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# Brown Carbon Production by Aqueous-Phase Interactions of Glyoxal and SO<sub>2</sub>

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# Brown Carbon Production by Aqueous-Phase Interactions of Glyoxal and SO<sub>2</sub>

## Abstract

Oxalic acid and sulfate salts are major components of aerosol particles. Here, we explore the potential for their respective precursor species, glyoxal and SO<sub>2</sub>, to form atmospheric brown carbon via aqueous-phase reactions in a series of bulk aqueous and flow chamber aerosol experiments. In bulk aqueous solutions, UV- and visible-light-absorbing products are observed at pH 3–4 and 5–6, respectively, with small but detectable yields of hydroxyquinone and polyketone products formed, especially at pH 6. Hydroxymethanesulfonate (HMS), C<sub>2</sub>, and C<sub>3</sub> sulfonates are major products detected by electrospray ionization mass spectrometry (ESI-MS) at pH 5. Past studies have assumed that the reaction of formaldehyde and sulfite was the only atmospheric source of HMS. In flow chamber experiments involving sulfite aerosol and gas-phase glyoxal with only 1 min residence times, significant aerosol growth is observed. Rapid brown carbon formation is seen with aqueous aerosol particles at >80% relative humidity (RH). Brown carbon formation slows at 50–60% RH and when the aerosol particles are acidified with sulfuric acid but stops entirely only under dry conditions. This chemistry may therefore contribute to brown carbon production in cloud-processed pollution plumes as oxidizing volatile organic compounds (VOCs) interact with SO<sub>2</sub> and water.

## Keywords

Absorption, Ions, Aerosols, pH, Oxidation

## Disciplines

Chemistry | Environmental Chemistry

## Notes

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1           Brown carbon production by aqueous-phase  
2                           interactions of glyoxal and SO<sub>2</sub>

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12

13

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26 chemistry may therefore contribute to brown carbon production in cloud-processed pollution  
27 plumes as oxidizing VOCs interact with SO<sub>2</sub> and water.

28 Keywords: cloud processing, sulfonate formation, secondary organic aerosol, sulfite oxidation  
29

### 30 **Introduction**

31 Sulfur dioxide, a S(IV) compound emitted from volcanoes, coal-burning power plants, smelters,  
32 and oil refineries, is oxidized to sulfate in the atmosphere with a lifetime of 4-12 h, as estimated  
33 from satellite retrievals.(1) This oxidation takes place mainly in cloudwater(2) or aqueous  
34 aerosol,(3) where dissolved SO<sub>2</sub> reacts with dissolved oxidants, especially HOOH(4) and organic  
35 peroxides.(5) The sulfate produced is a major component of submicron aerosol particles,(6) which  
36 affects human health and climate. Atmospheric sulfate concentrations are typically correlated with  
37 other products of oxidative cloud processing, such as oxalate ions,(7) produced from aqueous  
38 glyoxal oxidation. Recent observations of extremely rapid SO<sub>2</sub> oxidation at high RH during

39 pollution episodes over northeast China have highlighted remaining gaps in our understanding of  
40 relevant oxidation pathways.(8-10)

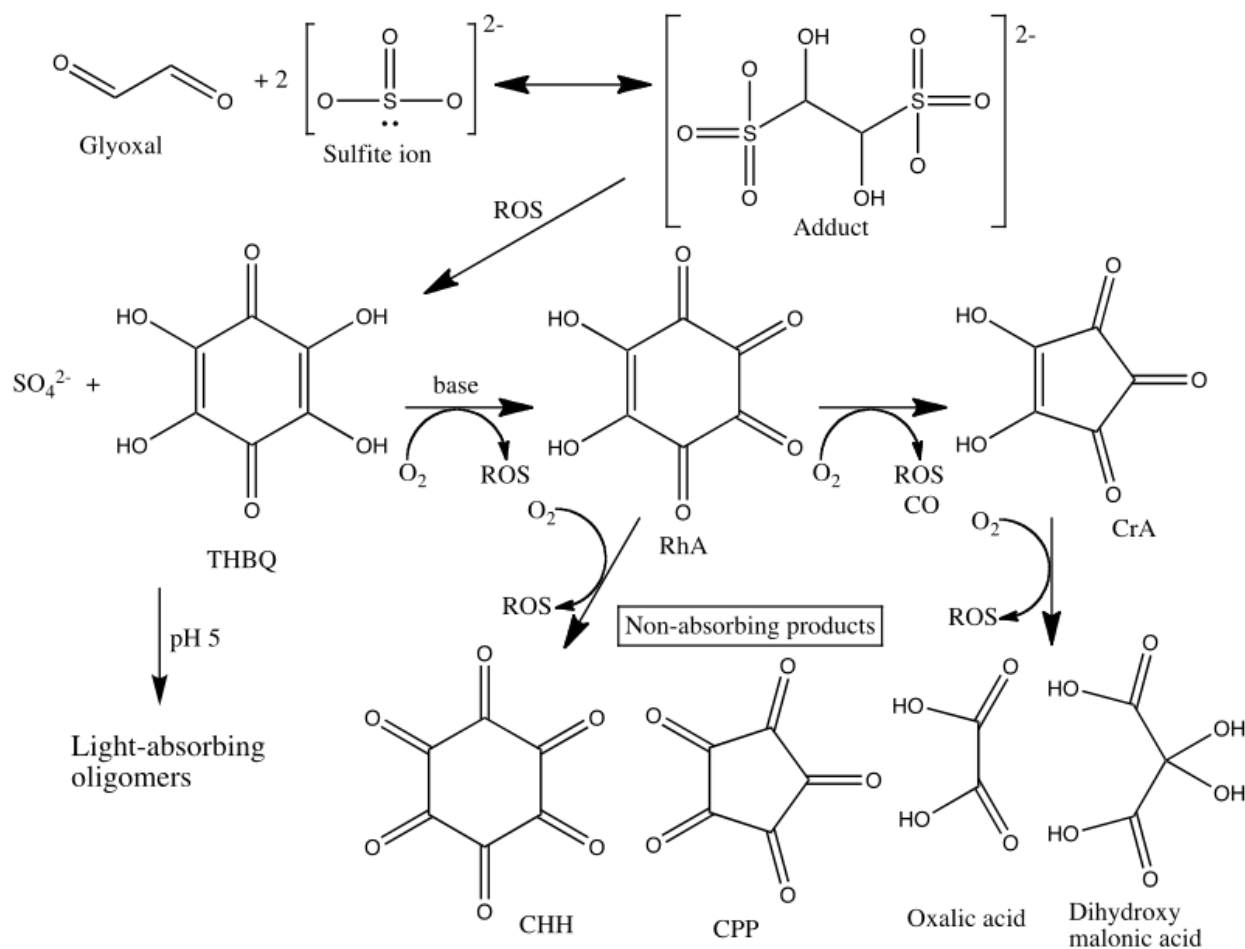
41 Oxidation is not the only chemical reaction that dissolved SO<sub>2</sub> participates in. Glyoxal, like  
42 other aldehydes,(4, 11) reacts rapidly with S(IV) compounds in aqueous media, reversibly forming  
43 sulfonate adduct molecules(12) containing C-S bonds.(13) No further products are observed in  
44 the dark when oxidants are excluded, leading to the conclusion that sulfonates serve only as  
45 condensed-phase atmospheric reservoirs for aldehydes and S(IV),(14) thereby increasing SO<sub>2</sub>  
46 partitioning(12) and glyoxal uptake into clouds.(15) However, when exposed to air, aqueous  
47 mixtures of glyoxal and sodium sulfite (which have pH > 7 due to sulfite basicity) quickly produce  
48 the redox-active, aromatic compound tetrahydroxybenzoquinone (THBQ)(16) at the air-water  
49 interface. THBQ is a black precipitate, and is red when dissolved in aqueous solution, strongly  
50 absorbing visible light ( $\sigma = 3.7 \times 10^{-17} \text{ cm}^2$  at  $\lambda_{\text{max}} = 485 \text{ nm}$ ). THBQ is itself oxidized under basic  
51 conditions to form the light-absorbing, redox-active species rhodizonic acid (RhA) and croconic  
52 acid (CrA), of which the latter is more stable. This oxidation pathway is summarized in Scheme  
53 1.

54 Redox-active quinone species have been implicated, along with transition metals ions, in the  
55 widespread toxicity of atmospheric aerosol.(17-21) These compounds can generate free radical  
56 oxidants in lung fluid for hours after inhalation, triggering adverse health effects.(20-25) Thus, it  
57 is critical to determine to what extent reactions between glyoxal and SO<sub>2</sub> dissolved in aqueous  
58 aerosol and cloud droplets might produce quinone species and brown carbon under  
59 atmospherically relevant conditions. In this work we performed a series of aerosol and bulk  
60 aqueous experiments involving glyoxal and dissolved SO<sub>2</sub> at pH < 7. We find that fast production  
61 of brown carbon products is maximized in aqueous aerosol at high RH and slowed by acidification

62 of the aerosol phase. In bulk phase simulations at  $\text{pH} < 6$ , sulfonates with C-S bonds and odd  
 63 carbon numbers are major products detected by ESI-MS, along with small yields of quinones  
 64 generated at  $\text{pH} \geq 5$ .

65

66 Scheme 1: Summary of Reported Glyoxal + Sulfite Reaction Products Under Basic Conditions



67

68 ROS = reactive oxidant species. Light absorbing products (middle row): THBQ =  
 69 tetrahydroxybenzoquinone; RhA = rhodizonic acid; CrA = croconic acid. Non-light-absorbing  
 70 products (bottom row): CHH = cyclohexahexanone; CPP = cyclopenta-pentanone. All structures  
 71 from ref (16). The pH 5 oligomer pathway is proposed in this work.

72

73

## 74 **Materials and Methods**

75 All chemicals were used as received from Sigma-Aldrich except as noted.

76 Bulk studies. Sodium sulfite (Spectrum) solutions were pH-buffered with formic acid (pH 3),  
77 acetic acid (pH 4 and 5.4) or malonic acid (pH 6) and reacted with aqueous glyoxal generated by  
78 hydrolysis of solid glyoxal trimer dihydrate (GTD, Fluka) at 0.25 M concentrations. Standards of  
79 tetrahydroxybenzoquinone (THBQ), rhodizonic acid (RhA, disodium salt), croconic acid (CrA,  
80 disodium salt), and glyoxal bis-disulfite adduct (GBDS, disodium salt hydrate) were made in N<sub>2</sub>-  
81 bubbled deionized water to minimize the presence of dissolved oxidants. Sodium sulfite - glyoxal  
82 reaction mixtures and standards were analyzed as a function of time by diode array UV/vis  
83 absorbance spectrometry (HP 8452A) and/or negative-mode electrospray ionization mass  
84 spectroscopy (Thermo LTQ).

85 Aerosol flow chamber studies. A schematic of the experimental system is shown in Figure S1.  
86 Aqueous aerosols were generated from 0.05 – 0.15% w/w aqueous sodium sulfite solutions (TSI  
87 3076 atomizer), pH buffered in one experiment with sulfuric acid. In certain experiments the  
88 aerosol flow was diffusion dried. Hydrogen peroxide gas was added in certain experiments by  
89 bubbling 0.2 L/min N<sub>2</sub> through a 30% w/w solution. A continuous flow of glyoxal gas was  
90 generated by flowing N<sub>2</sub> over a mixture of solid GTD and P<sub>2</sub>O<sub>5</sub> heated to 45 – 80 °C.(26) Glyoxal  
91 production was monitored by absorbance at 405 nm using a cavity ringdown (CRD) spectrometer  
92 and a cross section of  $4.491 \times 10^{-20}$  cm<sup>2</sup> molecule<sup>-1</sup>.(27) The various inlet flows totaling 2.5 L/min  
93 were mixed at the inlet to a 2.5 L Pyrex vessel, such that the average reaction time was 1 min.  
94 Aerosol particles exiting the reaction vessel were diffusion dried and monitored by Q-AMS  
95 (Aerodyne), CAPS-ssa (450 nm, Aerodyne), scanning mobility particle sizing (SMPS), CRD (530  
96 nm), and photoacoustic spectrometers (405 and 530 nm), with total sampling flows set to match

97 the inlet flows (2.5 L/min). Two-minute averaging of 1-Hz CAPS data allows albedo to be  
98 measured with precision typically between  $\pm 0.001$  and  $\pm 0.005$ , while geometric mean diameters  
99 extracted from SMPS size distributions have  $\pm 2$  nm precision. RH sensors monitored humidity  
100 levels at the aerosol inlet, chamber outlet, and dried chamber outlet flows.

101

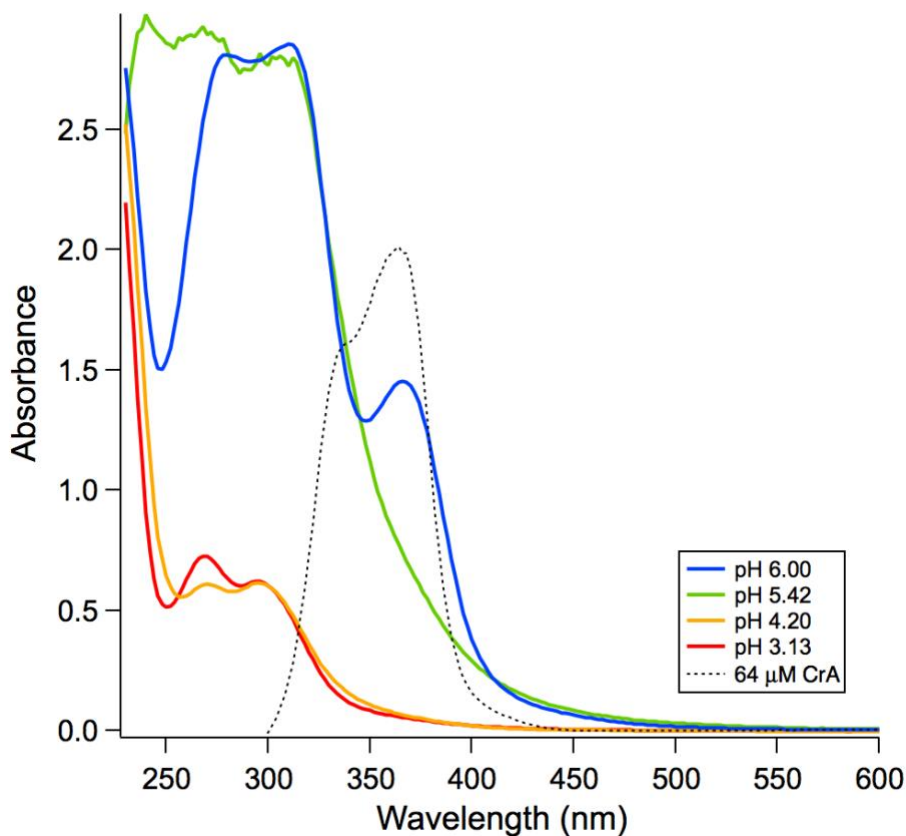
## 102 **Results and Discussion**

103 Bulk studies. In cloudwater (or other aqueous samples with pH between 2 and 7), acid-base  
104 equilibria will cause dissolved  $\text{SO}_2$  to exist mainly as bisulfite ions ( $\text{HSO}_3^-$ ) since  $\text{H}_2\text{SO}_3$  has  $pK_a$   
105 values of 1.9 and 7.2. The initial reaction between glyoxal and bisulfite is rapid. For example, in  
106  $\text{N}_2$ -bubbled pH 4 buffer, 0.1 M  $\text{HSO}_3^-$  reacted with 0.1 M glyoxal with  $t_{1/2} = 9$  s (Figure S2). These  
107 aqueous-phase concentrations are 40 and 80x higher, respectively, than estimated equilibrium  
108 concentrations in atmospheric cloud droplets at pH 6.(12) The measured half-life implies a rate  
109 constant  $k = 1.11 \text{ s}^{-1}\text{M}^{-1}$ , which is lower than (but within a factor of 7 of) earlier measurements  
110 conducted at pH = 3.26 and 0.0015 M.(12) This difference could be due to dehydration of glyoxal  
111 becoming rate-determining above pH 3.26.(12) The reversible formation of bisulfite dimer ions  
112 does not appear to be favorable enough to impact reaction rates even in our highest concentration  
113 experiments (Figure S3).(28)

114 The pH-dependence of brown carbon products generated in 2 days by glyoxal + bisulfite  
115 reactions is summarized in Figure 1. At pH 3.1 or 4.2, reaction products absorb light only in the  
116 UV range, while at pH 5.4 (Figure S4) and 6.0, visible light absorbers were produced. Importantly,  
117 at no point in the glyoxal + sulfite reaction in experiments at  $\text{pH} \leq 5.4$  do the characteristic visible  
118 absorbance bands of THBQ or RhA appear (both with  $\lambda_{\text{max}} = 485$  nm, Figures S5 and S6),  
119 suggesting that if these species are formed they are either reactive intermediates or minor products.



120 At pH 6.0, CrA can be quantified by its absorbance and fluorescence bands (Figures 1 and S7) at  
121 a 0.02% yield. The major products formed at mildly acidic pH are therefore different than the  
122 hydroquinones that form at high yields under basic conditions.



123  
124 **Figure 1:** UV-vis absorbance spectra of 0.25 M glyoxal + 0.25 M sodium sulfite solutions after  
125 2 days reaction time, buffered to initial pH 6.00 (blue), pH 5.42 (green), pH 4.20 (orange), and pH  
126 3.13 (red). Spectrum of 64  $\mu\text{M}$  aqueous croconic acid standard is overlaid for comparison.

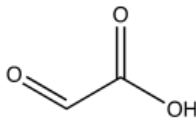
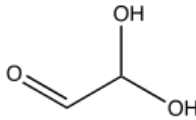
127  
128 The observed product differences may be due to pH-dependent hydroquinone instability. Both  
129 THBQ and RhA are unstable in aqueous solution at pH 5.5, having respective lifetimes of only 42  
130 and 70 min (Figures S5 and S6) even after initial  $\text{N}_2$  bubbling to remove oxidants. A 1 mM THBQ  
131 solution aged at pH 3 for 24 h turned from red to yellow and showed an unmistakable oligomer  
132 pattern(29) when analyzed by ESI-MS, with dominant peaks in the  $\text{C}_{10}$ - $\text{C}_{11}$  mass range (Figure

133 S8). Thus, it is plausible that glyoxal + sulfite reactions under slightly acidic conditions produce  
 134 a small amount THBQ as an intermediate, which then forms other light-absorbing oligomers.

135 To better characterize glyoxal + HSO<sub>3</sub><sup>-</sup> chemistry, a pH 5.4 reaction sample was analyzed by  
 136 negative ion mode ESI-MS after 12 d reaction time in capped vials. Major peaks detected are  
 137 listed in Table 1, along with proposed peak assignments. Even after 12 d, glyoxal and its self-  
 138 reaction oligomers are responsible for 5 peaks, including 3 of the 8 largest peaks. Bisulfite adducts  
 139 of these molecules (sulfonates) make up another 5 of the largest 15 peaks, and the HSO<sub>4</sub><sup>-</sup> (bisulfate,  
 140 *m/z* 97) peak is small, evidence that oxidation of the sample has been minimal. Glyoxal  
 141 monobisulfite (GMBS), *m/z* 139, and glyoxal dibisulfite, *m/z* 221, major products observed by  
 142 Olson and Hoffmann,<sup>(12)</sup> are the 2<sup>nd</sup> and 14<sup>th</sup> largest peaks detected in the mass spectrum,  
 143 respectively. The ESI-MS peak areas of these sulfonates were largest upon initial measurement (*t*  
 144 = 3 h) and showed a slow downward trend thereafter (Figure S9), evidence that they are quickly  
 145 formed and quite stable, consistent with prior work.<sup>(12)</sup>

146

147 Table 1: Peak Ions Detected in Solution Containing 0.25 M Glyoxal and NaHSO<sub>3</sub> at pH 5.42 After  
 148 13 d Reaction Time.

<i>m/z</i> of detected ion	assigned formula	identity	product generation	peak size ranking	proposed neutral structure
73	C <sub>2</sub> HO <sub>3</sub> <sup>-</sup>	glyoxylic acid	1 <sup>st</sup>	22	
75	C <sub>2</sub> H <sub>3</sub> O <sub>3</sub> <sup>-</sup>	glyoxal monohydrate GX.H <sub>2</sub> O	reactant	7	

81	$\text{HSO}_3^-$	bisulfite	reactant	13	
97	$\text{HSO}_4^-$	bisulfate	1 <sup>st</sup>	18	
111	$\text{CH}_3\text{SO}_4^-$	hydroxymethane -sulfonic acid, HMS	3 <sup>rd</sup>	3	
133	$\text{C}_4\text{H}_5\text{O}_5^-$	$\text{GX}_2 \cdot \text{H}_2\text{O}$	reactant oligomer	8	
139	$\text{C}_2\text{H}_3\text{SO}_5^-$	$\text{GX} \cdot \text{HSO}_3^-$ GMBS	1 <sup>st</sup>	2	
151	$\text{C}_4\text{H}_7\text{O}_6^-$	$\text{GX}_2 \cdot 2\text{H}_2\text{O}$	reactant oligomer	11	
155	$\text{C}_2\text{H}_3\text{SO}_6^-$	glyoxylic acid. $\text{HSO}_3^-$	2 <sup>nd</sup>	10	
157	$\text{C}_2\text{H}_5\text{SO}_6^-$	$\text{GX} \cdot \text{HSO}_3^- \cdot \text{H}_2\text{O}$	1 <sup>st</sup>	4	
169	$\text{C}_3\text{H}_5\text{SO}_6^-$	$\text{GX} \cdot \text{HMS}$	3 <sup>rd</sup>	1	
171	$\text{C}_2\text{H}_3\text{SO}_7^-$	$\text{HOO} \cdot \text{GX} \cdot \text{HSO}_3^-$	2 <sup>nd</sup>	6	

209	$C_6H_9O_8^-$	$GX_3 \cdot 2H_2O$	reactant oligomer	5	
215	$C_4H_7SO_8^-$	$GX_2 \cdot HSO_3^-$	1 <sup>st</sup>	9	
221	$C_2H_5S_2O_8^-$	$GX \cdot 2HSO_3^-$	2 <sup>nd</sup>	14	
267	$C_8H_{11}O_{10}^-$	$GX_4 \cdot 2H_2O$	reactant oligomer	16	
273	$C_6H_9SO_{10}^-$	$GX_3 \cdot HSO_3^-$	1 <sup>st</sup>	15	
335	$C_{10}H_7O_{13}^-$	$CrA_2 \cdot 3H_2O$	5 <sup>th</sup>	minor	

149 Notes: While  $m/z$  171 is also the unit mass of THBQ, the dominant product at high pH, the low  
 150 yields of THBQ determined by spectrophotometry in the previous section means that THBQ  
 151 cannot contribute more than 1% to the  $m/z$  171 ESI-MS signal. Similarly, RhA contributes less  
 152 than 0.05% of the signal at  $m/z$  169. These hydroquinone products are too unstable in aqueous  
 153 solution to build up to high concentrations at long reaction times. The ESI-MS spectrum is shown  
 154 in Figure S3.

155  
 156 Other detected peaks show evidence of oxidation, presumably caused by ambient oxidants  
 157 introduced when reaction vials were sampled (every 2 d on average). A small peak at  $m/z$  73 is  
 158 likely due to glyoxylic acid, formed by oxidation of glyoxal monomer. A minor peak at  $m/z$  335,  
 159 which was the largest peak in the 24-h aged THBQ solution (Figure S8), may be a light-absorbing

160 CrA dimer trihydrate formed via THBQ. If an OH radical abstracts a proton from GMBS, the  
161 addition of O<sub>2</sub> produces a peroxyacid sulfonate molecule at *m/z* 171. OH radical addition converts  
162 GMBS to a carboxylic sulfonic acid (*m/z* 155), which could also be produced by reaction between  
163 glyoxylic acid and bisulfite. OH radical oxidation of this carboxylic sulfonic acid followed by  
164 decarboxylation is the likely path to two major products with odd numbers of carbon:  
165 hydroxymethanesulfonate (HMS, *m/z* 111, 3<sup>rd</sup> largest peak) and a C<sub>3</sub> sulfonate (*m/z* 169, largest  
166 peak) likely formed via glyoxal addition to the HMS radical (as summarized in Scheme S1). The  
167 formation of HMS was confirmed by <sup>1</sup>H NMR through its characteristic CH<sub>2</sub> peak at 4.23 ppm  
168 (Figure S10).

169 Peak areas were examined as a function of reaction times between 3 h and 15 d for three oxidized  
170 products (*m/z* 97, bisulfate ion; *m/z* 169, C<sub>3</sub> sulfonate; and *m/z* 171, C<sub>2</sub> peroxy sulfonate). All 3  
171 slowly increased with reaction time (Figure S9). In contrast, the peak areas of four 1<sup>st</sup>-generation  
172 sulfonate products generated by direct (non-oxidative) reactions slowly decreased over the same  
173 time period, presumably after being formed earlier in the reaction (*t* < 3 h). This is consistent with  
174 oxidation reactions converting some 1<sup>st</sup> generation sulfonates into other sulfonate species, at rates  
175 limited by the supply of oxidant species.

176 It is notable that OH radical oxidation of GMBS appears to occur much more readily on the  
177 organic end of the molecule rather than at the sulfite group. The small size of the bisulfate ion  
178 peak at *m/z* 97 suggests that sulfur is protected from oxidation via incorporation into sulfonates,  
179 and that sulfonate C-S bonds are largely preserved during the limited oxidation of this sample.  
180 This is consistent with earlier studies that noted that while S(IV) can be oxidized by HOOH and  
181 ozone, once S(IV) is converted to HMS it does not react appreciably with either oxidant.(11)

182

183 Flow chamber studies. The ability of glyoxal gas to cause rapid browning of Na<sub>2</sub>SO<sub>3</sub> aerosol  
184 particles was tested in a series of 7 flow chamber experiments with 1-min residence times (Table  
185 2). Significant browning was observed at 405 and 450 nm by photoacoustic and cavity-attenuated  
186 phase-shift spectroscopy, respectively, in experiment 1 (Figure 2), where a constant flow of  
187 aqueous Na<sub>2</sub>SO<sub>3</sub> aerosol was mixed in this chamber with a smaller flow of dry N<sub>2</sub> / glyoxal to  
188 achieve 80% RH and 100 ppb glyoxal after mixing. In experiment 6, the only experiment with a  
189 gas-phase source of S(IV) and the only experiment with NaCl instead of Na<sub>2</sub>SO<sub>3</sub> seed particles, no  
190 gas-phase reaction between SO<sub>2</sub> and glyoxal was observed. However, NaCl seeds have been  
191 shown to catalyze SO<sub>2</sub> uptake,<sup>(30)</sup> and once aqueous NaCl seed particles were added, the second-  
192 lowest 450 nm albedo of 0.96 was achieved (Figure S11). AMS organic aerosol signals were also  
193 clearly present as soon as NaCl seeds were added. These observations suggest that both SO<sub>2</sub> and  
194 glyoxal were taken up by aqueous NaCl aerosol particles, where they reacted to form measurable  
195 brown carbon within on a 1-min timescale. In all other experiments (2-5 and 7), less browning  
196 was observed despite generally higher glyoxal concentrations and high SOA growth via glyoxal  
197 uptake. Browning in these experiments was likely slowed by much lower levels of aerosol-phase  
198 water (Expts. 3-5 and 7), or by the presence of 60% mole fraction aerosol-phase sulfuric acid  
199 (Expt. 2, Figure 3), which converted SO<sub>3</sub><sup>2-</sup> ions to a mixture of less reactive<sup>(31)</sup> HSO<sub>3</sub><sup>-</sup> and H<sub>2</sub>SO<sub>3</sub>.  
200 Experiments 1 and 2 are discussed in detail below.

201

202

203 Table 2: Summary of Flow Chamber Experiments: Sodium Sulfite Aerosol + Glyoxal (g)

expt.	figure	PAS <sub>abs</sub> , 405 nm (Mm <sup>-1</sup> )	albedo, 450 nm	[GX] (ppb) <sub>a</sub>	[Na <sub>2</sub> SO <sub>3</sub> ] (μg/m <sup>3</sup> )	% RH	AMS Org/SO <sub>4</sub> ratio	growth, (μg/m <sup>3</sup> )	notes
1	2	160	0.940	110	80 wet	80	0.9	55	
2	3	2	0.986	90	40 wet	80	0.4	24	Acidified pH 4 <sub>b</sub> (2:3 Na <sub>2</sub> SO <sub>3</sub> / H <sub>2</sub> SO <sub>4</sub> mole ratio)
3	S12	15	0.988	450	200 wet	50	0.9	150	
4	S12	10	0.980	500	180 wet	60	1.4	310	in air
5	S13	0.2	0.983	700	40 wet	50	1.0	52	HOOH (g) present
6	S11	<i>c</i>	0.960	~100 <sub>d</sub>	Wet NaCl	80	Org/Cl = 3	<i>c</i>	SO <sub>2</sub> (g) from Na <sub>2</sub> SO <sub>3</sub> (aq) bubbler
7	S14	<0.1	0.983	2500	420 dry	60-80	2.0	210	In 7% O <sub>2</sub> , 93% N <sub>2</sub>

204 \*Not measured. PAS = photoacoustic spectroscopy. GX = peak glyoxal conc. RH = relative  
 205 humidity. AMS = aerosol mass spectrometer. Aerosol particles had 1 min lifetime in flow  
 206 chamber. **a**: peak glyoxal concentrations are shown. **b**: before atomization into aerosol. **c**: no  
 207 measurement. **d**: estimated from glyoxal source temperature.

208

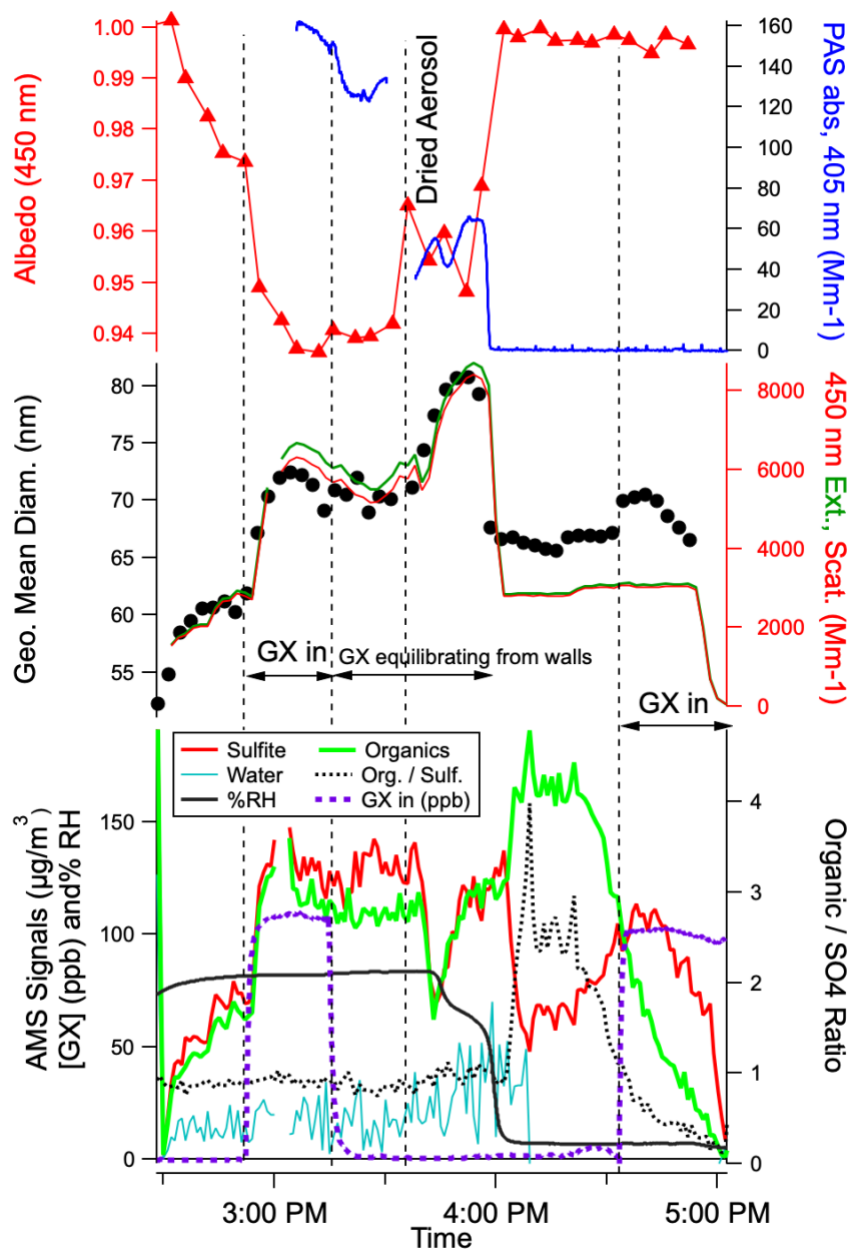
209 In experiment 1 (Figure 2), deliquesced Na<sub>2</sub>SO<sub>3</sub> aerosol were sent through the flow chamber in  
 210 humidified N<sub>2</sub> from 2:45 until 3:36 pm. At 2:50 pm the dry N<sub>2</sub> flow was routed through a heated  
 211 glyoxal source, rapidly reaching a calculated steady-state concentration of ~110 ppb glyoxal in the  
 212 mixing chamber. (Actual glyoxal concentrations may have been significantly lower due to uptake  
 213 by chamber walls at 80% RH.) Glyoxal addition caused SMPS particle diameters to increase by  
 214 20% and particle masses to increase by 70%, indicating significant and rapid glyoxal uptake. At  
 215 the same time, albedo at 450 nm declined from 0.97 to 0.94, indicating brown carbon formation

216 by glyoxal + sulfite reactions on a 1-min timescale. Interestingly, AMS signals for both organics  
217 and sulfate rose upon glyoxal addition, such that their ratio remains near 1. While sulfonates are  
218 efficiently broken down in the AMS inlet into organic and sulfate fragments,<sup>(3)</sup> the formation and  
219 destruction of sulfonates would not be expected to increase sulfate signals. Instead, this increase  
220 in sulfate signal indicates that the uptake of glyoxal (and formation of sulfonates) caused a  
221 significant shift in the effective Henry's Law equilibrium of S(IV) (SO<sub>2</sub> and sulfite) towards the  
222 aqueous phase, as predicted by Olson & Hoffmann.<sup>(12)</sup> The glyoxal source was turned off at 3:15  
223 pm (Figure 2), but albedo at 450 nm, aerosol absorbance at 405 nm, particle size, and AMS particle  
224 chemistry all remained constant, likely due to the preservation of glyoxal steady-state  
225 concentrations caused by equilibration from the glass walls in the humid chamber.<sup>(32, 33)</sup>

226 At 3:36 pm, the aerosol source was routed through a diffusion dryer, generating effloresced  
227 instead of aqueous Na<sub>2</sub>SO<sub>3</sub> aerosol even as RH remains between 60 and 84% for 20 more min due  
228 to water equilibrium from the walls. (Solid Na<sub>2</sub>SO<sub>3</sub> aerosol deliquesces above 85% RH.<sup>(31)</sup>) The  
229 change in particle phase from liquid to solid caused SMPS particle diameter to increase by an  
230 additional 11%. This suggests that glyoxal uptake is enhanced by oligomer formation in the high  
231 concentration environment of the surface water layer, such that particle growth is greater than it  
232 was on deliquesced aerosol. This effect has been seen in prior studies involving glyoxal.<sup>(34)</sup> At  
233 the same time, the switch to solid aerosol particles coincided with a 450 nm albedo rise from 0.94  
234 to 0.96, and a 60% decline in absorbance at 405 nm, both indicative of less brown carbon formation  
235 during the 1 min chamber residence time. This effect is likely due to aerosol-phase diffusion  
236 limitations that limit the supply of sulfite ions to the surface water layer where glyoxal is reacting.  
237 These observations show that glyoxal and sulfite ions can react in aqueous aerosol (and to a lesser  
238 extent in surface water layers on solid aerosol particles) to rapidly form brown carbon products.



239



**Figure 2:** Gas-phase glyoxal uptake experiment 1: aqueous  $\text{Na}_2\text{SO}_3$  aerosol (before 3:35 pm) and effloresced  $\text{Na}_2\text{SO}_3$  aerosol in flowing chamber (1 min residence time). **Top:** CAPS single-scattering albedo of dried aerosol at 450 nm (red triangles), recorded immediately after instrument baseline taken through filter; photoacoustic absorbance ( $\text{Mm}^{-1}$ , blue line) of dried aerosol at 405 nm. **Middle:** SMPS geometric mean diameters of dried aerosol (black circles); CAPS-ssa inlet-dilution-corrected 2-min-averaged extinction (green line), scattering (red line). **Bottom:** Glyoxal (g) concentrations in ppb, calculated based on dilution and cavity ringdown spectroscopic measurements made at 405 nm at the chamber inlet and no wall equilibria (purple line, left axis); relative humidity measured at chamber outlet (black line); dilution

corrected aerosol mass spectrometer loadings by category (left axis; water, light blue; sulfite, red; organics, green); and organic / sulfite ratio (gray dotted line, right axis). Vertical dotted lines mark beginning and ending of glyoxal addition, the switch from aqueous to deliquesced  $\text{Na}_2\text{SO}_3$  seed aerosol, and the start of 2<sup>nd</sup> glyoxal addition, as labeled. AMS water signals are qualitative due to drying in the low-pressure inlet; water signals are included to show that particles pass through the chamber and the AMS sampling line fully dry only after ~4:10 pm.

280

281 After 27 min. of dry gas and aerosol input (*i.e.*, ~4:00 pm in Figure 2), the flowing reaction cell  
282 surfaces were depleted of water, and RH in the chamber outflow declined to < 10%. Under these  
283 fully dry conditions, Na<sub>2</sub>SO<sub>3</sub> aerosol passed through the glyoxal-containing chamber without  
284 browning: aerosol albedo (450 nm) promptly rose to 1.00 and aerosol absorbance (405 nm)  
285 dropped to zero. At the same time, AMS sulfite signals declined by approximately 50%, back to  
286 pre-glyoxal-addition levels. These changes indicate that glyoxal and sulfite cannot react in the dry  
287 aerosol phase on a 1 min timescale, such that sulfite gas-particle partitioning is no longer perturbed  
288 and brown carbon is no longer formed.

289 Glyoxal uptake to Na<sub>2</sub>SO<sub>3</sub> particles did not end at this point, however. Although SMPS  
290 geometric mean diameters of the dried aerosol declined from 81 to 66 nm upon chamber drying,  
291 66 nm is still 6% larger than initial pre-glyoxal diameters. Furthermore, the organic AMS signal  
292 actually rises after the RH drops to below 10%, peaking at 16:09 just as the AMS water signal  
293 drops to zero. AMS data collected during this period (Figure S15) shows prominent increases at  
294 *m/z* 18, 44, 45, and 46 (likely oxalic acid), and relative increases in minor peaks at *m/z* 80 and 98  
295 (sulfuric acid). These increases suggest that glyoxal and sulfite ions are more susceptible to  
296 oxidation under dry conditions when they do not react with each other. When glyoxal addition  
297 was restarted in the fully dried chamber (100 ppb, 4:33 pm), a statistically significant 5% increase  
298 in aerosol diameters was observed, but albedo did not change. This is further evidence that a  
299 small amount of glyoxal can be taken up by residual surface water on dry Na<sub>2</sub>SO<sub>3</sub> aerosol, but no  
300 brown carbon is formed without an aqueous phase.

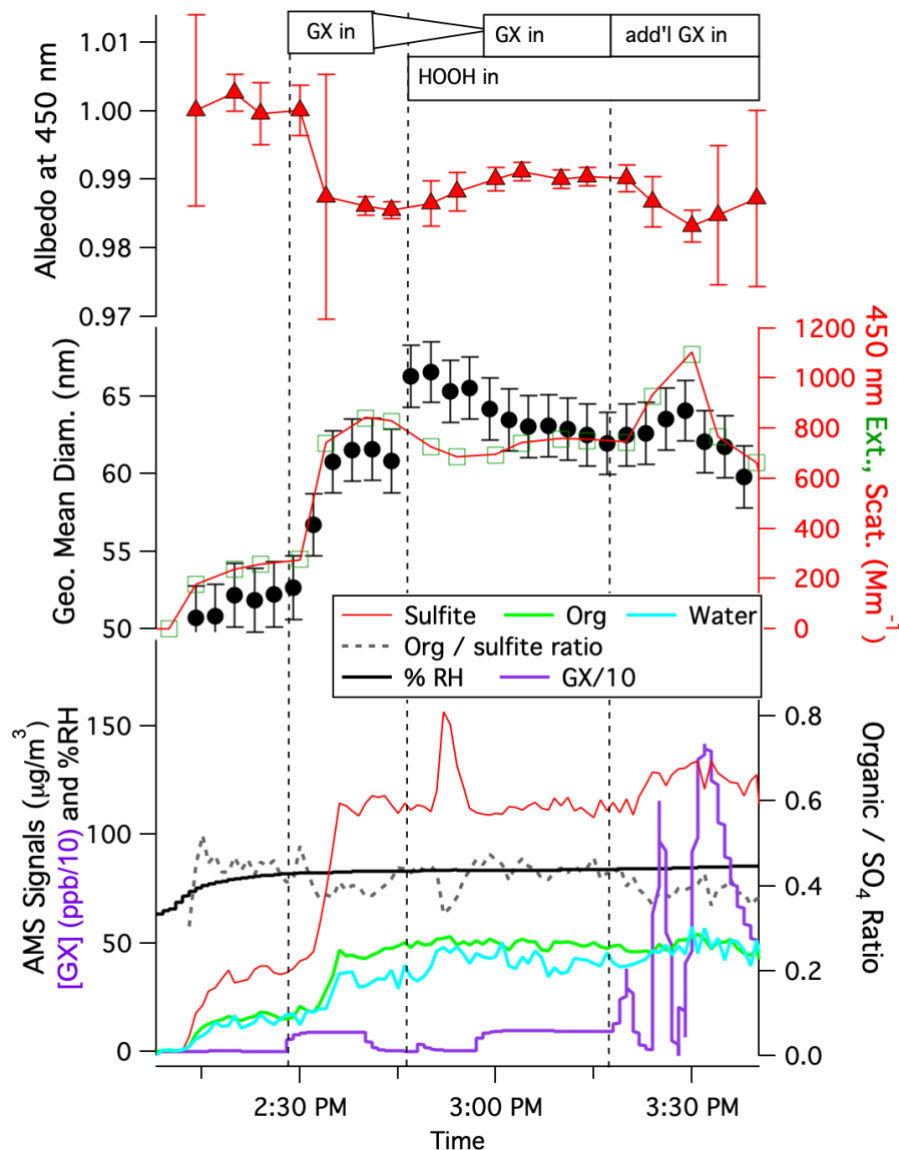
301 Experiment 2 (Figure 3) was conducted at the same RH as experiment 1, but with aqueous-phase  
302 sulfite ions converted to an equimolar mix of HSO<sub>3</sub><sup>-</sup> and H<sub>2</sub>SO<sub>3</sub> by the addition of sulfuric acid to  
303 pH 4.0. (Na<sub>2</sub>SO<sub>3</sub> / H<sub>2</sub>SO<sub>4</sub> were mixed at a 2:3 mole ratio). When 90 ppb glyoxal was added to the

304 flowing chamber at 2:28 pm, once again we observed a decline in albedo, an increase in SMPS  
305 particle mean diameter, and proportional (4×) increases in AMS signals for sulfate and organics,  
306 all occurring on a 1-min timescale (the residence time of aerosol particles in the flowing chamber).  
307 While the increases in particle size and AMS signals are comparable in magnitude to experiment  
308 1 with non-acidified sulfite aerosol, the albedo decline is at least a factor of 2 smaller. This  
309 suggests that glyoxal uptake and reaction with  $\text{HSO}_3^-$  to form sulfonates is still fast, but brown  
310 carbon formation is slowed, consistent with the pH-sensitivity observed in bulk-phase  
311 experiments.

312 The change in detected ions upon glyoxal addition is summarized in Figure S16. Because of the  
313 proportional 4× increase in AMS sulfate and organics, most signals fall on a new 4:1 line, with  
314  $m/z$  29, 30, 31 and 58 (glyoxal and its EI major fragments) being prominent organic ions detected.  
315 A few low-abundance ion signals increased by an order of magnitude, however, including  $m/z$  80  
316 and 97 (bisulfate ion) and 111 and 112 (HMS). These are some of the same products detected in  
317 bulk, acidified glyoxal + S(IV) solutions after very long reaction times, especially given that the  
318 glyoxal hydrates and oligomers (and perhaps adducts with S(IV)) detected by ESI-MS would  
319 undergo thermal breakdown to glyoxal monomer(35) during vaporization in the high-temperature  
320 AMS inlet.

321 The addition of  $\text{HOOH}$  gas from a bubbler at 2:45 pm (Figure 3) caused further growth in particle  
322 size, but brown carbon formation declined slightly (450 nm albedo increased). Starting at 3:20  
323 pm, three pulses of very high (ppm) levels of glyoxal were introduced to the flowing chamber, but  
324 these additions caused only minor changes in physical or optical properties of the aerosol (max  
325 change in albedo = -0.007, max change in particle mass = +10%). It appears that the effects of

326 glyoxal exposure on S(IV)-containing aerosol particles became saturated due to chamber wall  
 327 uptake / wall equilibrium at 80% RH.



**Figure 3:** Gas-phase glyoxal uptake experiment 2: aqueous pH 4  $\text{Na}_2\text{SO}_3$  /  $\text{H}_2\text{SO}_4$  aerosol in flowing chamber (1 min residence time). **Top:** CAPS single-scattering albedo of dried aerosol at 450 nm (red triangles), recorded immediately after instrument baseline taken through filter, error bars show standard deviation of the 2-min. averages; **Middle:** SMPS geometric mean diameters of dried aerosol (black circles); CAPS-ssa inlet-dilution-corrected 2-min-averaged extinction (green squares), scattering (red line). **Bottom:** Glyoxal (g) concentrations in ppb after dividing by 10,

359 calculated based on dilution and cavity ringdown spectroscopic measurements made at 405 nm at  
 360 the chamber inlet and no wall equilibria (purple line, left scale); relative humidity measured at  
 361 chamber outlet (black line); dilution corrected AMS loadings by category (left scale; water, light  
 362 blue; sulfite, red; organics, green); and organic / sulfite ratio (gray dotted line, right axis). Vertical  
 363 dotted lines mark beginnings of glyoxal or HOOH additions, as labeled.  
 364

365 In summary, fast particle growth due to glyoxal uptake is most pronounced in the surface water  
 366 layer of solid  $\text{Na}_2\text{SO}_3$  aerosol at high RH, but brown carbon formation on a 1-min timescale is

367 maximized when Na<sub>2</sub>SO<sub>3</sub> aerosol particles are deliquesced. Some glyoxal uptake onto solid  
368 Na<sub>2</sub>SO<sub>3</sub> aerosol is observed even under completely dry conditions (< 5% RH), but brown carbon  
369 is not formed. In aqueous Na<sub>2</sub>SO<sub>3</sub> aerosol particles acidified to pH 4, aerosol growth and  
370 partitioning of S(IV) to the aqueous aerosol phase are observed that are similar in magnitude to  
371 unacidified experiments, but brown carbon formation is lessened. On the other hand, while in bulk  
372 liquid studies no visible light absorbers were produced at pH 4.2 or less over 2 d reaction times, in  
373 aerosol particles generated from pH 4 solution measurable absorbance at 450 nm was generated in  
374 only 1 min. Thus, it appears that glyoxal uptake, reaction with S(IV) to form sulfonic acids, and  
375 to a lesser extent brown carbon formation from these precursors can all occur rapidly at acidic pH  
376 in aqueous aerosol. Reaction acceleration in aerosol particles (relative to bulk liquid experiments)  
377 has been observed in many other systems,(30, 36-40) and is likely caused by surface-reactive  
378 species. Such reactions are likely to show a particle size dependence. We note that dried particle  
379 sizes in this study (50-80 nm) were slightly smaller than atmospheric accumulation mode particles  
380 (> 100 nm).

381

### 382 **Atmospheric Significance**

383 In the flowing aerosol experiments with deliquesced Na<sub>2</sub>SO<sub>3</sub> aerosol at 80% RH, glyoxal  
384 concentrations were ~110 ppb, and reaction times were 1 minute. If the initial reaction between  
385 glyoxal (g) and sulfite ions is the rate-limiting step in brown carbon formation, and since that step  
386 is first order with respect to glyoxal,(12) then we can scale down to atmospheric conditions using  
387 an “integrated glyoxal” concept that is analogous to “integrated OH” in oxidation studies using  
388 OH reactors. Using this concept, the 1-minute lifetime in our aerosol experiments corresponds to  
389 about 18 h of glyoxal exposure at atmospheric concentrations of 100 ppt. Thus, given that glyoxal

390 is efficiently scavenged by aqueous aerosol, it appears that glyoxal exposure could reasonably  
391 depress the albedo of atmospheric aerosol particles in humid, polluted regions where aerosol  
392 particles are liquid and contain significant quantities of dissolved SO<sub>2</sub>.

393 The pH dependence seen in our aerosol and bulk studies suggests that brown carbon formation  
394 by glyoxal-SO<sub>2</sub> reactions would be most pronounced in aerosol that are neutralized by ammonia  
395 and amines, a situation that is becoming more common in the atmosphere as ammonia and amine  
396 emissions are uncontrolled and rising. It should also be noted that aqueous reactions between  
397 glyoxal and ammonia and amines under neutral conditions have also been identified as a source of  
398 brown carbon.(41-45) Aqueous-phase glyoxal + S(IV) reactions produce hydroquinones at very  
399 low yields at pH ≤ 6, but oligomer products in this pathway may nevertheless be contributing  
400 significantly to light absorption.

401 Recent work has suggested that HMS is the most abundant organosulfate compound in the  
402 aerosol phase during Chinese winter haze events.(3) Because it can be easily converted to sulfate  
403 by typical AMS and ion chromatography methods, HMS may be responsible for 1/3 of the  
404 unexplained “sulfate” formation reported there. In this work we have shown that HMS, long  
405 assumed to be formed only from formaldehyde and S(IV),(3, 46) is also an important product of  
406 aqueous phase glyoxal + S(IV) reactions under mildly acidic conditions. Cloudwater  
407 concentrations of formaldehyde and glyoxal in the atmosphere are comparable, with measured  
408 formaldehyde:glyoxal ratios between 0.7 and 4.(47-50) Given that bisulfite reaction rates with  
409 formaldehyde in bulk aqueous solution are 6000x faster than with glyoxal,(14) it seems at first  
410 glance unlikely that glyoxal + S(IV) could be a significant source of atmospheric HMS. However,  
411 glyoxal + S(IV) reactions begin with a nucleophilic attack by the S(IV) lone pair on a non-hydrated  
412 carbonyl functional group. Glyoxal preferentially forms a monohydrate (with a non-hydrated

413 carbonyl) at air-water interfaces, causing nucleophilic attack reaction rates on glyoxal to be  
414 enhanced by orders of magnitude in aerosol experiments, compared with bulk solution  
415 measurements.(36) Even in Los Angeles, where cloud formaldehyde levels are typically in excess  
416 of S(IV) levels,(51) Richards *et al.* determined that only 1/3 of the S(IV) in clouds and fog had  
417 reacted with formaldehyde to form HMS, based on measurements of free formaldehyde.(52) It  
418 thus appears that there is enough S(IV) in clouds and aqueous aerosol to react with glyoxal, and it  
419 is at least possible that glyoxal + S(IV) reactions contribute to observed HMS concentrations.

420 Field measurements of the glyoxal sulfonate C<sub>2</sub> adduct molecule could establish an upper limit  
421 on the size of this HMS source. Based on comparative ESI-MS and NMR peak heights in this  
422 work, the ratio of glyoxal sulfonate C<sub>2</sub> adduct to HMS produced in glyoxal + sulfite reactions at  
423 pH 5 is 9 +/-4 even after long reaction times. Production of HMS at moderate yield by glyoxal +  
424 S(IV) reactions may help explain the correlation between HMS, oxalic acid, and sulfate noted in  
425 field measurements, where elevated levels are associated with aged, cloud-processed pollution  
426 plumes.(13)

427

428 **Supporting Information Available:** Experimental schematic, additional UV/vis, fluorescence,  
429 NMR, and mass spectra for reaction mixtures and standard compounds, AMS spectra comparisons,  
430 summaries of flow chamber experiments 3 – 7, and reaction scheme.

431

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433

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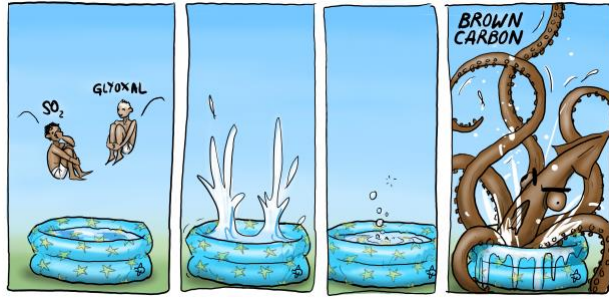


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