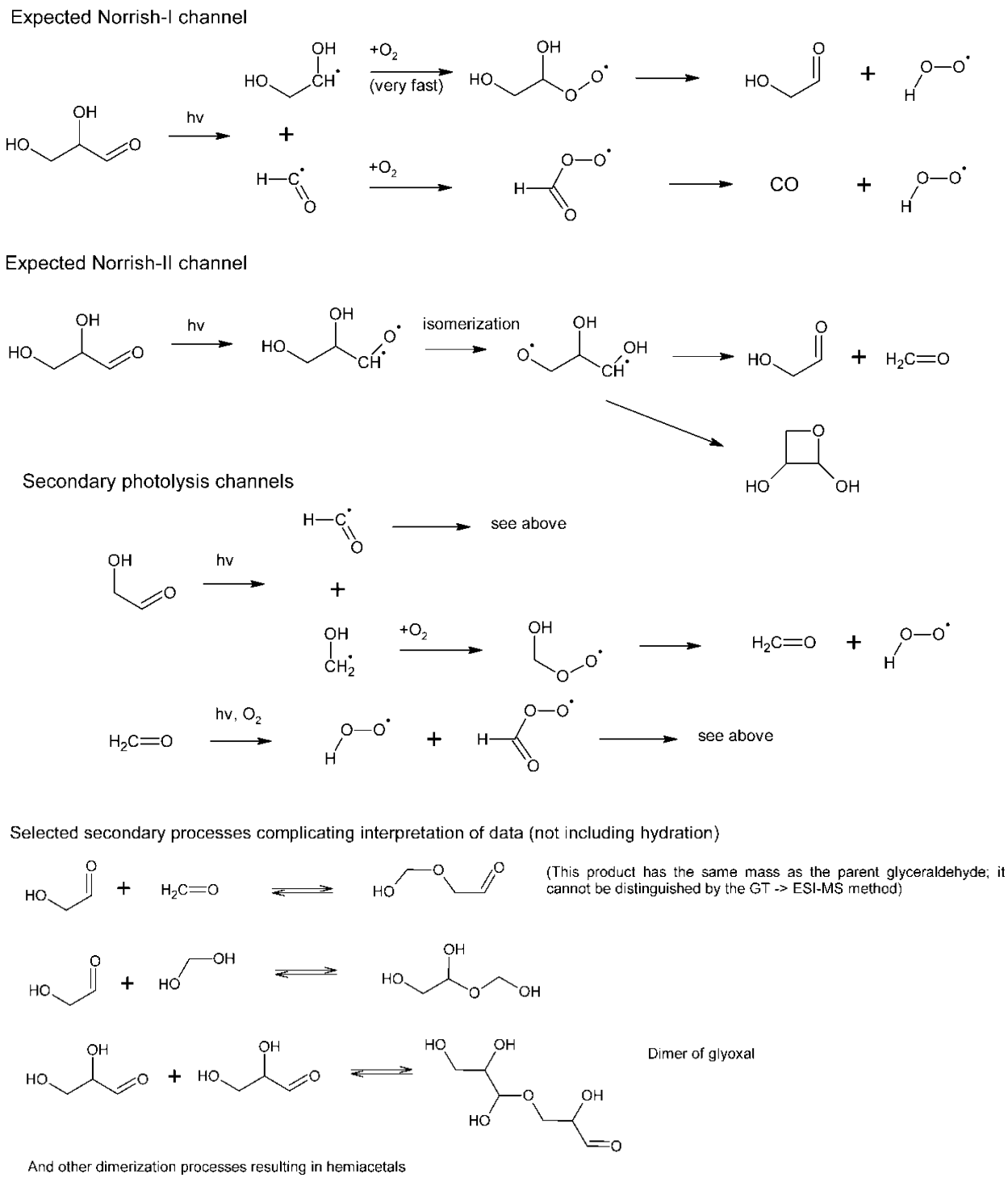



Figure S28: Chemical Mechanism of Glyceraldehyde Photolysis

**15. Comparison of Aqueous Photolysis and Aqueous Oxidation by OH for 4-hydroxy-3-methyl-but-2-enal, 3,6-oxoheptanoic acid, ketolimonaldehyde, and ketonorlimonic acid**

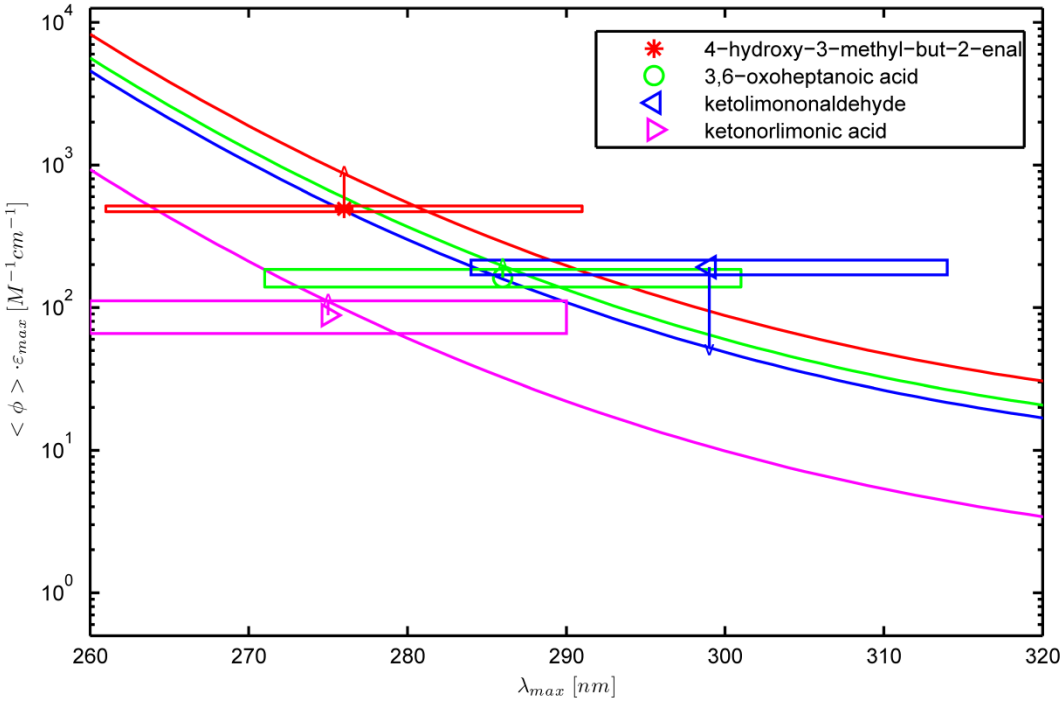



Figure S29**:** **C**omparison of aqueous photolysis at a solar zenith angle of 20$^o$ and aqueous oxidation by OH at a typical daytime concentration of $10^{-13}$ M and a pH of 2. Molecules, denoted by the markers in the key, have arrows that point to their corresponding $k_{OH}$. Isopleths correspond to $\lambda_{max}$ and $\varepsilon_{max}\cdot\langle\Phi\rangle$ values where Q = 1 at the $k_{OH}$ value of the molecule indicated with the same color. Rectangles indicate the bounds of the mean absolute errors calculated from TDDFT predictions of compounds with published extinction coefficients. Molecules with values of $\lambda_{max}$ and $\varepsilon_{max}\cdot\langle\Phi\rangle$ that are below their corresponding $k_{OH}$ value will be preferentially removed with oxidation by OH. Conversely, molecules with values of $\lambda_{max}$ and $\varepsilon_{max}\cdot\langle\Phi\rangle$ that are above their corresponding $k_{OH}$ value will be preferentially removed by aqueous photolysis.

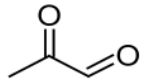
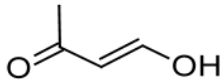
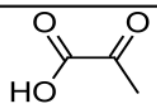
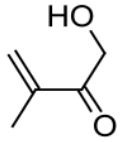
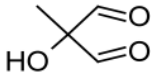
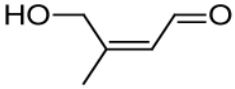
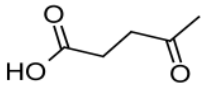
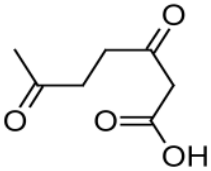
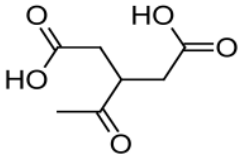
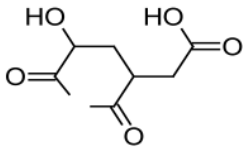
## 16. Parameters Used to Construct Figure 3

Table S6: Computational and experimental parameters used to model the SOA relevant compounds plotted in Figure 3.

| Molecule Name | Molecule Ref. | KH (atm-m^3/mol) | log(Khyd) | log(Khyd) 2nd most likely | KH Ref. | Khyd Ref. | kOH Aqueous pH = 2 | kOH Aqueous pH = 6 | kOH Aq. Ref. |
|---|---|---|---|---|---|---|---|---|---|
| methyl glyoxal | Fang (2012) | 2.70E-07 | 1.82 | -0.13 | Betterton (1998) | SPARC | - | - | - |
| 4-hydroxybut-3-en-2-one (keto-enol equilibrium forms 3-oxobutanal) | Fang (2012) | 4.56E-08 | 1.53 | 0.71 | HENRYWIN bond | SPARC | - | - | - |
| pyruvic acid | Fang (2012) | 3.32E-09 | -1.3 | - | Khan (1992) | SPARC | - | - | - |
| 1-hydroxy-3-methylbut-3-en-2-one | Fang (2012) | 6.39E-06 | -3.11 | - | HENRYWIN bond | SPARC | - | - | - |
| 2-methyl-2-oxidanyl-propanedial | Fang (2012) | 1.29E-08 | 1.83 | 0.55 | HENRYWIN bond | SPARC | - | - | - |
| 4-hydroxy-3-methyl-but-2-enal | Fang (2012) | 8.88E-10 | -2.17 | - | HENRYWIN group | SPARC | 5.88E+09 | 5.88E+09 | Buxton (1988) + SAR |
| levulinic acid | Jaoui (2006) | 5.48E-11 | -3.64 | - | HENRYWIN group | SPARC | - | - | - |
| 3,6-oxoheptanoic acid | Jaoui (2006) | 3.29E-13 | -1.28 | -0.2 | HENRYWIN group | SPARC | 6.00E+08 | 4.00E+09 | SAR |
| ketonorlimonic acid | Jaoui (2006) | 1.17E-16 | -5.34 | - | HENRYWIN group | SPARC | 2.10E+08 | 6.60E+08 | SAR |
| ketolimonaldehyde | Jaoui (2006) | 4.55E-12 | -1.09 | -3.69 | HENRYWIN group | SPARC | 3.25E+09 | 3.25E+09 | SAR |

## 17. Structure of Molecules in Figure 3

Table S7: Molecular structures of SOA relevant compounds investigated in Figure 3

| Label in Figure 3 | Molecule Name | Molecule Reference | Structure |
|---|---|---|---|
| A | methyl glyoxal | Fang (2012) |  |
| B | 4-hydroxybut-3-en-2-one | Fang (2012) |  |
| C | pyruvic acid | Fang (2012) |  |
| D | 1-hydroxy-3-methylbut-3-en-2-one | Fang (2012) |  |
| E | 2-methyl-2-oxidanyl-propanedial | Fang (2012) |  |
| F | 4-hydroxy-3-methyl-but-2-enal | Fang (2012) |  |
| G | levulinic acid | Jaoui (2006) |  |
| H | 3,6-oxoheptanoic acid | Jaoui (2006) |  |
| I | ketonorlimonic acid | Jaoui (2006) |  |
| J | ketolimonaldehyde | Jaoui (2006) |  |

## 18. Parameters Used to Construct Figures 4 and 5

Table S8: References and parameters used to generate Figures 4 and 5

| Name | εmax | λmax | Reference | aq. kOH pH = 2 | aq. kOH pH = 6 | Reference |
|---|---|---|---|---|---|---|
| ethanal | 9 | 277 | Xu (1993) | 7.30E+08 | 7.30E+08 | Buxton (1988) |
| acetone [2-propanone] | 16.5 | 265.1 | Xu (1993) | 1.10E+08 | 1.10E+08 | Buxton (1988) |
| 2–pentanone | 25.5 | 270.6 | Xu (1993) | 1.90E+09 | 1.90E+09 | Buxton (1988) |
| methyl glyoxal [2-oxopropanal] | 27.5 | 282.5 | Mackinney (1948) | 6.56E+08 | 6.56E+08 | Lim (2005) |
| glyoxal [1,2-ethanedione] | 5.8 | 267.5 | Mackinney (1948) | 1.05E+09 | 1.05E+09 | Buxton (1988) |
| levulinic acid [4-oxopentanoic acid] | 25.1 | 270 | Mackinney (1948) | 4.90E+08 | 6.00E+08 | SAR |
| hydroxyacetone [1-hydroxy-2-propanone] | 20 | 267 | Steenken (1975) | 5.11E+08 | 5.11E+08 | SAR |
| dihydroxyacetone [1,3-Dihydroxy-2-propanone] | 17.95 | 270 | This Work | 8.11E+08 | 8.11E+08 | SAR |
| glyceraldehyde [2,3-dihydroxypropanal] | 3.6 | 271 | This Work | 1.88E+09 | 1.88E+09 | SAR |
| pyruvic acid [2-oxo-propanoic acid] | 19.9 | 317.5 | Mackinney (1948) | 2.70E+08 | 7.00E+08 | Ervens (2003) |
| methacrolein [2-methyl-2-propenal] | 30 | 311 | Liu (2009) | 5.80E+09 | 5.80E+09 | Liu (2009) |
| propanal | 10.5 | 278 | Xu (1993) | 3.65E+09 | 3.65E+09 | Monod (2005) |
| acrolein [2-propenal] | 25 | 315 | Sham (1995) | 7.00E+09 | 7.00E+09 | Buxton (1988) |
| butanal | 14 | 284 | Xu (1993) | 3.77E+09 | 3.77E+09 | Buxton (1988) |
| crotonaldehyde [2-butenal] | 31.8 | 310 | Mackinney (1948) | 5.80E+09 | 5.80E+09 | Buxton (1988) |
| 2-butanone | 20.5 | 267.6 | Xu (1993) | 9.00E+08 | 9.00E+08 | Buxton (1988) |
| methylvinylketone [3-butene-2-one] | 30 | 296 | Renard (2013) | 8.50E+09 | 8.50E+09 | Buxton (1988) |

## 19. Parameters Used to Construct Figures 2, 6, and S9-S13

**Table S9: Henry's Law constants used to construct Figures 2, 6, and S9-13**

| Name | Functional Group | C# | kH (atm-m^3/mol) | kH Ref. |
|---|---|---|---|---|
| formaldehyde | Aldehyde | 1 | 3.37E-07 | Betterton (1988) |
| ethanal (acetaldehyde) | Aldehyde | 2 | 6.67E-05 | Betterton (1988) |
| propanal | Aldehyde | 3 | 7.34E-05 | Betterton (1988) |
| butanal | Aldehyde | 4 | 1.00E-04 | Zhou (1990) |
| pentanal | Aldehyde | 5 | 1.58E-04 | Zhou (1990) |
| hexanal | Aldehyde | 6 | 2.00E-04 | Zhou (1990) |
| heptanal | Aldehyde | 7 | 3.16E-04 | Zhou (1990) |
| octanal | Aldehyde | 8 | 5.01E-04 | Zhou (1990) |
| nonanal | Aldehyde | 9 | 1.00E-03 | Zhou (1990) |
| decanal | Aldehyde | 10 | 1.58E-03 | Zhou (1990) |
| propan-2-one (acetone) | Ketone | 3 | 3.16E-05 | Staudingers (1996) |
| butan-2-one | Ketone | 4 | 5.01E-05 | Staudingers (1996) |
| pentan-2-one | Ketone | 5 | 6.31E-05 | Buttery (1971) |
| hexan-2-one | Ketone | 6 | 1.58E-04 | Buttery (1971) |
| heptan-2-one | Ketone | 7 | 2.00E-04 | Buttery (1971) |
| octan-2-one | Ketone | 8 | 3.98E-04 | Buttery (1971) |
| nonan-2-one | Ketone | 9 | 6.31E-04 | Buttery (1971) |
| ethanedial (glyoxal) | Dialdehyde | 2 | 2.38E-09 | Ip (2009) |
| propanedial | Dialdehyde | 3 | 6.25E-08 | HENRYWIN group estimate |
| butanedial | Dialdehyde | 4 | 1.69E-08 | HENRYWIN group estimate |
| pentanedial | Dialdehyde | 5 | 2.39E-08 | HENRYWIN group estimate |
| hexanedial | Dialdehyde | 6 | 3.38E-08 | HENRYWIN group estimate |
| heptanedial | Dialdehyde | 7 | 4.77E-08 | HENRYWIN group estimate |

Table S9 (continued)

| | | | | |
|---|---|---|---|---|
| octanedial | Dialdehyde | 8 | 6.74E-08 | HENRYWIN group estimate |
| nonanedial | Dialdehyde | 9 | 9.52E-08 | HENRYWIN group estimate |
| decanedial | Dialdehyde | 10 | 1.34E-07 | HENRYWIN group estimate |
| undecanedial | Dialdehyde | 11 | 1.90E-07 | HENRYWIN group estimate |
| dodecanedial | Dialdehyde | 12 | 2.68E-07 | HENRYWIN group estimate |
| 2-oxopropanal (methyl glyoxal) | Ketoaldehyde | 3 | 2.70E-07 | Betterton (1988) |
| 3-oxobutanal | Ketoaldehyde | 4 | 4.56E-08 | HENRYWIN bond estimate |
| 4-oxopentanal | Ketoaldehyde | 5 | 1.12E-08 | HENRYWIN group estimate |
| 5-oxohexanal | Ketoaldehyde | 6 | 1.58E-08 | HENRYWIN group estimate |
| 6-oxoheptanal | Ketoaldehyde | 7 | 2.23E-08 | HENRYWIN group estimate |
| 7-oxooctanal | Ketoaldehyde | 8 | 3.15E-08 | HENRYWIN group estimate |
| 8-oxononanal | Ketoaldehyde | 9 | 4.45E-08 | HENRYWIN group estimate |
| 9-oxodecanal | Ketoaldehyde | 10 | 6.29E-08 | HENRYWIN group estimate |
| 10-oxoundecanal | Ketoaldehyde | 11 | 8.88E-08 | HENRYWIN group estimate |
| butane-2,3-dione (biacetyl) | Diketone | 4 | 1.33E-05 | Betterton (1981) |
| pentane-2,4-dione | Diketone | 5 | 2.35E-06 | HENRYWIN experimental database |
| hexane-2,5-dione (acetonylacetone) | Diketone | 6 | 7.39E-09 | HENRYWIN group estimate |
| heptane-2,6-dione | Diketone | 7 | 1.04E-08 | HENRYWIN group estimate |
| octane-2,7-dione | Diketone | 8 | 1.47E-08 | HENRYWIN group estimate |
| nonane-2,8-dione | Diketone | 9 | 2.08E-08 | HENRYWIN group estimate |
| decane-2,9-dione | Diketone | 10 | 2.94E-08 | HENRYWIN group estimate |
| undecane-2,10-dione | Diketone | 11 | 4.15E-08 | HENRYWIN group estimate |

Table S9 (continued)

| | | | | |
|---|---|---|---|---|
| dodecane-2,11-dione | Diketone | 12 | 5.87E-08 | HENRYWIN group estimate |
| tridecane-2,12-dione | Diketone | 13 | 8.29E-08 | HENRYWIN group estimate |
| 1-hydroxypropan-2-one (hydroxyacetone) | Hydroxyketone | 3 | 8.48E-09 | HENRYWIN group estimate |
| 4-hydroxybutan-2-one | Hydroxyketone | 4 | 6.43E-10 | HENRYWIN group estimate |
| 5-hydroxypentan-2-one | Hydroxyketone | 5 | 9.09E-10 | HENRYWIN group estimate |
| 6-hydroxyhexan-2-one | Hydroxyketone | 6 | 1.28E-09 | HENRYWIN group estimate |
| 7-hydroxyheptan-2-one | Hydroxyketone | 7 | 1.81E-09 | HENRYWIN group estimate |
| 8-hydroxyoctan-2-one | Hydroxyketone | 8 | 2.56E-09 | HENRYWIN group estimate |
| 9-hydroxynonan-2-one | Hydroxyketone | 9 | 3.62E-09 | HENRYWIN group estimate |
| 10-hydroxydecan-2-one | Hydroxyketone | 10 | 5.11E-09 | HENRYWIN group estimate |
| 11-hydroxyundecan-2-one | Hydroxyketone | 11 | 7.22E-09 | HENRYWIN group estimate |
| 12-hydroxydodecan-2-one | Hydroxyketone | 12 | 1.02E-08 | HENRYWIN group estimate |
| 13-hydroxytridecan-2-one | Hydroxyketone | 13 | 1.44E-08 | HENRYWIN group estimate |
| 14-hydroxytetradecan-2-one | Hydroxyketone | 14 | 2.03E-08 | HENRYWIN group estimate |
| 2-oxoethanoic acid (glyoxylic acid) | Aldehydic Acid | 2 | 9.17E-08 | Ip (2009) |
| 3-oxopropanoic acid | Aldehydic Acid | 3 | 1.43E-10 | Saxena and Hildeman (1996) |
| 4-oxobutanoic acid | Aldehydic Acid | 4 | 8.29E-11 | HENRYWIN group estimate |
| 5-oxopentanoic acid | Aldehydic Acid | 5 | 1.17E-10 | HENRYWIN group estimate |
| 6-oxohexanoic acid | Aldehydic Acid | 6 | 1.65E-10 | HENRYWIN group estimate |
| 7-oxoheptanoic acid | Aldehydic Acid | 7 | 2.34E-10 | HENRYWIN group estimate |
| 8-oxooctanoic acid | Aldehydic Acid | 8 | 3.30E-10 | HENRYWIN group estimate |
| 9-oxononanoic acid | Aldehydic Acid | 9 | 4.66E-10 | HENRYWIN group estimate |
| 10-oxodecanoic acid | Aldehydic Acid | 10 | 6.58E-10 | HENRYWIN group estimate |

Table S9 (continued)

| | | | | |
|---|---|---|---|---|
| 11-oxoundecanoic acid | Aldehydic Acid | 11 | 9.30E-10 | HENRYWIN group estimate |
| 2-hydroxyethanal (formic acid) | Hydroxyaldehyde | 2 | 2.51E-08 | Betterton (1988) |
| 3-hydroxypropanal | Hydroxyaldehyde | 3 | 9.74E-10 | HENRYWIN group estimate |
| 4-hydroxybutanal | Hydroxyaldehyde | 4 | 1.38E-09 | HENRYWIN group estimate |
| 5-hydroxypentanal | Hydroxyaldehyde | 5 | 1.94E-09 | HENRYWIN group estimate |
| 6-hydroxyhexanal | Hydroxyaldehyde | 6 | 2.74E-09 | HENRYWIN group estimate |
| 7-hydroxyheptanal | Hydroxyaldehyde | 7 | 3.88E-09 | HENRYWIN group estimate |
| 8-hydroxyoctanal | Hydroxyaldehyde | 8 | 5.48E-09 | HENRYWIN group estimate |
| 9-hydroxynonanal | Hydroxyaldehyde | 9 | 7.73E-09 | HENRYWIN group estimate |
| 10-hydroxydecanal | Hydroxyaldehyde | 10 | 1.09E-08 | HENRYWIN group estimate |
| 11-hydroxyundecanal | Hydroxyaldehyde | 11 | 1.54E-08 | HENRYWIN group estimate |
| 12-hydroxydodecanal | Hydroxyaldehyde | 12 | 2.18E-08 | HENRYWIN group estimate |
| 13-hydroxytridecanal | Hydroxyaldehyde | 13 | 3.08E-08 | HENRYWIN group estimate |
| 14-hydroxytetradecanal | Hydroxyaldehyde | 14 | 4.35E-08 | HENRYWIN group estimate |
| 15-hydroxypentadecanal | Hydroxyaldehyde | 15 | 6.14E-08 | HENRYWIN group estimate |
| 2-oxopropanoic acid (pyruvic acid) | Keto Acid | 3 | 3.23E-09 | Pocker (1969) |
| 3-oxobutanoic acid (acetoacetic acid) | Keto Acid | 4 | 3.69E-10 | HENRYWIN bond estimate |
| 4-oxopentanoic acid (levulinic acid) | Keto Acid | 5 | 4.89E-10 | HENRYWIN bond estimate |
| 5-oxohexanoic acid | Keto Acid | 6 | 6.49E-10 | HENRYWIN bond estimate |
| 6-oxoheptanoic acid | Keto Acid | 7 | 8.62E-10 | HENRYWIN bond estimate |
| 7-oxooctanoic acid | Keto Acid | 8 | 1.14E-09 | HENRYWIN bond estimate |
| 8-oxononanoic acid | Keto Acid | 9 | 1.52E-09 | HENRYWIN bond estimate |
| 9-oxodecanoic acid | Keto Acid | 10 | 2.02E-09 | HENRYWIN bond estimate |

Table S10: Hydration equilibrium constants and acid-dissociation constants used to construct Figures 2, 6, and S9-13

| Name | log(Khyd)1 A | log(Khyd)1 B | log(Khyd)2 A | log(Khyd)2 B | Khyd Ref. | pKa | pKa Ref. |
|---|---|---|---|---|---|---|---|
| formaldehyde | 3.30103 | | | | Doussin (2013) | | |
| ethanal (acetaldehyde) | 0.079181 | | | | Doussin (2013) | | |
| propanal | -0.070581 | | | | Doussin (2013) | | |
| butanal | -0.221849 | | | | Doussin (2013) | | |
| pentanal | -0.259637 | | | | Sham and Joens (1995) | | |
| hexanal | -0.31 | | | | Sham and Joens (1995) | | |
| heptanal | -0.27 | | | | SPARC | | |
| octanal | -0.28 | | | | SPARC | | |
| nonanal | -0.28 | | | | SPARC | | |
| decanal | -0.29 | | | | SPARC | | |
| propan-2-one (acetone) | -2.69897 | | | | Bell (1966) | | |
| butan-2-one | -2.17 | | | | SPARC | | |
| pentan-2-one | -2.21 | | | | SPARC | | |
| hexan-2-one | -2.24 | | | | SPARC | | |
| heptan-2-one | -2.26 | | | | SPARC | | |
| octan-2-one | -2.27 | | | | SPARC | | |
| nonan-2-one | -2.28 | | | | SPARC | | |
| ethanedial (glyoxal) | 2.31597 | | 4.30103 | | Doussin (2013) | | |
| propanedial | 1.48 | | 1.34 | | SPARC | | |
| butanedial | 1.16 | | -0.67 | | SPARC | | |
| pentanedial | 1.17 | | 0.11 | | SPARC | | |
| hexanedial | 0.9 | | 0.02 | | SPARC | | |
| heptanedial | -0.02 | | -0.42 | | SPARC | | |

Table S10 (continued)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| octanedial | -0.07 | | -0.5 | | SPARC | | |
| nonanedial | -0.09 | | -0.59 | | SPARC | | |
| decanedial | -0.11 | | -0.68 | | SPARC | | |
| undecanedial | -0.12 | | -0.76 | | SPARC | | |
| dodecanedial | -0.19 | | -0.78 | | SPARC | | |
| 2-oxopropanal (methyl glyoxal) | 3.30103 | -0.18 | -0.13 | 1.1 | Doussin (2013) & SPARC | | |
| 3-oxobutanal | 1.53 | -0.47 | -0.49 | 0.71 | SPARC | | |
| 4-oxopentanal | 1.09 | -1.15 | -2.85 | -1.28 | SPARC | | |
| 5-oxohexanal | 0.95 | -1.32 | -2.05 | -0.33 | SPARC | | |
| 6-oxoheptanal | 0.72 | -1.51 | -2.13 | -0.44 | SPARC | | |
| 7-oxooctanal | -0.02 | -1.88 | -2.37 | -0.56768 | quad fit from adjacent data | | |
| 8-oxononanal | -0.07 | -1.92 | -2.46 | -0.65739 | quad fit from adjacent data | | |
| 9-oxodecanal | -0.09 | -1.93 | -2.54 | -0.74 | SPARC | | |
| 10-oxoundecanal | -0.1 | -2 | -2.63 | -0.76 | SPARC | | |
| butane-2,3-dione (biacetyl) | 0.30103 | | -1.08 | | Doussin (2013) | | |
| pentane-2,4-dione | -0.39 | | -0.6 | | SPARC | | |
| hexane-2,5-dione (acetonylacetone) | -1.35 | | -3.28 | | SPARC | | |
| heptane-2,6-dione | -1.43 | | -2.34 | | SPARC | | |
| octane-2,7-dione | -1.61 | | -2.43 | | SPARC | | |
| nonane-2,8-dione | -1.89 | | -2.5 | | SPARC | | |
| decane-2,9-dione | -1.92 | | -2.59 | | SPARC | | |
| undecane-2,10-dione | -1.93 | | -2.69 | | SPARC | | |

Table S10 (continued)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| dodecane-2,11-dione | -1.93 | | -2.78 | | SPARC | | |
| tridecane-2,12-dione | -1.93 | | -2.88 | | SPARC | | |
| 1-hydroxypropan-2-one (hydroxyacetone) | -1.05 | | | | SPARC | | |
| 4-hydroxybutan-2-one | -0.79 | | | | SPARC | | |
| 5-hydroxypentan-2-one | -2.94 | | | | SPARC | | |
| 6-hydroxyhexan-2-one | -2.19 | | | | SPARC | | |
| 7-hydroxyheptan-2-one | -2.27 | | | | SPARC | | |
| 8-hydroxyoctan-2-one | -2.36 | | | | SPARC | | |
| 9-hydroxynonan-2-one | -2.43 | | | | SPARC | | |
| 10-hydroxydecan-2-one | -2.51 | | | | SPARC | | |
| 11-hydroxyundecan-2-one | -2.6 | | | | SPARC | | |
| 12-hydroxydodecan-2-one | -2.6 | | | | SPARC | | |
| 13-hydroxytridecan-2-one | -2.75 | | | | SPARC | | |
| 14-hydroxytetradecan-2-one | -2.77 | | | | SPARC | | |
| 2-oxoethanoic acid (glyoxylic acid) | 3.041393 | | | | Tur'yan (1998) | 3.32 | Dawson (1959) |
| 3-oxopropanoic acid | 1.46 | | | | SPARC | 4.63 | SPARC |
| 4-oxobutanoic acid | -1.66 | | | | SPARC | 4.37 | SPARC |
| 5-oxopentanoic acid | -0.47 | | | | SPARC | 4.51 | SPARC |
| 6-oxohexanoic acid | -0.54 | | | | SPARC | 4.6 | SPARC |
| 7-oxoheptanoic acid | -0.48 | | | | SPARC | 4.68 | SPARC |
| 8-oxooctanoic acid | -0.58 | | | | SPARC | 4.72 | SPARC |
| 9-oxononanoic acid | -0.69 | | | | SPARC | 4.73 | SPARC |
| 10-oxodecanoic acid | -0.79 | | | | SPARC | 4.74 | SPARC |

Table S10 (continued)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 11-oxoundecanoic acid | -0.89 | | | | SPARC | 4.74 | SPARC |
| 2-hydroxyethanal (formic acid) | 1.1959 | | | | Amyes (2007) | 3.77 | Brown (1955) |
| 3-hydroxypropanal | 1.36 | | | | SPARC | | |
| 4-hydroxybutanal | -1.16 | | | | SPARC | | |
| 5-hydroxypentanal | -0.23 | | | | SPARC | | |
| 6-hydroxyhexanal | -0.32 | | | | SPARC | | |
| 7-hydroxyheptanal | -0.41 | | | | SPARC | | |
| 8-hydroxyoctanal | -0.49 | | | | SPARC | | |
| 9-hydroxynonanal | -0.57 | | | | SPARC | | |
| 10-hydroxydecanal | -0.65 | | | | SPARC | | |
| 11-hydroxyundecanal | -0.67 | | | | SPARC | | |
| 12-hydroxydodecanal | -0.68 | | | | SPARC | | |
| 13-hydroxytridecanal | -0.7 | | | | SPARC | | |
| 14-hydroxytetradecanal | -0.71 | | | | SPARC | | |
| 15-hydroxypentadecanal | -0.73 | | | | SPARC | | |
| 2-oxopropanoic acid (pyruvic acid) | 0.146128 | | | | Esposito (1999) | 2.45 | IUPAC (1979) |
| 3-oxobutanoic acid (acetoacetic acid) | -0.69 | | | | SPARC | 3.59 | IUPAC (1979) |
| 4-oxopentanoic acid (levulinic acid) | -3.64 | | | | SPARC | 4.6 | IUPAC (1979) |
| 5-oxohexanoic acid | -2.48 | | | | SPARC | 4.8 | IUPAC (1979) |
| 6-oxoheptanoic acid | -2.62 | | | | SPARC | 4.6 | SPARC |
| 7-oxooctanoic acid | -2.49 | | | | SPARC | 4.68 | SPARC |
| 8-oxononanoic acid | -2.59 | | | | SPARC | 4.72 | SPARC |
| 9-oxodecanoic acid | -2.69 | | | | SPARC | 4.73 | SPARC |

Table S11: Aqueous and gas-phase OH oxidation rate constants used to construct Figures 2, 6, and S9-13

| Name | KOH Aq pH = 2 [M^-1 s^-1] | KOH Aq pH = 6 [M^-1 s^-1] | KOH Aq Ref. | KOH Gas [cm^3/ molec/s] | KOH Gas Ref. |
|---|---|---|---|---|---|
| formaldehyde | 1.00E+09 | 1.00E+09 | Buxton (1998) | 8.50E-12 | Atkinson (2006) |
| ethanal (acetaldehyde) | 7.30E+08 | 7.30E+08 | Buxton (1998) | 1.50E-11 | Atkinson (2006) |
| propanal | 3.29E+09 | 3.29E+09 | Monod (2005) | 2.00E-11 | Atkinson (2006) |
| butanal | 3.77E+09 | 3.77E+09 | (2005) | 2.40E-11 | (2006) |
| pentanal | 3.90E+09 | 3.90E+09 | Monod (2005) | 2.48E-11 | Albaladejo (2002) |
| hexanal | 2.50E+09 | 2.50E+09 | Jurgens (2007) | 2.60E-11 | Albaladejo (2002) |
| heptanal | 6.53E+09 | 6.53E+09 | SAR | 2.96E-11 | Albaladejo (2002) |
| octanal | 7.68E+09 | 7.68E+09 | SAR | 3.17E-11 | SAR |
| nonanal | 8.83E+09 | 8.83E+09 | SAR | 3.60E-11 | Bowman (2003) |
| decanal | 9.99E+09 | 9.99E+09 | SAR | 3.45E-11 | SAR |
| propan-2-one (acetone) | 1.10E+08 | 1.10E+08 | Buxton (1998) | 1.80E-13 | Atkinson (2006) |
| butan-2-one | 9.00E+08 | 9.00E+08 | Buxton (1998) | 1.20E-12 | Atkinson (2006) |
| pentan-2-one | 1.90E+09 | 1.90E+09 | Buxton (1998) | 4.56E-12 | Atkinson (2000) |
| hexan-2-one | 2.93E+09 | 2.93E+09 | SAR | 6.37E-12 | Jiminez (2005) |
| heptan-2-one | 4.09E+09 | 4.09E+09 | SAR | 1.17E-11 | Atkinson (2000) |
| octan-2-one | 5.25E+09 | 5.25E+09 | SAR | 1.10E-11 | Wallington 1987 |
| nonan-2-one | 6.40E+09 | 6.40E+09 | SAR | 1.10E-11 | SAR |
| ethanedial (glyoxal) | 1.05E+09 | 1.05E+09 | Buxton (1997) | 1.10E-11 | Atkinson (2006) |
| propanedial | 2.46E+09 | 2.46E+09 | SAR | 1.32E-10 | SAR |
| butanedial | 2.86E+09 | 2.86E+09 | SAR | 4.70E-11 | SAR |
| pentanedial | 3.93E+09 | 3.93E+09 | SAR | 2.52E-11 | Rogers (1989) |
| hexanedial | 5.08E+09 | 5.08E+09 | SAR | 5.22E-11 | SAR |
| heptanedial | 6.23E+09 | 6.23E+09 | SAR | 5.36E-11 | SAR |

Table S11 (continued)

| | | | | | |
|---|---|---|---|---|---|
| octanedial | 7.38E+09 | 7.38E+09 | SAR | 5.50E-11 | SAR |
| nonanedial | 8.53E+09 | 8.53E+09 | SAR | 5.64E-11 | SAR |
| decanedial | 1.00E+10 | 1.00E+10 | SAR | 5.79E-11 | SAR |
| undecanedial | 1.00E+10 | 1.00E+10 | SAR | 5.93E-11 | SAR |
| dodecanedial | 1.00E+10 | 1.00E+10 | SAR | 6.07E-11 | SAR |
| 2-oxopropanal (methyl glyoxal) | 6.56E+08 | 6.56E+08 | SAR | 1.30E-11 | SAR |
| 3-oxobutanal | 1.34E+09 | 1.34E+09 | SAR | 6.65E-11 | SAR |
| 4-oxopentanal | 1.82E+09 | 1.82E+09 | SAR | 2.63E-11 | SAR |
| 5-oxohexanal | 2.78E+09 | 2.78E+09 | SAR | 3.68E-11 | SAR |
| 6-oxoheptanal | 3.92E+09 | 3.92E+09 | SAR | 3.15E-11 | SAR |
| 7-oxooctanal | 5.07E+09 | 5.07E+09 | SAR | 3.30E-11 | SAR |
| 8-oxononanal | 6.22E+09 | 6.22E+09 | SAR | 3.44E-11 | SAR |
| 9-oxodecanal | 7.37E+09 | 7.37E+09 | SAR | 3.58E-11 | SAR |
| 10-oxoundecanal | 8.52E+09 | 8.52E+09 | SAR | 3.72E-11 | SAR |
| butane-2,3-dione (biacetyl) | 1.86E+09 | 1.86E+09 | Schaefer (2012) | 2.48E-13 | Dagaut (1988) |
| pentane-2,4-dione | 9.90E+09 | 9.90E+09 | Buxton (1998) | 9.07E-11 | Zhou (2008) |
| hexane-2,5-dione (acetonylacetone) | 6.10E+08 | 6.10E+08 | Schaefer (2012) | 5.67E-12 | SAR |
| heptane-2,6-dione | 1.41E+09 | 1.41E+09 | SAR | 1.61E-11 | SAR |
| octane-2,7-dione | 2.52E+09 | 2.52E+09 | SAR | 1.09E-11 | SAR |
| nonane-2,8-dione | 3.67E+09 | 3.67E+09 | SAR | 1.23E-11 | SAR |
| decane-2,9-dione | 4.82E+09 | 4.82E+09 | SAR | 1.37E-11 | SAR |
| undecane-2,10-dione | 5.97E+09 | 5.97E+09 | SAR | 1.51E-11 | SAR |

Table S11 (continued)

| | | | | | |
|---|---|---|---|---|---|
| dodecane-2,11-dione | 7.13E+09 | 7.13E+09 | SAR | 1.65E-11 | SAR |
| tridecane-2,12-dione | 8.28E+09 | 8.28E+09 | SAR | 1.80E-11 | SAR |
| 1-hydroxypropan-2-one (hydroxyacetone) | 1.00E+09 | 1.00E+09 | SAR | 3.00E-12 | Atkinson (2006) |
| 4-hydroxybutan-2-one | 2.59E+09 | 2.59E+09 | Buxton (1998) | 1.39E-11 | SAR |
| 5-hydroxypentan-2-one | 3.62E+09 | 3.62E+09 | SAR | 9.64E-12 | SAR |
| 6-hydroxyhexan-2-one | 4.77E+09 | 4.77E+09 | SAR | 1.11E-11 | SAR |
| 7-hydroxyheptan-2-one | 5.92E+09 | 5.92E+09 | SAR | 1.25E-11 | SAR |
| 8-hydroxyoctan-2-one | 7.07E+09 | 7.07E+09 | SAR | 1.39E-11 | SAR |
| 9-hydroxynonan-2-one | 1.00E+10 | 1.00E+10 | SAR | 1.53E-11 | SAR |
| 10-hydroxydecan-2-one | 1.00E+10 | 1.00E+10 | SAR | 1.67E-11 | SAR |
| 11-hydroxyundecan-2-one | 1.00E+10 | 1.00E+10 | SAR | 1.81E-11 | SAR |
| 12-hydroxydodecan-2-one | 1.00E+10 | 1.00E+10 | SAR | 1.95E-11 | SAR |
| 13-hydroxytridecan-2-one | 1.00E+10 | 1.00E+10 | SAR | 2.09E-11 | SAR |
| 14-hydroxytetradecan-2-one | 1.00E+10 | 1.00E+10 | SAR | 2.24E-11 | SAR |
| 2-oxoethanoic acid (glyoxylic acid) | 4.70E+08 | 2.60E+09 | Ervens (2003) | 1.28E-11 | SAR |
| 3-oxopropanoic acid | 9.73E+08 | 1.39E+09 | SAR | 6.64E-11 | SAR |
| 4-oxobutanoic acid | 1.42E+09 | 1.66E+09 | SAR | 2.63E-11 | SAR |
| 5-oxopentanoic acid | 2.20E+09 | 2.88E+09 | SAR | 3.68E-11 | SAR |
| 6-oxohexanoic acid | 3.34E+09 | 4.03E+09 | SAR | 3.15E-11 | SAR |
| 7-oxoheptanoic acid | 4.49E+09 | 5.18E+09 | SAR | 3.29E-11 | SAR |
| 8-oxooctanoic acid | 5.64E+09 | 6.34E+09 | SAR | 3.44E-11 | SAR |
| 9-oxononanoic acid | 6.79E+09 | 7.49E+09 | SAR | 3.58E-11 | SAR |
| 10-oxodecanoic acid | 7.94E+09 | 8.64E+09 | SAR | 3.72E-11 | SAR |

Table S11 (continued)

| | | | | | |
|---|---|---|---|---|---|
| 11-oxoundecanoic acid | 9.09E+09 | 9.79E+09 | SAR | 3.86E-11 | SAR |
| 2-hydroxyethanal (formic acid) | 1.14E+09 | 1.14E+09 | SAR | 1.10E-11 | Atkinson (2006) |
| 3-hydroxypropanal | 3.21E+09 | 3.21E+09 | SAR | 3.45E-11 | SAR |
| 4-hydroxybutanal | 3.86E+09 | 3.86E+09 | SAR | 3.03E-11 | SAR |
| 5-hydroxypentanal | 4.97E+09 | 4.97E+09 | SAR | 3.17E-11 | SAR |
| 6-hydroxyhexanal | 6.12E+09 | 6.12E+09 | SAR | 3.31E-11 | SAR |
| 7-hydroxyheptanal | 7.27E+09 | 7.27E+09 | SAR | 3.45E-11 | SAR |
| 8-hydroxyoctanal | 8.43E+09 | 8.43E+09 | SAR | 3.59E-11 | SAR |
| 9-hydroxynonanal | 9.58E+09 | 9.58E+09 | SAR | 3.74E-11 | SAR |
| 10-hydroxydecanal | 1.00E+10 | 1.00E+10 | SAR | 3.88E-11 | SAR |
| 11-hydroxyundecanal | 1.00E+10 | 1.00E+10 | SAR | 4.02E-11 | SAR |
| 12-hydroxydodecanal | 1.00E+10 | 1.00E+10 | SAR | 4.16E-11 | SAR |
| 13-hydroxytridecanal | 1.00E+10 | 1.00E+10 | SAR | 4.30E-11 | SAR |
| 14-hydroxytetradecanal | 1.00E+10 | 1.00E+10 | SAR | 4.44E-11 | SAR |
| 15-hydroxypentadecanal | 1.00E+10 | 1.00E+10 | SAR | 4.58E-11 | SAR |
| 2-oxopropanoic acid (pyruvic acid) | 2.70E+08 | 7.00E+08 | Ervens (2003) | 6.52E-13 | SAR |
| 3-oxobutanoic acid (acetoacetic acid) | 2.27E+08 | 2.73E+08 | SAR | 2.10E-12 | SAR |
| 4-oxopentanoic acid (levulinic acid) | 4.94E+08 | 6.01E+08 | SAR | 1.18E-11 | SAR |
| 5-oxohexanoic acid | 1.35E+09 | 1.48E+09 | SAR | 1.82E-11 | SAR |
| 6-oxoheptanoic acid | 2.47E+09 | 2.60E+09 | SAR | 1.30E-11 | SAR |
| 7-oxooctanoic acid | 3.62E+09 | 3.75E+09 | SAR | 1.44E-11 | SAR |
| 8-oxononanoic acid | 4.78E+09 | 4.90E+09 | SAR | 1.58E-11 | SAR |
| 9-oxodecanoic acid | 5.93E+09 | 6.05E+09 | SAR | 1.72E-11 | SAR |

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