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Technical note: Updated parameterization of the reactive uptake of glyoxal and methylglyoxal by atmospheric aerosols and cloud droplets

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Abstract

We present updated recommendations for the reactive uptake coefficients for glyoxal and methylglyoxal uptake to aqueous aerosol particles and cloud droplets. The particle and droplet types considered were based on definitions in GEOS-Chem v11, but the approach is general. Liquid maritime and continental cloud droplets were considered. Aerosol types include sea salt (fine and coarse) with varying relative humidity and particle size, and sulfate/nitrate/ammonium as a function of relative humidity, particle composition, and aerosol pH. We take into account salting effects, aerosol thermodynamics, mass transfer, and aqueous phase chemical kinetics. The new recommended values for the reactive uptake coefficients in most cases are lower than those currently used in large-scale models, such as GEOS-Chem. We expect application of these parameterizations will result in improved representation of aqueous secondary organic aerosol formation in atmospheric chemistry models.

1 Introduction

The uptake and reaction of water soluble volatile organic compounds (VOCs) in cloud droplets and aerosol liquid water is likely a significant source of secondary organic aerosol (SOA) material (Carlton et al., 2008; Fu et al., 2008, 2009; McNeill, 2015; McNeill et al., 2012). These processes may be referred to, collectively, as aqueous SOA (or aqSOA) formation.

Glyoxal (CHOCHO, GLYX) and methylglyoxal ($CH_3C(O)CHO$, MGLY) are both atmospherically abundant gas-phase oxidation products of multiple VOC precursors, including isoprene and toluene. Both GLYX and MGLY are water-soluble, GLYX more so than MGLY (Betterton and Hoffmann, 1988; Zhou and Mopper, 1990). Taking into account salting effects, the effective Henry's Law constant for GLYX in aerosol water can be several orders of magnitude higher than that of MGLY, depending on the aerosol ionic content (Kampf et al., 2013; Waxman et al., 2015). As α-dicarbonyl species, GLYX and MGLY exhibit similar aqueous-phase chemistry: they undergo reversible hydration and self-oligomerization (Ervens and Volkamer, 2010; Hastings et al., 2005; Sareen et al., 2010; Shapiro et al., 2009), they can be oxidized by aqueous-phase radicals to form organic acids or organosulfates (Carlton et al., 2007; Lim et al., 2013; Perri et al., 2010; Schaefer et al., 2012, 2015), and they can react with nitrogen-containing species to form brown carbon (Lee et al., 2013; Maxut et al., 2015; Nozière et al., 2009; Sareen et al., 2010; Schwier et al., 2010; Shapiro et al., 2009; Yu et al., 2011).

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GLYX and MGLY received significant attention in the atmospheric chemistry modelling community (Carlton et al., 2008; Fu et al., 2008, 2009) following early experimental demonstrations of their potential significance as aqSOA precursors (Carlton et al., 2007; Hastings et al., 2005; Kroll et al., 2005; Loeffler et al., 2006). Fu and co-workers predicted that uptake of GLYX and MGLY to low-level clouds was a significant source of organic aerosol over North America, with MGLY producing more than three times more SOA than GLYX (Fu et al., 2009). Carlton et al. (2008) found that including in-cloud aqSOA production by GLYX in CMAQ improved agreement with aircraft observations.

Since these initial studies, more information has become available regarding the gas-particle partitioning of glyoxal and methylglyoxal (Ip et al., 2009; Kampf et al., 2013; Waxman et al., 2015; Yu et al., 2011) and their chemical processing in the aqueous phase, allowing a refinement of their representation in models.

Here, we calculate reactive uptake coefficients for glyoxal and methylglyoxal for several cloud and aerosol types for application in large-scale atmospheric chemistry modelling. We take into account salting effects, aerosol thermodynamics, mass transfer considerations, and aqueous phase chemical kinetics. We base our calculations on the cloud and aerosol types used in GEOS-Chem v11, so these recommendations can be applied directly to that model, but the approach is general.

2 Methods and Data

Following Hanson et al. (1994), the reactive uptake coefficient, γ, is calculated according to:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4H^{*}\mathbb{R}T\sqrt{k^{I}D_{aq}}}\left(\frac{1}{cothq - 1/q}\right) \quad (1)$$

where α is the mass accommodation coefficient, ω is the gas-phase thermal velocity of the organic species, H^* is the effective Henry's Law constant (Schwartz, 1986), ℝ is the universal gas constant, T is temperature in Kelvin, k^I is the first order aqueous loss rate, and D_{aq} is the aqueous-phase diffusion coefficient for the organic. Particle radius, R_p, and in-particle diffusion limitations are taken into account through the parameter $q = R_p/l$, where l is the diffuso-reactive length:

$$l = \left(\frac{D_{aq}}{k^{I}}\right)^{1/2} \quad (2)$$

Particle types. Although the approach described here is general, we applied it to the liquid cloud and aerosol particle types in GEOS-Chem v11. A complete listing can be found in the Supporting Information. Briefly, we considered marine and remote continental liquid cloud droplets, coarse and fine sea salt aerosol particles as a function of relative humidity, and sulfate/nitrate/ammonium (SNA) aerosols as a function of relative humidity, pH, and composition. Sea salt aerosols are assumed to be composed of 100% NaCl. The Windows stand-alone executable for ISORROPIA-II (Fountoukis and Nenes,

2007) was used in forward mode to calculate the equilibrium inorganic ion composition of the aerosols, in order to calculate the Henry's constant. The temperature was held constant at 280 K and calculations were performed for each of the desired relative humilities (99, 95, 90, 80, 70, 50 and 0%). Solid formation was suppressed (metastable mode). For the SNA aerosols, the amount of NO_3^- was held constant at 2 μmol/m^3 air, while the SO_4^{-2} and NH_3 amounts were each varied from 1-8 μmol/m^3.

Aqueous-phase reaction. The formulation in eq (1) and (2) describes uptake due to irreversible aqueous-phase loss processes only. Based on our previous analysis of the system using the multiphase photochemical box model GAMMA, the dominant irreversible atmospheric aqueous-phase reactive process for GLYX and MGLY is reaction with OH (McNeill, 2015; McNeill et al., 2012). Therefore, the aqueous loss is represented by the pseudo first order rate constant for the reaction between the organic species of choice and OH (i.e., $k^{I}= k_{OH}$[OH]). Reversible reactive processes, e.g. spontaneous hydration and self-oligomerization of glyoxal and methylglyoxal, which substantially promote uptake of GLYX and MGLY to the aqueous phase, may be taken into account by the use of an effective Henry's Law constant (McNeill et al., 2012). However, we note that the form of eq. 1 implies no uptake (reversible or irreversible) in the absence of OH.

Considerable uncertainty exists in the aqueous concentration of OH in cloudwater and especially aerosol particles. In order to calculate k^{I}, we use OH concentrations for maritime and remote continental clouds and aerosols following Herrmann et al. (2010) (Table 1). They reported a range of [OH] for each scenario calculated using the CAPRAM 3.0 model. This [OH] range was used to calculate the uncertainty in γ.

Table 1. Mean values and range of in-particle hydroxyl radical concentrations, as reported by Herrmann et al., (2010).

Cloud/aerosol type	Mean [OH] (M)	Max [OH] (M)	Min [OH] (M)
Maritime aerosols	10^{-13}	3.3×10^{-12}	4.6×10^{-15}
Remote aerosols	3.0×10^{-12}	8×10^{-12}	5.5×10^{-14}
Maritime clouds	2.0×10^{-12}	5.3×10^{-12}	3.8×10^{-14}
Remote clouds	2.2×10^{-14}	6.9×10^{-14}	4.8×10^{-15}

Calculating the Henry's constant. The solubility of glyoxal and methylglyoxal in aqueous solutions depends on the salt content (Ip et al., 2009; Kampf et al., 2013; Waxman et al., 2015; Yu et al., 2011). Glyoxal becomes more soluble with increasing salt concentration (i.e., it exhibits "salting in"), whereas the opposite is true for methylglyoxal (it "salts out"). Therefore, the Henry's constants for glyoxal and methylglyoxal are a function of particle type and liquid water content (and therefore relative humidity).

The Henry's constants are calculated for sea salt aerosols following Waxman et al. (2015) using the equation:

$$\log\left(\frac{K_{H,w}}{K_{H,NaCl}}\right) = K_{s,NaCl}c_{NaCl} \qquad (3)$$

where $K_{H,w}$ is the Henry's constant for pure water, $K_{H,NaCl}$ is the Henry's constant for the salt-containing aerosol, c_{NaCl} is the NaCl concentration in molality as calculated using ISORROPIA-II, and and $K_{s,NaCl}$ is the salting constant (Table 2). Waxman and coworkers showed that salting constants were additive for a mixed $(NH_4)_2SO_4/NH_4NO_3$ system, following:

$$\log\left(\frac{K_{H,w}}{K_{H,salt}}\right) = K_{s,(NH4)2SO4}c_{(NH4)2SO4} + K_{s,NH4NO3}c_{NH4NO3} \qquad (4)$$

where $K_{H,salt}$ is the Henry's constant for the salt mixture, $c_{(NH4)2SO4}$ and c_{NH4NO3} are the concentrations in molality and $K_{s,(NH4)2SO4}$ and $K_{s,NH4NO3}$ are the salting constants. The sum of sulfate and bisulfate was used to calculate $c_{(NH4)2SO4}$.

For cloud droplets, $K_{H,w}$ is used due to the low ion concentrations in cloudwater (Ervens, 2015; McNeill, 2015).

Table 2. Reaction and mass transfer parameters

Species	k_{OH} (M^{-1} s^{-1})	$K_{H,w}$ (M atm^{-1})	$K_{s, NaCl}$ [1/m]	$K_{s, (NH4)2SO4}$ [1/m]	$K_{s, NH4NO3}$ [1/m]
Glyoxal	1.1×10^{9} [a]	3.5×10^{5} [c]	-0.10 [e]	-0.24 [d]	-0.07 [e]
Methylglyoxal	7×10^{8} [b]	3.71×10^{3} [c]	0.06 [e]	0.16 [e]	0.075 [e]

a (Schaefer et al., 2015)
b (Schaefer et al., 2012)
c (Betterton and Hoffmann, 1988)
d (Kampf et al., 2013)
e (Waxman et al., 2015)

Statistical analysis and parameter estimation. The calculated reactive uptake coefficient, γ, for MGLY and GLYX and each particle type was parameterized as a function of relative humidity via weighted least squares regression. Assuming that the errors in the reactive uptake coefficients are log-normally distributed, a covariance matrix for the model parameters was calculated based on the mean square errors of the data and the design matrix of the linear regression. The standard deviations of the model parameters were then determined from the diagonal of the covariance matrix (Aster et al., 2005). Student's t-tests were then performed on each model parameter for the hypothesis that the model parameter in question is equivalent to zero in order to assess the necessity of each parameter. The nonzero model parameter was kept for t-tests in which there was at least 98% confidence that the hypothesis of the model parameter being zero could be rejected.

3 Results and Discussion

The reactive uptake coefficient, γ, was calculated for MGLY and GLYX as a function of [OH], RH, particle size, and in the case of SNA aerosol, particle composition. Calculated values of γ varied over several orders of magnitude. In most cases these values are lower than those previously used to model reactive uptake of these species in large-scale models.

3.1 Liquid cloud droplets.

The results for marine and remote continental cloud droplets are shown in Table 3 with the mean value and error bars given. The uncertainty reflects the uncertainty in [OH]. γ_{MGLY} is lower than γ_{GLYX} by a factor of roughly 100 in each case, consistent with its lower $K_{H,w}$ and k_{OH}.

Table 3. Recommended γ for liquid cloud droplets. Cloud types and size as defined in GEOS-Chem v11.

Cloud type	R_{eff} (µm)	γ_{GLYX}	γ_{MGLY}
Marine	10	7.5×10^{-4} ($+0.001,-7.4\times10^{-4}$)	5.7×10^{-6} ($+9.4\times10^{-6},-5.6\times10^{-6}$)
Remote continental	6	4.3×10^{-6} ($+9.2\times10^{-6},-3.4\times10^{-6}$)	3.2×10^{-8} ($+6.7\times10^{-8},-2.5\times10^{-8}$)

3.2 Aerosols.

For aerosols, the reactive uptake coefficients were found to vary significantly with RH due to salting effects. No clear correlation of γ with S:A, S:N or aerosol pH is apparent (see Supporting Information). Therefore, in developing the parameterization, we examine the dependence of each reactive uptake coefficient on RH only.

Figure 1 shows calculated values of γ_{GLYX} for the three particle types as a function of RH. The range of uncertainty in the calculated values, indicated by the red shading, is due to the uncertainty in [OH] (Table 1). The black lines indicate the weighted least squares fit to the data, and the grey lines indicate the confidence interval for the fit. The average values and the results of the least squares fits are summarized in Table 4.

γ_{GLYX} decreases with increasing RH, due to salting in. Therefore, the maximum γ_{GLYX} (10^{-2} for SNA, 50% RH) exceeds the dilute (cloudwater) case. It also exceeds the general case used by Fu et al. (2008) ($\gamma_{GLYX, Fu} = 2.9\times10^{-3}$), which was based on the experimental observations of Liggio et al. (2005) for $(NH_4)_2SO_4$ aerosols at 55% RH.

In the case of coarse sea salt, in-particle diffusion limitations led to smaller γ_{GLYX} at the mean [OH] than at the minimum [OH] for some RH values. The scatter in the calculated γ_{GLYX} led to a low-confidence result from the weighted least squares regression. For this reason, we recommend use of the average γ_{GLYX} value in lieu of a parameterization (Table 4).

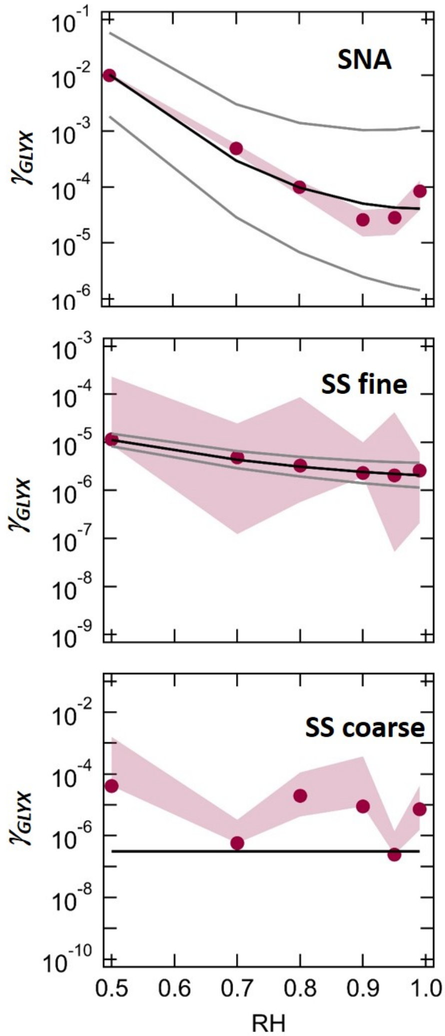

Figure 1. Calculated reactive uptake coefficients for uptake of glyoxal to sulfate/nitrate/ammonium (SNA) aerosols, and fine and coarse sea salt (SS) aerosols, as defined in GEOS-Chem v11. Red shading indicates the uncertainty in γ_{GLYX}. The black lines show the results of weighted least squares regression, with the confidence intervals in grey.

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Table 4. Summary of γ_{GLYX} recommendations for aerosols. Aerosol types and specifications as defined in GEOS-Chem v11.

Aerosol type	**γ_{GLYX} average value**	**γ_{GLYX} Parameterization** x: RH as fraction
SNA	$1.0(\pm0.1)\times10^{-2}$ (RH = 50%) $4.9(\pm1.0)\times10^{-4}$ (RH = 70%) $1.0(\pm0.3)\times10^{-4}$ (RH = 80%) $2.6(\pm1.3)\times10^{-5}$ (RH = 90%) $2.8(\pm1.4)\times10^{-5}$ (RH = 95%) $8.5(\pm4.6)\times10^{-5}$ (RH = 99%)	$\gamma = \exp(a + bx + cx^2)$ a = 12.1 (± 0.6) b = -44.5 (± 1.7) c = 22.3 (± 1.1) conf = 0.9997
Sea salt (fine)	2.6×10^{-6} (+0.04,-2.6×10^{-6})	$\gamma = \exp(a + bx + cx^2)$ a = -7.5 (± 0.1) b = -10.0 (± 0.3) c = 4.4 (± 0.2) conf = 0.9998
Sea salt (coarse mode)	4.8×10^{-7} (+0.013,-4.8×10^{-7})	Average value recommended

Figure 2 shows calculated values of γ_{MGLY} as a function of RH. The average values and the results of the least squares fits are summarized in Table 5. In contrast to glyoxal, methylglyoxal salts out, so γ_{MGLY} increases with increasing RH. All calculated values ($10^{-10} < \gamma_{MGLY} < 10^{-6}$) are much smaller than the general case used by Fu et al. (2008) ($\gamma_{MGLY, Fu} = 2.9\times10^{-3}$). Those investigators had assumed that the reactive uptake coefficient for methylglyoxal would be equal to that for glyoxal as measured by Liggio et al. (2005).

Similar to the glyoxal case, the variability in γ_{MGLY} for the coarse mode sea salt aerosols due to in-particle diffusion limitations led to a low-confidence weighted least squares fit. The average value is recommended.

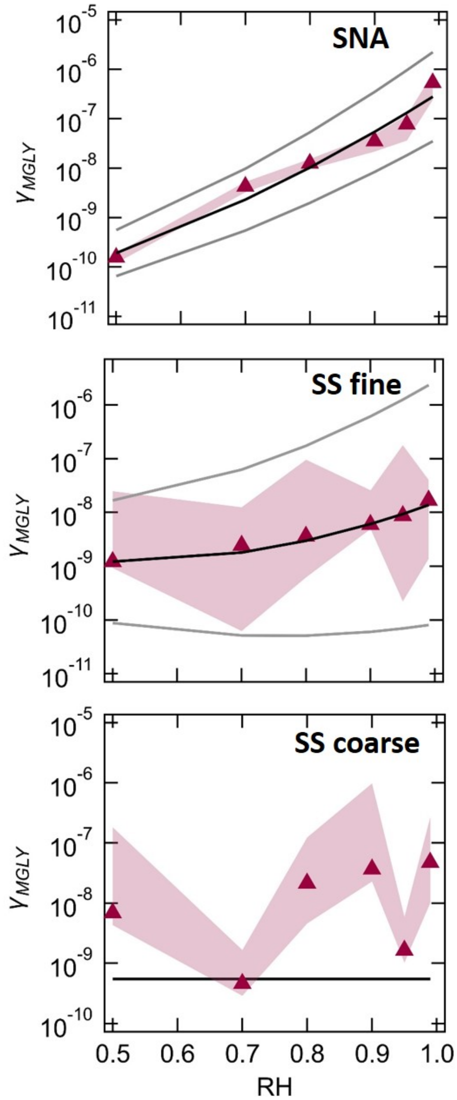

Figure 2 Calculated reactive uptake coefficients for uptake of methylglyoxal to sulfate/nitrate/ammonium (SNA) and sea salt (SS) aerosols. See text for details.

Table 5. Summary of γ_{MGLY} recommendations for aerosols.

Aerosol type	γ_{MGLY} average value	γ_{MGLY} Parameterization x: RH as fraction
SNA	1.6(±0.4)×10^{-10} (RH = 50%) 4.3(±1.0)×10^{-9} (RH = 70%) 1.3(±0.3)×10^{-8} (RH = 80%) 3.5(±1.5)×10^{-8} (RH = 90%) 7.7(±4.1)×10^{-8} (RH = 95%) 5.3(±2.9)×10^{-7} (RH = 99%)	$\gamma = \exp(a + bx + cx^2)$ a = -25.7 (± 0.4) b = 2.5 (± 1.0) c = 8.3 (± 0.7) conf = 0.9990
Sea salt (fine)	6.5 (±1.3) × 10^{-9}	$\gamma = \exp(a + bx + cx^2)$ a = -17.9 (± 0.9) b = -10.4 (± 2.6) c = 10.3 (± 1.7) conf = 0.9909
Sea salt (coarse mode)	5.5 × 10^{-10} (+0.016,-5.5×10^{-10})	Average value recommended

4 Atmospheric Implications

We present revised recommendations for the reactive uptake coefficient for glyoxal and methylglyoxal for several cloud and aerosol types. The values we calculated in most cases are lower than those currently used in large-scale models such as GEOS-Chem. We expect application of these parameterizations will result in a dramatic decrease in the calculated contribution of MGLY uptake to aqueous SOA formation and better representation of spatial variability in aqSOA formed from glyoxal.

Reactive uptake of glyoxal and methylglyoxal to other hygroscopic aerosols such as organics is possible, although given the importance of salting effects on this chemistry, and the low expected [OH] concentration in organic aerosols (McNeill, 2015), we expect the contribution of these processes to aqSOA formation to be minor.

This representation of aqueous SOA formation by GLYX and MGLY, with the treatment of Henry's constants described here, does not take into account the contribution of reversible uptake of GLYX, which could be a significant, although transient, source of aerosol mass under some conditions (McNeill et al., 2012; Woo and McNeill, 2015). The use of this parameterization together with simpleGAMMA (Woo and McNeill, 2015) would give representation of both aqSOA formation types by GLYX.

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Supplementary Information

Details of the GEOS-Chem v11 cloud and aerosol specifications, plots of the dependence of γ on aerosol composition, and the MATLAB routine for calculating γ can be found in the supplementary information.

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