Aqueous-phase chemistry of glyoxal with multifunctional reduced nitrogen compound: A potential missing route of secondary brown carbon

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Abstract. Aqueous-phase chemistry of glyoxal (GL) with reduced nitrogen compounds (RNCs) plays a significant source of secondary brown carbon (SBrC), which is one of the largest uncertainties in climate predictions. However, few studies have revealed that SBrC formation is affected by multifunctional RNCs, which has a non-negligible atmospheric abundance. Hence, we performed theoretical and experimental approaches to investigate the reaction mechanisms and kinetics of the mixtures for ammonium sulfate (AS), multifunctional amine (monoethanolamine, MEA) and GL. Our experiments indicate that the light-absorption and the growth rate are enhanced in MEA-GL mixture relative to AS-GL and MEA-AS-GL mixtures, and MEA reactions of the chromophores by more efficiently than the analogous AS reactions. Quantum chemical calculations show that the formation and propagation of oligomers proceed via four-step nucleophilic addition reactions in three reaction systems. The presence of MEA provides the extra two branched chains to affect the natural charges and steric hindrance of intermediates, facilitated the formation of chromophores. Molecule dynamics simulations reveal that the interfacial and interior attraction on the aqueous aerosols with MEA is more pronounced for small α-dicarbonyls, to facilitate the further engagement in the aqueous-phase reactions. Our results show a possible missing source for SBrC formation on urban, regional and global scales.

1 Introduction

Brown carbon (BrC) represents the most important source of carbonaceous aerosols, with profound implications to the global climate, air quality and human health (Laskin et al., 2015; Marrero-Ortiz et al., 2018; Li et al., 2022; Yan et al., 2018; Yuan et al., 2023). Chemical transport models reveal that a non-negligible radiative forcing by BrC is range from 0.05 to 0.27 W m^{-2} averaged globally (Tuccella et al., 2020; Wang et al., 2018; De Haan et al., 2020; Zhang et al., 2020; Laskin et al., 2015; Moise et al., 2015). Large differences in these estimated data result from the uncertainties of BrC on its formation mechanisms,

chemical composition and optical properties (An et al., 2019; Shi et al., 2020; Kasthuriarachchi et al., 2020; Corbin et al., 2019). It affects understanding the radiative effect in current climate models (Liu et al., 2020; Zhang et al., 2020; Zhang et al., 2023). Compared with primary BrC, sources and formation of secondary BrC (SBrC) are more complex and lack of understanding in detail (Lin et al., 2015; Yuan et al., 2020; Srivastava et al., 2022). Hence, in recent years, great efforts have been made to better understand the chemical composition and formation mechanisms of SBrC chromophores.

There is compelling evidence that the heterogeneous reactions of reduced nitrogen compounds (RNCs) and small α-dicarbonyls have been recognized as significant sources of SBrC (Hawkins et al., 2018; De Haan et al., 2018; George et al., 2015). These SBrC chromophores are normally conjugated and possibly heteroaromatic species, such as imidazole (IML) and its derivatives (De Haan et al., 2009b; De Haan et al., 2009a; Yang et al., 2022). Numerous previous studies paid much attention to BrC from the secondary processes of small α-dicarbonyls with ammonium sulfate (AS) and methylamine (MA) (De Haan et al., 2020; De Haan et al., 2019; De Haan et al., 2009a; Lin et al., 2015). For example, nearly 30 chromophores were detected in AS-methylglyoxal (MG) mixture by HPLC/PDA/HRMS and nitrogen-containing compounds account for more than 70% of the overall light absorption within 300−500 nm range (Lin et al., 2015). Some studies have also revealed that the absorption of BrC generated in AS- or MA-MG mixture increases with pH value (Hawkins et al., 2018; Sedehi et al., 2013) Also, the iminium pathway is predominant while pH < 4 to form IML and its derivatives but is suppressed at pH 4.(Nozière et al., 2009; Sedehi et al., 2013; Yu et al., 2011). Hence, pH value has a large effect on the formation of SBrC chromophores, but the chemical mechanisms of BrC formation under the different pH values remain unclear, hindering a systematical understanding its integrated atmospheric chemistry and nonnegligible environmental impacts.

On the other hand, multifunctional RNCs (such as ethanolamines and amino acids) display a strong atmospheric activity to the formation of SBrC with an unneglected atmospheric concentration (Huang et al., 2016; Ge et al., 2011; Powelson et al., 2014b; Trainic et al., 2012; Laskin et al., 2015; Ning et al., 2022). For example, a rapid BrC formation was detected in glycine reactions with small α-dicarbonyls, and sub-micrometer amino acids particles exhibited a high growth upon exposure to small α-dicarbonyls (Powelson et al., 2014b; Sedehi et al., 2013; De Haan et al., 2009b; Trainic et al., 2012). On the other hand, monoethanolamine (MEA) is an amine-based solvent for post-combustion CO_2 capture (PCCC) technology with a relatively high vapor pressure, emitting 80 tons per year into the atmosphere for each 1 million tons of CO2 removed per year (Karl et al., 2011; Puxty et al., 2009; Shen et al., 2019). Recent field measurement has shown that MEA is the second most abundant organic amine in PM2.5 in Shanghai besides MA (Huang et al., 2016). However, to the best of our knowledge, few previous results are available on the participation of MEA in the SBrC formation with small α-dicarbonyls and its potential role in the atmosphere and human health were also not attempted.

Hence, we elucidated the chemical mechanisms of BrC chromophores from the mixtures of typical reaction of RCNs (i.e., MEA and AS) with small α-dicarbonyls using combined theoretical and experimental methods. Herein, glyoxal (GL) is selected as the representative of small α-dicarbonyls due to its high global emissions and significant contribution to BrC (Fu et al., 2008; Myriokefalitakis et al., 2008; Shi et al., 2020; Nie et al., 2022; Gomez et al., 2015). The chemical composition of the BrC chromophores was characterized by mass spectrometry in different initial pH values, and the optical properties were

66 measured using UV-Vis spectrophotometry. Possible pathways were calculated using density functional theory, and the

67 mechanism of BrC chromophore formation was also simulated. The effects of multifunctional amine in formation of SBrC

68 chromophores were elaborated further. Additionally, the potential implications of multifunctional amine on climate radiative

69 forcing were stated and discussed briefly.

70 **2 Experimental methods and theoretical calculations**

71 **2.1 Experimental section**

72 The procedures of each experiment are summarized in Fig. S1. All reagents were used as described in Supporting Information

73 (SI). Three mixtures were prepared under atmospheric relevant aqueous conditions to generate SBrC: AS-GL, MEA-GL and

74 MEA-AS-GL. Briefly, AS-GL (1 M) mixture was prepared by adding AS to aqueous GL (in ultrapure water) for a final

75 concentration of 1 M of each reactant in the volumetric flasks. For the two MEA-containing mixtures, MEA was acidified with

76 diluted sulfuric acid (20%) to prevent GL from reacting with MEA in alkaline condition. The acidified MEA was then combined

77 with aqueous GL similar to that described for the AS-GL (1 M) mixture. All three solutions mentioned above were then diluted

78 to reach a final concentration of 1 M in three 50mL volumetric flasks. To explore the effects of pH values, three mixtures were

79 prepared with an initial pH values of 3 or 4 via addition of sulfuric acid (20%) or sodium hydroxide solution (2 M) prior to the

80 mixing of RNCs and GL (Kampf et al., 2016; Yu et al., 2011). Each mixture was transported into brown vials, which has been

81 proven to avoid the photolysis and light-induced reactions of light-absorbing products (Kampf et al., 2012), to guarantee

82 efficiently produce chromophores in droplet evaporation collecting on the timescales of seconds (Zhao et al., 2015; Lee et al.,

83 2014).

84 The absorption spectra of all mixtures were recorded by using an UV-Vis spectrophotometer (Agilent Cary 300, USA).

85 All experimental solutions were diluted by a factor of 200 or 400 before each measurement to avoid saturation of the absorption

86 peaks. The diluted samples were added into a quartz cuvette with 1 cm optical path length right away to prevent the diluted

87 samples from photolysis. The spectra recorded between 200 – 500 nm were shown in Fig. 1. And the blank experiments of GL

88 and RNCs solution were performed and presented in Fig. S2. The absorption spectra of all samples were measured with three

89 times. The wavelength-dependent mass absorption coefficients (MACs) of experimental solutions were calculated from initial

90 base-10 absorbance (A_{10}),

91
$$\text{MAC}(\lambda) = \frac{A_{10}^{\text{solution}}(\lambda) \times \ln(10)}{b \times C_{\text{mass}}}$$

92 where C_{mass} is the mass concentration of reactants and b is path length (Aiona et al., 2017; Chen and Bond, 2010). The different

93 dilution factors were normalized by using MAC formula.

94 Samples used for mass spectrometry analysis were diluted by a factor of 800 or 1000 followed by syringe filtration. The

95 filters were stored in brown chromatography injection vials to block the light. Ultra-performance liquid chromatography

96 coupled to hybrid Quadrupole-Exactive Orbitrap mass spectrometry (UPLC-Q-Orbitrap HRMS, Thermo Scientific[TM], USA)

97 (Wang et al., 2017) was employed to obtain structural data of chromophores in this study. MS^2 analysis were used for all

98 chromophores with a weight error of less than 10 ppm compared with the theoretical mass to obtain fragments information for

99 the identification of structure analysis. Detailed description of the mass spectrometry and chromatographic conditions are all

100 described in SI.

2.2 Quantum calculations and molecular dynamics simulations

102 Quantum chemical calculations were performed using the Gaussian 09 package (M. J.Frisch, 2013). Structures for all

103 stationary points (SPs), including reactants, intermediates, transient states (TSs), and products, were optimized using the hybrid

104 density functional of M06-2X method(Zhao and Truhlar, 2007) with 6-311G(d,p) basis set, i.e., at the M06-2X/6-311G(d,p)

105 level (Ji et al., 2017). The solvent effect was considered using the solvation model based on density (SMD) to simulate the

106 aqueous environment (Gao et al., 2016; Marenich et al., 2009). Harmonic frequency calculation was carried out at the same

107 level as structural optimization to verify whether SP is a TS (with one and only imaginary frequency) or a minimum (without

108 imaginary frequencies) (Ji et al., 2022). Intrinsic reaction coordinate calculation was performed to confirm that the TSs

109 connected with the corresponding reactants and products. Single point energy (SPE) calculation was executed using the M06-

110 2X method with a more flexible 6-311+G(3df,3pd) basis set to obtain more accurate potential energy surfaces (PESs). For the

111 pathways with TSs, the rate constants (k) were calculated via conventional transition state theory (TST) (Evans and Polanyi,

112 1935; Eyring, 1935; Galano and Alvarez-Idaboy, 2009; Gao et al., 2014). To simulate real atmospheric conditions in the

113 solution, the calculated k values were refined by solvent cage effects(Okuno, 1997) and diffusion-limited effects (Collins and

114 Kimball, 1949), of which the calculation details of diffusion-limited rate constant k_d can be seen in SI. For the pathways without

115 TSs, the corresponding k values are predominated by the diffusion-limit effect which equal to the diffusion-limited rate

116 constants.

117 Classical molecular dynamics (MD) was performed using NAMD package (Phillips et al., 2005) to simulate the

118 heterogeneous processes of GL from gas to the AS and MEA particles. The AS particle is composed of 39 SO_4^{2-}, 78 NH_4^+ and

119 2046 H_2O in a box size of $40 \times 40 \times 40$ $Å^3$, while the MEA particle consists of 39 MEA and 2036 H_2O. The 5 ns equilibration

120 at the time step of 1 fs was executed in the isothermal-isochoric (NVT) ensemble (T = 298 K) to ensure the thermodynamic

121 equilibrium of particles (Shi et al., 2020; Zhang et al., 2019). The MD simulation of 2 ns is run via the NVT ensemble. MEA

122 and GL were described using CHARMM force field (Jorgensen et al., 1996), and H_2O using TIP3P model (Martins-Costa et

123 al., 2012). The fixed charges on NH_4^+ and SO_4^{2-} are scaled by 0.75 to account for the electronic polarizability (Leontyev and

124 Stuchebrukhov, 2011; Mosallanejad et al., 2020). The periodic boundary conditions were selected for three dimensions. In

125 order to calculate the kinetic trajectories of GL from gas to two target particles, the free energy profile along the distance of

126 the center of mass between each particle and GL was calculated via umbrella sampling (Torrie and Valleau, 1977) and

127 weighted-histogram analysis method (Kumar et al., 1992) based on the above equilibrated molecular dynamics trajectories.

128 The bias potential force constant was equal to 10 kcal mol^{-1} Å^{-2}.

3 RESULTS AND DISCUSSION

3.1 Mass absorption coefficients of BrC chromophores

The mass absorption coefficients (MACs) identified in AS-GL, MEA-GL, and MEA-AS-GL mixtures at the initial pH of 3 and 4 (denoted as pH = 3 and pH = 4) are shown in Fig. S3. The maximum adsorption peaks locate at 207, 212, and 209 nm for AS-GL, MEA-GL, and MEA-AS-GL mixtures at pH = 3, respectively, and the corresponding location is not changed at pH = 4. The MAC values of the maximum adsorption peaks are in the range of 1080−17909 cm^2 g^{-1} for three mixtures. In addition, each mixture has an absorption peak between 285 - 324 nm (Fig. S4), with a range of 42 - 228 cm^2 g^{-1}, which are consistent with the MAC values measured by Powelson et al. at the reaction time of 4 days (Powelson et al., 2014a) but are smaller than the values measured by Zhao et al. with a long reaction time of 2 - 3 months (Zhao et al., 2015). The MAC values at 207 - 212 and 285 - 324 nm exhibit a similar trend (Fig. S4). Therefore, to easily compare the absorbance in three mixtures, we focus on the adsorption peaks in the range of 207 - 212 nm, which exhibits an obvious variation, and the effect of the initial pH on reaction systems is also discussed in this range. The MAC values at pH = 4 are higher than those at pH = 3 for three mixtures. For example, the MAC value in AS-GL mixture is 2037 cm^2 g^{-1} at pH = 4, which is almost twice higher than that at pH = 3. Hence, the initial pH values of solution mainly affect the MAC values rather than the locations of absorption peaks.

In order to explore the influence of the initial pH values on the MAC values, a comparison of MAC values at initial pH 3 and 4 is performed for all three mixtures (Fig. 1a).Fig. 1a shows a comparison of the MAC values of all three mixtures at the initial pH of 3 and 4. The MAC values of maximum adsorption peaks increase from AS-GL to MEA-GL to MEA-AS-GL mixture, ranging from 1080 to 6345 cm^2 g^{-1} at pH = 3 and 2037 to 7617 cm^2 g^{-1} at pH = 4. The highest MAC value of MEA-AS-GL is explained by the different initial total concentration of reactants (see in Method), since the initial concentration of AS and MEA in MEA-AS-GL mixture is twice times than that in MEA-GL or AS-GL mixture. In addition, the MAC value of maximum adsorption peak in MEA-AS-GL mixture is higher than the sum of those in MEA-GL and AS-GL mixtures, and the location of maximum absorption peak in MEA-AS-GL mixture is between those in MEA-GL and AS-GL mixtures. It implies that the extra chromophores are yielded in MEA-AS-GL mixture in addition to producing the same chromophores as AS-GL and MEA-GL mixtures.

To compare the formation rate of chromophore between the different mixtures, the growth rates (GRs) of the maximum absorption peaks as a function of reaction time is shown in Fig. 2. The trend of the GR variation with reaction time at pH = 3 is similar to that at pH = 4, while the GRs of three mixtures at pH = 4 are larger than those at pH = 3 at the beginning of the reactions. The GRs are nearly invariant after 6−9 days, implying that the chromophore formation for three mixtures is irreversible. MEA-AS-GL mixture exhibits the larger GRs than other mixtures at the beginning of reaction because of its higher initial concentration of reactants. As the reaction proceeds, the GRs of MEA-GL mixture are increased and finally larger than those of other mixtures. Hence, MEA reactions form the chromophores by more efficiently than the analogous AS reactions.

The GRs dependence of the pH values of three mixtures is also plotted as a function of reaction time as shown in Fig. 2. The pH values rapidly degrade within the first 2 days in three mixtures, which is the same trend as GRs that decrease by a

162 factor of more than 1−3 at pH = 3 and 4. This trend is explained by ambient pH values, since a known byproduct (i.e., formic

163 acid) is formed (De Haan et al., 2009b; De Haan et al., 2020; Galloway et al., 2009; Hamilton et al., 2013; Kampf et al., 2012;

164 Yu et al., 2011). Note that the trend of GRs shows a decrease from MEA-AS-GL, MEA-GL, to AS-GL mixtures at the beginning

165 of the reaction time, while the MAC values of MEA-GL mixture are larger than those of two mixtures accompanied by the

166 more rapid decrease of pH values in solution after the reaction is equilibrium (Figs. 1b and 2), suggesting that chromophore

167 formation of three mixtures depends on the ambient pH value..

3.2 Chemical composition characterization of BrC chromophores

169 The chemical composition characterization of formed BrC chromophore was conducted by UPLC-Q-Orbitrap HRMS. The

170 formulas, m/z values, characteristic fragments, and structures of chromophores and intermediates are identified based on

171 obtained mass spectrum data in AS-GL, MEA-GL, and MEA-AS -GL mixtures (Table S1). The corresponding MS and MS^2

172 spectra of chromophores and intermediates are exhibited in Figs. 3, S8-S12. For all mixtures, imidazole (IML) compounds are

173 identified with a characteristic peak at m/z 69.045 in MS^2 spectra. Therefore, various IML compounds are observed based on

174 several representative peaks at m/z 69.045, including imidazole (IML_{AS} and IML_{MEA}), imidazole-2-carboxaldehyde (IC_{AS} and

175 IC_{MEA}), and their hydrated forms (HIC_{AS} and HIC_{MEA}) for AS-GL and MEA-GL mixtures (Table S1, Figs. 3a-b and S8-S9).

176 For MEA-GL mixture, extra catenulate intermediates without IML-structure characteristics are obtained at m/z values of

177 102.055 and 120.065 (Table S1, Figs. 3a and S10), corresponding to $C_4H_7O_2N$ (IA_{MEA}) and $C_4H_9O_3N$ (AHA_{MEA} and ID_{MEA})

178 compounds, respectively. However, no catenulate intermediates in AS-GL mixture are observed in this study because of their

179 low concentrations and short lifetimes, although they are observed by previous studies using MS/AMS and ^1H nuclear magnetic

180 resonance spectroscopy (Galloway et al., 2009; Lee et al., 2013; Yu et al., 2011). In addition, as shown in Figs. 3b and S11,

181 some IML-based products at m/z values of 145.061, 135.066, and 193.072 were obtained in AS-GL mixture correspond to

182 hydrated N-glyoxal substituted imidazole (HGI_{AS}), 2,2'-biimidazole (BIM_{AS}), and its glyoxal substituted analog (GBI_{AS}),

183 respectively. As discussed above, an important distinction between AS-GL and MEA-GL mixtures is whether formation of

184 bicyclic IML products (Fig. 3a-b), indicating that the optical properties of chromophores are mainly determined by mono-

185 imidazole compounds rather than bicyclic IML compounds.

186   To further explore the difference of identified products in MEA-GL and AS-GL mixtures, the possible pathways leading

187 to the identified intermediates and chromophores are illustrated in Fig. 4, along with the reaction energies (ΔG_r) of all pathways

188 calculated at the M06-2X/6-311+G(3df,3pd)//M06-2X/6-311G(d,p) level. As shown in Fig. 4, the formation and propagation

189 of oligomers was proposed to proceed via four-step nucleophilic addition (NA) reactions. For MEA-GL mixture, three

190 catenulate intermediates (AHA_{MEA}, IA_{MEA}, and ID_{MEA}) are successively yielded by the nucleophilic attack of MEA at the

191 reactive carbonyl site via dehydration and hydration, with the total ΔG_r value of −7.8 kcal mol^{-1} (Fig. 4a). Subsequently, two-

192 step NA reactions between ID_{MEA} and MEA and between DI_{MEA} and GL-diol (DL), followed by protonation and dehydration,

193 yields two intermediates (HA_{MEA} and PIC_{MEA}) in sequence. Although the third NA reaction between DI_{MEA} and DL is

194 endothermic (ΔG_r = 12.7 kcal mol^{-1}), the total ΔG_r value of DI_{MEA} formation in MEA-GL mixture is −18.7 kcal mol^{-1} for

proceeding the NA reaction to yield PIC_{MEA}. Similarly, the formation of PIC_{AS} in AS-GL mixture is also thermodynamically feasible, with the total ΔG_r value of −10.9 kcal mol^{-1}. However, PIC_{MEA} or PIC_{AS} is thermodynamically unstable, since there is a large exothermicity of the subsequent reaction pathway (ΔG_r = −78.6 or −50.0 kcal mol^{-1}) for proceeding cyclization leading to the formation of IC_{MEA} or IC_{AS}. It should be noted that for AS-GL mixture, the fate of IC_{AS} is dependent of the competition between the pathways of hydration to yield HIC_{AS} and NA reaction with DL to form BI_{AS}, while for MEA-GL mixture, there are no nucleophilic sites of IC_{MEA} for further oligomerization to form bicyclic IML compounds because IC_{MEA} is imidazolium cation. Similarly, IC_{MEA} also undergoes a hydration reaction to form HIC_{MEA} with a similar structure to HIC_{AS}. Subsequently, HIC_{AS} and HIC_{MEA} are decomposed to yield IML_{AS} and IML_{MEA}, respectively, accompanied by the formation of formic acid (ΔG_r = -10.2 and -15.6 kcal mol^{-1}), which is the reason for the decrease in pH in Section 3.1. However, as a reaction byproduct, formic acid hardly participates in the formation of light-absorbing products, so it has little influence on the reaction mechanisms. Current results further explain our experimental results mentioned above that higher MAC and larger GR values in MEA-GL mixture than that in AS-GL mixture.

For MEA-AS-GL mixture, the products in AS-GL and MEA-GL mixtures are also observed (Fig. 3c). Beyond that, four extra IML compounds are also observed at m/z values of 113.071, 141.066, 159.076 and 171.076, corresponding to IML (IML_{MAG}), imidazole-2-carboxaldehyde (IC_{MAG}) and its hydrated form (HIC_{MAG}), and N-glyoxal substituted imidazole (GI_{MAG}) (Figs. 3c and S12). An extra -C_2H_4O group exists in the geometries of the above four IML compounds relative to the products of AL-GL mixture, indicating that there exist the cross reactions between MEA and AS in the MEA-AS-GL mixture. As shown in Fig. 5, the cross NA reaction between ID_{AS} and MEA or ID_{MEA} and AS possesses a negative ΔG_r value of −4.8 or −5.4 kcal mol^{-1}, followed by dehydration to form the same intermediate, diimine (DI_{MAG}). It implies that the cross reactions in MEA-AS-GL mixture are thermodynamical favorable. Therefore, the formation and propagation of chromophores in MEA-AS-GL mixture also proceed via NA reactions, which is the key route for the formation of BrC chromophores.

As shown in Fig. 3c, no bicyclic IML compounds are produced in MEA-AS-GL mixture because the precursors of bicyclic IML compound (i.e., imidazole-2-carboxaldehyde) is fully hydrated under more acidic condition than AS-GL mixture (see pH values in Table S2). It leads to the formation of N-glyoxal substituted imidazole (i.e., GI_{MAG}) instead of bicyclic IML compounds. The similar phenomenon is also found in the previous studies (Ackendorf et al., 2017; Kampf et al., 2012; Yu et al., 2011) that bicyclic IML compounds are hardly yield from imidazole-2-carboxaldehyde in acidic condition. As discussed above, imidazole-based structural characteristics in chromophores are maintained in the presence of MEA, but the nucleophilicity of chromophores is reduced because the nucleophilic sites are occupied. Also, the positively charged quaternary amine salts (such as IC_{MEA} and GI_{MAG}) are also yield in MEA-GL and MEA-AS-GL mixtures, and thereby the chemical composition and optical properties of chromophores are affected.

3.3 Chemical reaction mechanism leading to BrC chromophores

As discussed above, the four-step NA reactions are the key pathways to form and propagate oligomers including intermediates and chromophores for three mixtures. Therefore, all possible pathways involved in the four key NA reactions of three mixtures

228 are calculated using density functional theory. The corresponding PESs stablished by the M06-2X/6-311+G(3df,3pd)//M06-

229 2X/6-311G(d,p) level are also presented in dotted boxes of Figs. 4-5. The optimized geometries of key stationary points,

230 including transition states (TSs), intermediates, and products, are depicted in Figs. S13-S15 at the M06-2X/6-311G(d,p) level.

231 We first performed quantum chemistry calculation to evaluated the direct nucleophilic attack of GL by MEA or AS, which

232 proceeds a large activation energy ($\Delta G^{\ddagger}$) value of 6.3 or 8.6 kcal mol^{-1}, following by H-shift reaction to yield AHA$_{MEA}$ or

233 AHA$_{AS}$, with also a large $\Delta G^{\ddagger}$ value of 15.2 or 18.2 kcal mol^{-1} (see NA1a' and NA2a' in Fig. 4). The high $\Delta G^{\ddagger}$ values and

234 large endothermicity of the direct NA reactions leading to AHA$_{MEA}$ and AHA$_{AS}$ imply that their occurrences are kinetically

235 and thermodynamically hindered.

236 Hence, we explored the cationic oligomerization of chromophore formation under acidic condition, which involves three

237 essential steps, (1) protonation and dehydration to form cationic intermediates (CIs) or carbenium ions (CBs), (2) nucleophilic

238 attack of CIs or CBs by MEA and AS, and (3) formation of intermediates and chromophores by deprotonation or dehydration.

239 As shown in Figs. 4-5, each pathway involved in the cationic-mediated reaction mechanism proceeds without a TS, except

240 deprotonation of CIs, in line with the results of the previous studies (Ji et al., 2020; Ji et al., 2022). However, deprotonation of

241 CIs by sulfate ion (SO$_4^{2-}$) possesses a negative $\Delta G^{\ddagger}$ value in this study, implying an approximate barrierless process of this

242 kind of deprotonation.

243 For the first-step NA reaction (NA1a in Fig. 4) in MEA-GL mixture, the electrophilic cationic site of CB$_{DL}$ is attacked by

244 the nucleophilic -NH$_2$ group of MEA with the ΔG_r value of -40.3 kcal mol^{-1}. CB$_{DL}$ is broadly produced from GL and reflected

245 from the large particle growth and formation of IML products (Ji et al., 2020; Li et al., 2021). The deprotonation of CI$_{MEA}$1

246 possesses a negative $\Delta G^{\ddagger}$ value of -4.5 kcal mol^{-1}, and a pre-reactive complex is identified prior the corresponding TS (detailed

247 in SI). Similarly, the other two NA1b and NA1c reactions (Fig. 4) also include protonation, dehydration, nucleophilic attack,

248 and deprotonation to yield HA$_{MEA}$ and PIC$_{MEA}$. Kinetic data listed in Table S3 show that the rate constants of most pathways

249 involved in the NA1a-1b and NA2a-2c reactions fall in the range of ~10^9 M^{-1} s^{-1}. The similar results can be drawn for AS-GL

250 mixture, suggesting that the electrostatic attraction is a significant factor to affect the NA reactions.

251 To further evaluate the cationic reaction mechanism, the natural bond orbital (NBO) analysis reveals that the N atom of

252 NH$_3$ exhibits more negative charge (-1.1 e) relative to MEA (-0.9 e), suggesting the stronger electrostatic attraction between

253 CB$_{DL}$ and NH$_3$ to yield CI$_{AS}$1 in the first-step NA reaction (see NA1a and NA2a in Fig. 4). However, the second-step NA

254 reaction between CB$_{MEA}$ and MEA are promoted by MEA because the presence of MEA enhances the positive charge in CB$_{MEA}$

255 (0.6 e), facilitating the electrostatic attraction (see NA1b and NA2b in Fig. 4). For the third-step NA reaction (see NA1c and

256 NA2c in Fig. 4), due to the steric hindrance, the deprotonation of CI$_{MEA}$8 possesses a larger $\Delta G^{\ddagger}$ value relative to that of CI$_{AS}$8.

257 Hence, the NA reactions are regulated by both electrostatic attraction and steric hindrance effect.

258 The fourth-step NA reactions in MEA-GL and AS-GL mixtures exhibit two distinct chemical reaction mechanisms in

259 cyclization to yield N-heterocycles (see NA1d and NA2d in Fig. 4). The protonation of PIC$_{MEA}$ and PIC$_{AS}$ occurs at the

260 hydroxyl group to form CI$_{MEA}$9 and CI$_{AS}$9. For MEA-GL mixture, the barrierless dehydration and cyclization of CI$_{MEA}$9 occur

261 in one step to yield N-heterocycle (i.e., IC$_{MEA}$), with the total ΔG_r value of -78.6 kcal mol^{-1} (NA1d in Fig. 4a). However, for

AS-GL mixture, the cyclization of PIC$_{AS}$ to IC$_{AS}$ includes protonation, dehydration, cyclization, and deprotonation. Note that cyclization and deprotonation proceed via two TSs in sequence, with the corresponding $\Delta G^{\ddagger}$ values of 3.9 and −0.6 kcal mol^{-1} (NA2d in Fig. 4b), respectively, forming IC$_{AS}$. As discussed above, cyclization in MEA-GL and AS-GL mixtures is the rate-limiting step to chromophore formation.

For MEA-AS-GL mixture, AHA$_{MEA/AS}$, and ID $_{MEA/AS}$ are yielded via the same first NA reactions (NA1a/2a) as MEA-GL and AS-GL mixtures. Also, the formation of ID$_{MEA/AS}$ proceeds via protonation and dehydration to form CB$_{MEA/AS}$. However, the second NA reaction includes the cross-NA reaction of CB$_{MEA}$ with AS (NA3b-1) or CB$_{AS}$ with MEA (NA3b-2) to produce extra oligomers (i.e., HA$_{MAG}$1 and HA$_{MAG}$2), in contrast to MEA-GL and AS-GL mixtures. Hence, the fate of CB$_{MEA/AS}$ is dependent of the competition reaction between the pathways of self-NA reaction to form HA $_{MEA/AS}$ (NA1b/2b) and cross-NA reaction to yield HA$_{MAG}$1/2 (NA3b-1/2). The ΔG_r values of the cross-NA reactions to yield HA$_{MAG}$1 and HA$_{MAG}$2 are −30.3 and −30.4 kcal mol^{-1}, respectively, comparable with those of self-NA reactions. It suggests both NA reactions to form HAs are equally accessible. Subsequently, HA$_{MAG}$1/2 undergoes dehydration to form DI$_{MAG}$, further proceeds the third NA reaction to yield PIC$_{MAG}$, in line with the mechanisms of the third NA reactions for MEA-GL and AS-GL mixtures. The cyclization of CI$_{MAG}$10 (the fourth NA reaction) possesses with two successive TSs, similar to that of AS-GL mixture but different to that of MEA-GL mixture. The corresponding $\Delta G^{\ddagger}$ values are obtained as 5.0 and 1.6 kcal mol^{-1}, respectively, which are larger than those of AS-GL mixture. In summary, compared with the AS-containing mixtures, the presence of MEA provides the extra two branched chains in N atoms, which affect the natural charges and molecular steric hindrance of intermediates, to thereby facilitate the intramolecular interaction between N and C atoms to form SBrC chromophores.

4 Conclusions and atmospheric implications

BrC chromophores play an important role in the Earth's radiative balance, air quality and human health. However, the formation mechanisms of BrC chromophores are not fully understood, hindering a comprehensive assessment of BrC chromophores on atmospheric chemistry and environmental impacts. Hence, using combined theoretical and experimental methods, we investigated the aqueous chemistry of typical RNCs with GL and evaluated the impact of typical multifunctional RNCs on the formation of BrC chromophores. Experimental studies show that the MAC values of chromophores are affected by the initial pH value for AS-GL, MEA-GL and MEA-AS-GL mixtures, and the growth rates of chromophores are enhanced in the presence of MEA. The optical properties of chromophores are regulated by monocyclic and bicyclic IML compounds in AS-GL mixture but by monocyclic IML compounds in MEA-containing mixtures (i.e., MEA-GL and MEA-AS-GL). Combined with the results of quantum chemical calculations, chromophore formation is characterized by nucleophilic addition with large exothermicity and strong electrostatic attraction among the MEA-derived intermediates, which are also enhanced by MEA.

In addition, to simply evaluate the impacts of MEA and AS on chromosphere formation in the aqueous aerosols and fog/cloud droplets, the dynamics process of GL from gas to aqueous phase was carried out (Fig. S16). The free energy

difference reflects whether the liquid particles with MEA and AS (denoted as MEA and AS particles) prefer to adsorb and accommodate GL. As shown in Fig. S16, a larger decrease in the free energy (-3.7 kcal mol^{-1}) occurs when GL approaches the interface of the MEA particle relative to the AS particle, indicating a thermodynamically favorable process. Subsequently, the stabilized GL enters into the interior region of the MEA and AS particles, with slightly endothermic (1.6 and 2.4 kcal mol^{-1}). A smaller free energy difference from the interface into the interior region of the MEA particle implies that the interfacial GL is more readily promoted to enter the interior region of the particle when the particles contain MEA compared with AS. Hence, the interfacial and interior attraction on the MEA particle is more pronounced for small α-dicarbonyls, to facilitate the further engagement in the aqueous-phase reactions with RNCs in the particle.

Formation of SBrC from multifunctional RNCs and small α-dicarbonyls occurs widely on aqueous aerosols and fog/cloud droplets under typical atmospheric conditions. Compared with the ubiquitous coexistence between AS and small α-dicarbonyls from global aerosol measurement, SBrC aerosol formation from multifunctional RNC mixtures should be paid attention to during serious haze formation in China because of their atmospheric reactivities and non-negligible concentrations. Our results also imply that SBrC aerosols, if formed from the aqueous reactions between MEA and GL, likely contribute to atmospheric warming because the presence of MEA enhances the MACs of the mixture. Hence, recognition of this aerosol formation mechanism in the radiative transfer atmospheric model is needed, reparenting a possible missing source for BrC formation on urban, regional and global scales.

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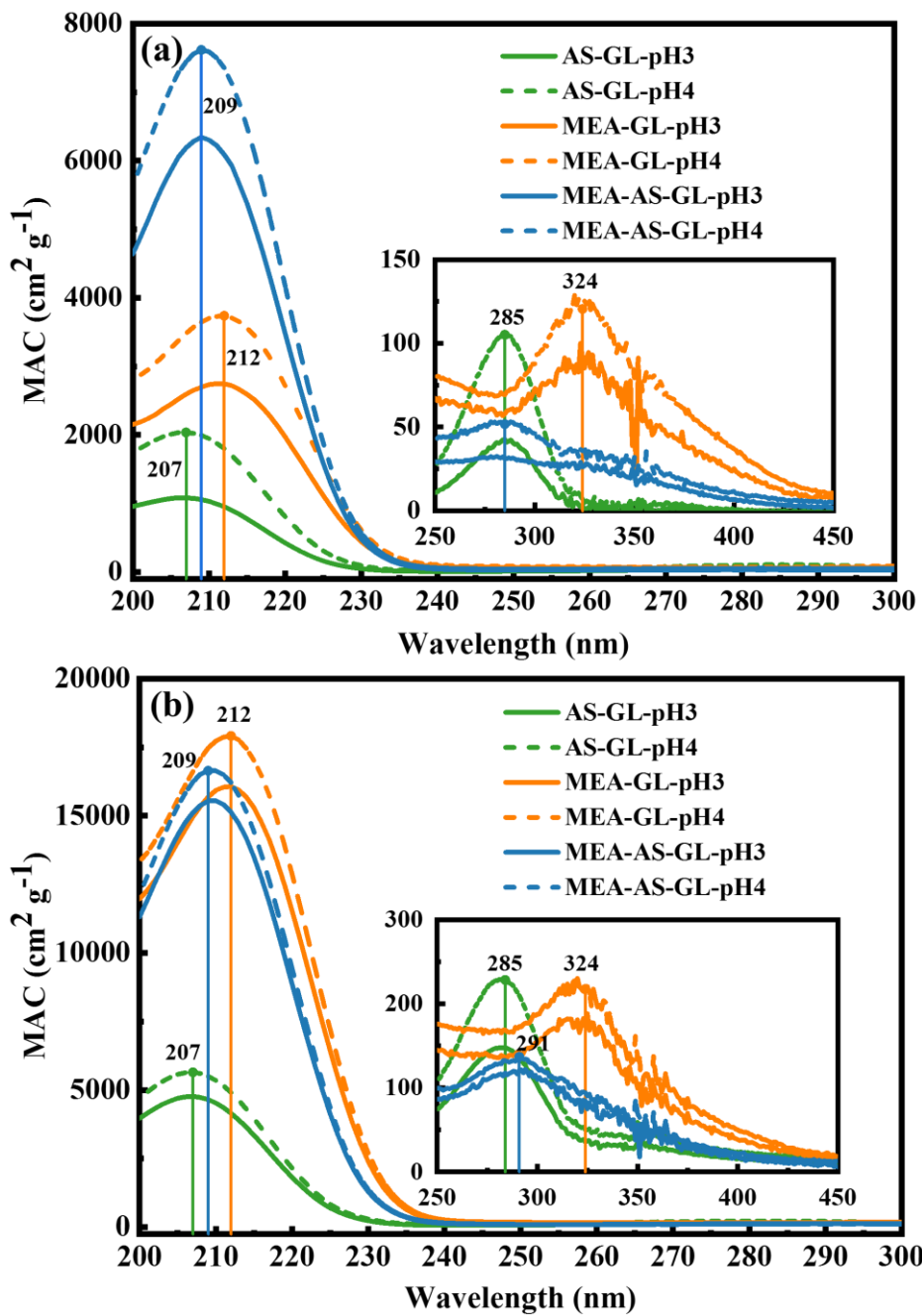
Figure 1: The MAC values for AS-GL, MEA-GL and MEA-AS-GL mixtures at the initial pH of 3 and 4 at 1d (a) and 15d (b).

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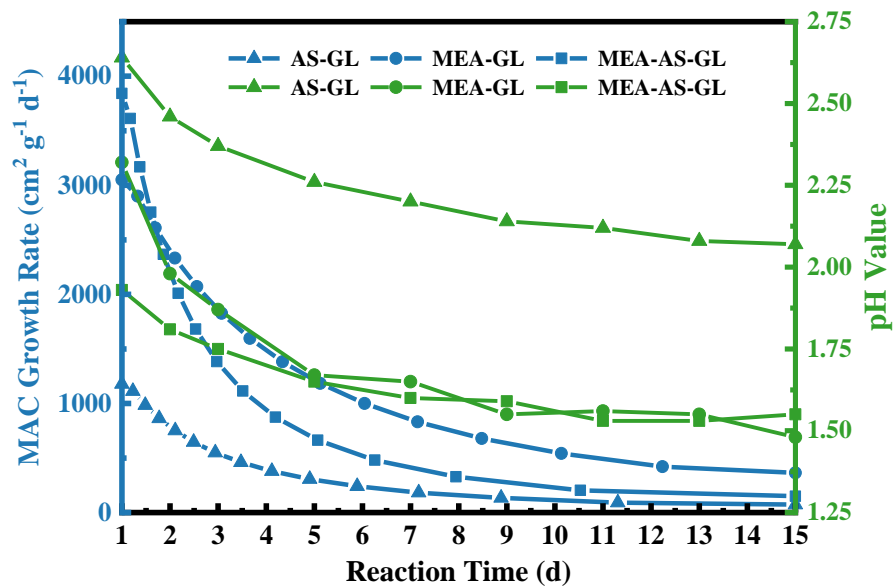
Figure 2: Dependence of the growth rates (blue line) and pH values (green line) on reaction time for AS-GL, MEA-GL and MEA-AS-GL mixtures.
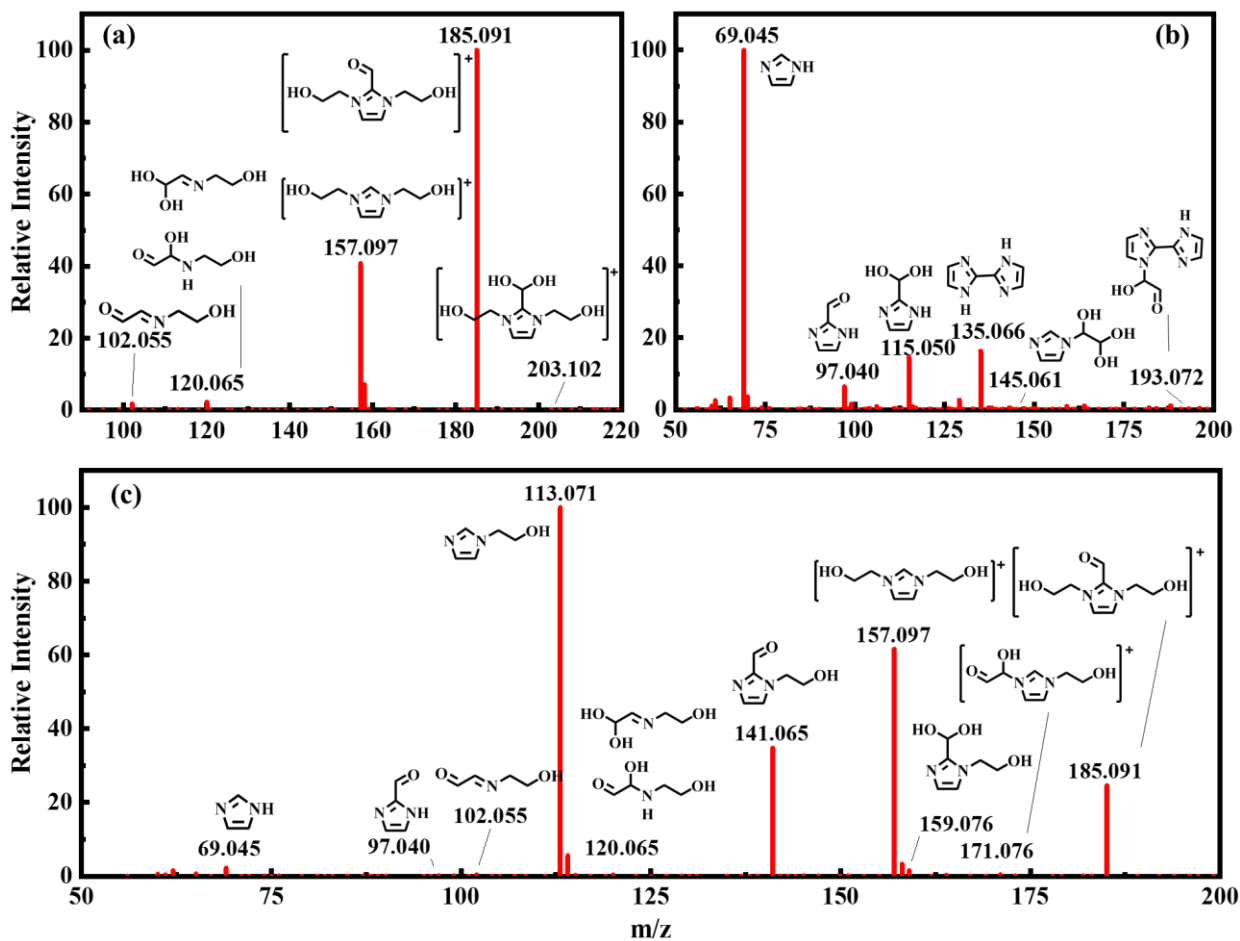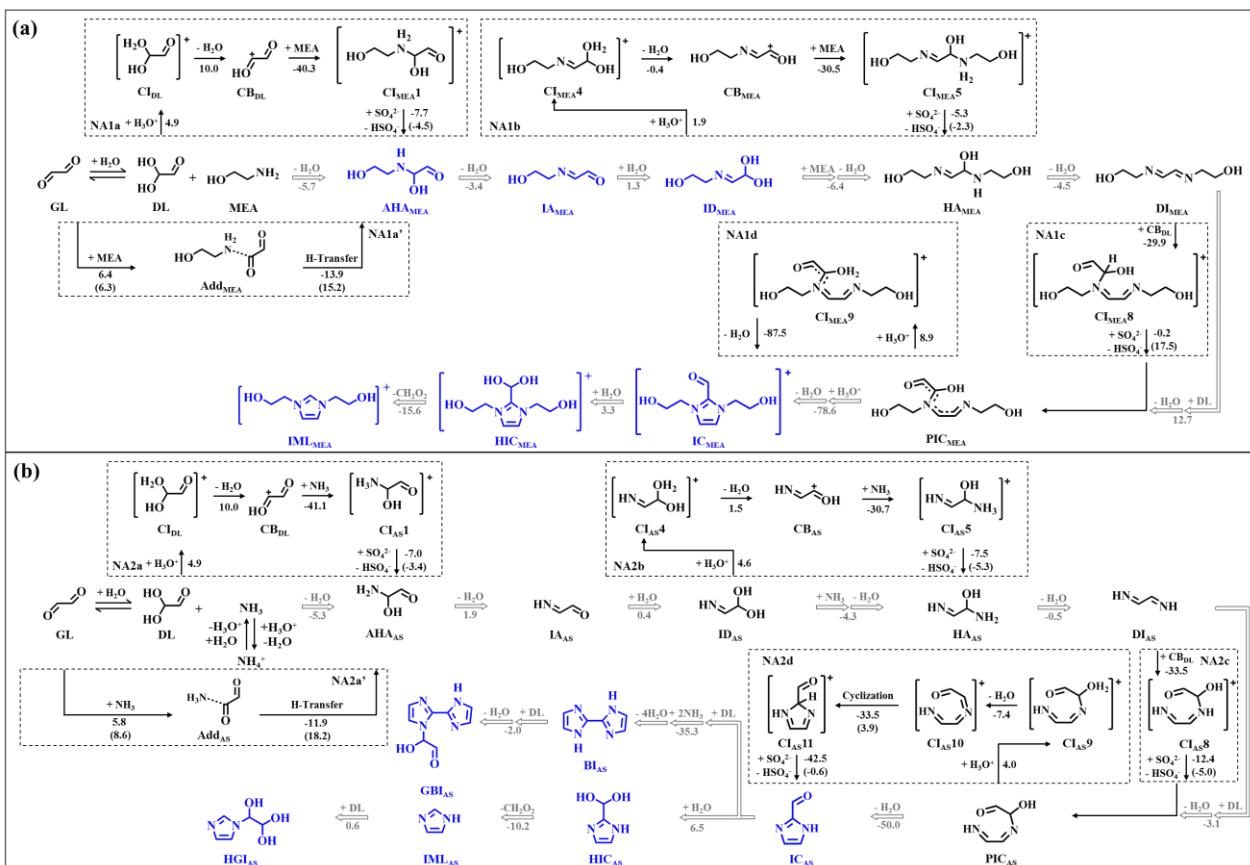
Figure 3: Mass spectra monitoring of chromophores for (a) MEA-GL (b) AS-GL and (c) MEA-AS-GL mixtures.

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547 **Figure 4: Possible pathways leading to chromophores for (a) MEA-GL and (b) AS-GL mixtures (oriented by gray arrows). Detailed**
548 **PESs of the four NA reactions are presented in dotted boxes. The number denotes the values of ΔG_r and $\Delta G^{\ddagger}$ (in brackets) for each**
549 **reaction step (in kcal mol^{-1}), and all energies are relative to the corresponding reactants.**

Figure 5: Possible pathways leading to chromophores for MEA-AS-GL mixture (oriented by gray arrows). Detailed PESs of the four NA reactions are presented in dotted box. The shaded area is the overlapping part with the pathways of MEA-GL and AS-GL mixtures. The number denotes the value of ΔG_r and $\Delta G^{\ddagger}$ (in brackets) for each reaction step (in kcal mol^{-1}), and all energies are relative to the corresponding reactants.