Contribution of carbonyl chromophores to secondary brown carbon from nighttime oxidation of unsaturated heterocyclic volatile organic compounds

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ABSTRACT

The light absorption properties of brown carbon (BrC), which are linked to molecular chromophores, may play a significant role in the Earth's energy budget. While nitroaromatic compounds have been identified as strong chromophores in wildfire-driven BrC, other types of chromophores remain to be investigated. As an electron-withdrawing group ubiquitous in the atmosphere, we characterized carbonyl chromophores in BrC samples from the nighttime oxidation of furan and pyrrole derivatives, which are important but understudied precursors of secondary organic aerosols (SOA) primarily found in wildfire emissions. Various carbonyl chromophores were characterized and quantified in BrC samples, and their ultraviolet-visible (UV-Vis) spectra were simulated using time-dependent density functional theory (TD-DFT). Our findings suggest that chromophores with carbonyls bonded to nitrogen (i.e., imides and amides) derived from N-containing heterocyclic precursors substantially contribute to BrC light absorption. The quantified N-containing carbonyl chromophores contributed to over 40% of the total light absorption at wavelengths below 350 nm and above 430 nm in pyrrole BrC. The contributions of chromophores to total light absorption differed significantly by wavelength, highlighting their divergent importance in different wavelength ranges. Overall, our findings highlight the significance of carbonyl chromophores in secondary BrC and underscore the need for further investigation.

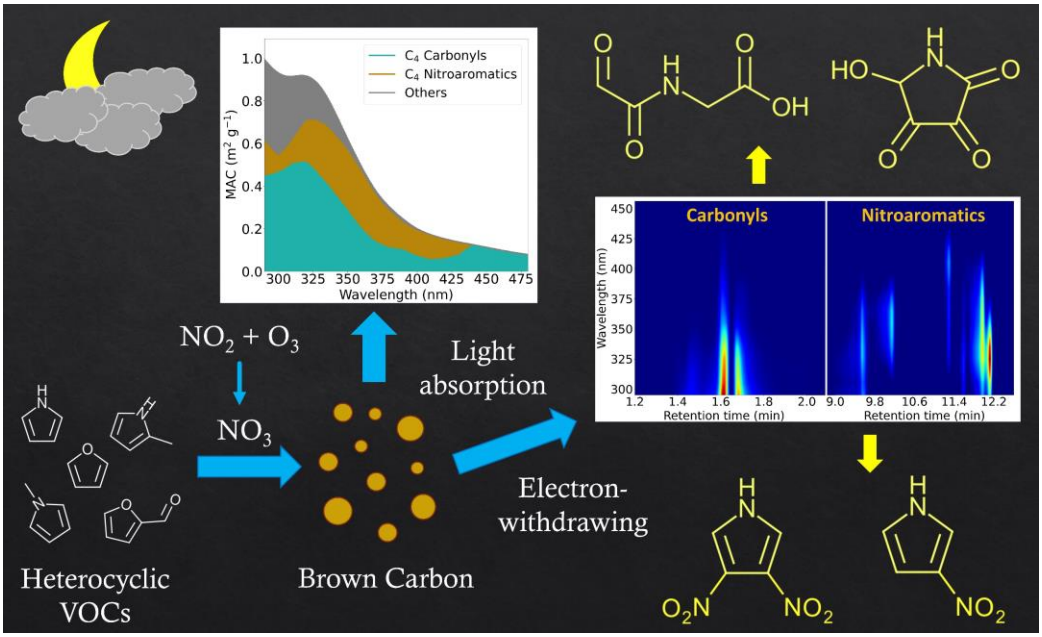
KEYWORDS

furan and pyrrole derivatives, secondary organic aerosols, imides and amides, light absorption contribution, wavelength dependency

Synopsis

Atmospheric carbonyls are formed by the oxidation of various volatile organic compounds (VOCs), and they have the potential to be important chromophores in secondary brown carbon, especially those from nighttime oxidation of N-containing heterocyclic VOC precursors.

TOC Graphic


C4 Carbonyls
C4 Nitroaromatics
Others
MAC (m² g⁻¹)
Wavelength (nm)
Carbonyls
Nitroaromatics
Wavelength (nm)
Retention time (min)
Retention time (min)
NO2 + O3
NO3
Light absorption
Electron-withdrawing
Heterocyclic VOCs
Brown Carbon

INTRODUCTION

Atmospheric brown carbon (BrC) is an important contributor to global warming, with a +0.10-0.55 W m^{-2} direct radiative effect[1-3] (~20-24% contribution) on the top-of-atmosphere direct radiative forcing.[4, 5] The contribution of BrC absorption is enhanced at higher altitudes[6] and varies by both daily and seasonal cycles,[7] especially due to changes in air pollution and cloud coverage.[7, 8] Conversely, the light absorption of BrC may also indirectly reduce the global coverage of clouds and decrease their cooling effects.[9] The spatial and temporal variations of BrC light absorption, and consequently their impacts, are strongly related to the changes in chemical composition.[8, 10] However, parameterization pertinent to BrC constituents remains underdeveloped in climate models,[11] hindering accurate evaluations of BrC optical properties and climate change prediction.[12, 13]

Accurate representations of BrC's effects on climate change require a comprehensive process-level understanding of the formation and evolution of molecular chromophores, which play a key role in regulating the light absorption properties of BrC. Nitroaromatic chromophores, also known as nitrated aromatic compounds, have been recognized as significant contributors to BrC light absorption. For example, Li et al. and Frka et al. reported that nitroaromatic chromophores may contribute to ~17-31% light absorption of BrC at 365-370 nm,[14, 15] while Bluvshtein et al. and Lin et al. indicated an even higher ratio (i.e., 50-80%) at wavelengths above 350 nm in biomass burning events.[16, 17] Although nitroaromatic chromophores may not account for a large fraction of aerosol mass, their contribution to BrC light absorption at 365 nm can be ~2-10 times that of their mass contribution in BrC samples.[14, 15, 18, 19] Among a variety of nitroaromatic chromophores, nitrophenols and nitrocatechols have been identified as two major groups of nitroaromatic chromophores in ambient aerosols,[19, 20] and they have been widely

74 investigated to characterize the BrC formation and evolution due to photooxidation or
75 photolysis.[21-26]

76 While nitroaromatic chromophores have been identified as potential tracers of BrC in
77 atmospheric processing due to their significant role in the light absorption of BrC at 365 nm,[27] the
78 contributors to the BrC absorption spectra in the near ultraviolet (UV) range below 365 nm have
79 not been fully deconvoluted. In contrast to the >50% contribution of light absorption above 350
80 nm, nitroaromatic chromophores only accounted for ~20% of light absorption at 300 nm in
81 biomass burning events, according to studies reported by Bluvshtein et al. and Lin et al.[16, 17] The
82 wavelength-dependent contributions to BrC light absorption suggest the critical role of other types
83 of chromophores in UV absorption. Since the light absorption of BrC chromophores is induced by
84 electronic transitions, similar to nitroaromatics, which have strongly electron-withdrawing nitro
85 groups attached to the aromatic rings, unsaturated organic compounds or conjugated systems
86 coupled with other types of electron-withdrawing groups such as carbonyls could also be
87 chromophore candidates.[13, 28] For instance, the simplest unsaturated carbonyl compound (i.e.,
88 acrolein) can absorb sunlight above 290 nm.[29, 30] From field studies, it has been reported that
89 carbonyls may contribute to a large mass fraction of biomass burning aerosols[31, 32] and significant
90 light absorption in the BrC.[10, 33, 34] The molecular absorptivity of numerous carbonyl compounds
91 observed in ambient aerosols is comparable to the absorptivity of nitroaromatic chromophores at
92 290-350 nm.[35] Therefore, it is essential to characterize carbonyl chromophores and constrain their
93 roles in BrC light absorption.

94 In this study, we characterized carbonyl chromophores in secondary organic aerosols (SOA)
95 from the nighttime oxidation of a series of unsaturated heterocyclic volatile organic compounds
96 (VOCs), including pyrrole, 1-methylpyrrole (1-MP), 2-methylpyrrole (2-MP), furan, and furfural,

that have been widely observed in biomass burning events,[36-40] and may account for ~30% of the initial nitrate radical (NO_3) reactivity in wildfire-driven nighttime chemistry.[40] Recently, these VOCs were reported as potentially important precursors for secondary BrC formation during nighttime oxidation,[41-44] in which several carbonyl chromophores were observed.[43] Multi-instrumental characterization along with theoretical calculations of ultraviolet-visible (UV-Vis) spectra were employed here to elucidate the structures of carbonyl chromophores and their spectral light absorptivity. This study focuses on the light absorption contribution of carbonyl chromophores in pyrrole SOA and 2-MP SOA; because nitroaromatic chromophores have been identified as critical contributors to BrC light absorption in these systems, they can serve as a benchmark for comparisons.[42] Characterizing BrC chromophores at the molecular level can contribute to a deeper process-level understanding of the formation and evolution of secondary BrC light absorption in changing environments.

METHODS

Experimental setup. Experiments were performed in a 10 m^3 Teflon FEP chamber at room temperature (20-25 °C) and low relative humidity (RH< 20%) in the dark. Details of the experimental setup and SOA properties, including number and size distribution, aerosol effective density, and mass fraction of organics, were introduced in our previous studies.[42, 43] In brief, 450 ppb NO_2 and 1500 ppb O_3 (initial $[NO_2]/[O_3]$ = 0.3) were first injected into the chamber and allowed to react for one hour, producing ~22 ppb nitrate radicals (NO_3).[42] To investigate the effects of NO_3 radical levels on the light absorption contributions of BrC chromophores, additional experiments were carried out with 150 ppb NO_2 and 1500 ppb O_3 (initial $[NO_2]/[O_3]$ = 0.1), producing ~8 ppb NO_3.[42] The concentrations of NO_2 and O_3 were monitored by a NO_x analyzer

(Teledyne Instruments) and an O_3 analyzer (Advanced Pollution Instrumentation, Inc.), respectively. Our previous studies indicated that the nighttime oxidation of pyrroles and furans under both conditions was predominantly initiated by NO_3 radicals.[42, 44] After the one-hour reaction between O_3 and NO_2 to produce NO_3 radicals, one of the studied heterocyclic VOCs was first vaporized in a heated jar and then injected into the chamber with ~15 lpm of nitrogen gas. The target concentration of VOCs in the chamber was ~200 ppb. After the mass concentration reached a plateau, the generated SOA particles were collected on polytetrafluoroethylene (PTFE) membrane filters (46.2 mm, 2.0 μm, Tisch Scientific) for one hour with a flowrate of 16.7 lpm; each filter collected the aerosols from 1 m^3 of chamber air and served for subsequent offline analysis. Although chamber experiments have some limitations in simulating the real atmosphere (e.g., size-dependent particulate wall loss rate (Fig. S1) that may affect the chromophore quantification),[45] the controlled chamber conditions can systematically facilitate the characterization of carbonyl chromophores and the evaluation of their roles in secondary BrC.

Compositional analysis. The compositional analysis was conducted using a suite of complementary analytical instruments. A liquid chromatography coupled with a diode array detector, an electrospray ionization source (negative ion mode), and a quadruple-time-of-flight tandem mass spectrometer (LC-DAD-ESI(-)-Q-TOFMS, Agilent Technologies 1260 Infinity II, and 6545 Q-TOF LC/MS) was used to identify light-absorbing carbonyl products and to characterize their molecular structures. The gradient elution for the changing LC mobile phase composition over time is shown in Fig. S2A. A gas chromatography-electron ionization mass spectrometry (GC/EI-MS, Agilent Technologies 6890N GC System, and 5975 inert XL Mass Selective Detector) was also used to complementarily identify carbonyl products. An iodide-adduct time-of-flight chemical ion mass spectrometry coupled with the Filter Inlet for Gases and

AEROsols system (FIGAERO-ToF-CIMS, Aerodyne Research Inc.)[46] and an ion mobility spectrometry time-of-flight mass spectrometer (IMS-TOF, Tofwerk Inc.) were used to characterize SOA composition in real time and offline, respectively. All the characterization methods were the same as those in our prior studies.[42, 43] Detailed instrumental setups and operational parameters have been described previously.[42, 43, 47-49]

N-containing carbonyl chromophores were characterized by LC-DAD-ESI-Q-TOFMS and GC/EI-MS, and their mass contributions were estimated semi-quantitatively using maleimide ($C_4H_3NO_2$) as a surrogate standard. The mass ratio of the characterized N-containing carbonyl chromophores ($MR_{carbonyl}$) (Eq. (1)), and the mass ratio of maleimide ($MR_{maleimide}$) in SOA samples from pyrrole and its derivatives had been previously determined by GC/EI-MS using a similar approach.[43]

$$MR_{carbonyl} = MR_{maleimide}\frac{c_{carbonyl}M_{carbonyl}}{c_{maleimide}M_{maleimide}} = MR_{maleimide}R_F\frac{A_{carbonyl}M_{carbonyl}}{A_{maleimide}M_{maleimide}} \quad (1)$$

Here, $c_{carbonyl}$ and $c_{maleimide}$ are the molar concentrations of the characterized carbonyl chromophores and maleimide in the extracted SOA samples (mol L^{-1}); $M_{carbonyl}$ and $M_{maleimide}$ are the molar masses of the characterized carbonyl chromophores and maleimide in the extracted SOA samples (g mol^{-1}); $A_{carbonyl}$ and $A_{maleimide}$ are the peak areas of parent ions of the characterized carbonyl chromophores and maleimide in their extracted ion chromatograms (EICs) measured by LC-DAD-ESI-Q-TOFMS. Although response factors (R_F) of the characterized N-containing carbonyl chromophores may differ slightly from the surrogate standard (Fig. S2B), semi-quantification can provide approximate mass ratios and still support comparisons of the representation of various N-containing carbonyl chromophores in SOA samples.

Light absorption measurements. The absorbance of SOA samples (290-700 nm) was measured by a UV-Vis spectrophotometer (Beckman DU-640). The SOA mass on each filter sample varied within 10-350 μg, depending on the type of VOCs. Each filter sample was extracted with 22 mL of acetonitrile (ACN), which has been shown to be a suitable solvent for the analysis of secondary BrC due to its chemical stability (aprotic) and solubility for polar compounds.[43] It is noted that ACN may not completely extract the SOA constituents from filters (Table S1), so the BrC light absorption estimated in this study is the lower limit. The contribution of BrC carbonyl marker compounds (i.e., maleimide and phthalic anhydride)[43] to the total light absorption of SOA samples (*AbsC*), which can vary greatly with wavelength (λ), is estimated by Eq. (2).

$$AbsC\ (\lambda) = \frac{Abs_{chro}(\lambda)}{Abs_{BrC}(\lambda)} \quad (2)$$

$Abs_{BrC}(\lambda)$ is the total light absorbance of the BrC samples, directly measured by the UV-Vis spectrophotometer, while $Abs_{chro}(\lambda)$ is the light absorbance of the investigated BrC chromophores, calculated by the Beer-Lambert law (Eq. (3)).

$$Abs_{chro}(\lambda) = \varepsilon_{chro}(\lambda) \times \frac{m_{chro}}{M_{chro}} \times b \quad (3)$$

$\varepsilon_{chro}(\lambda)$ is the molecular absorptivity of the investigated BrC chromophores (L mol^{-1} cm^{-1}), which has been reported in our previous work;[43] m_{chro} is the mass concentration of molecular chromophores in the SOA solution samples (ng μL^{-1}); M_{chro} is the molar mass of the molecular chromophores (g mol^{-1}); and b is the instrumental light path (i.e., 1 cm).

Computations of theoretical UV-Vis spectra. The time-dependent density functional theory (TD-DFT) was used to simulate the wavelength-dependent light absorptivity of the characterized carbonyl products, for which no authentic standards were available. The Gaussian 16 program (revision C. 01)[50] was used for all computations, with the B3LYP functional[51, 52] and the 6-

311++G(d,p) basis set[53] as suggested in previous studies.[54, 55] The ACN solvent environment was simulated by the integral equation formalism extension of the polarizable continuum model (IEFPCM).[56] The GaussView 6 program was used to generate the theoretical UV-Vis spectra. All the Cartesian coordinates for geometrical structures were summarized in Table S2.

RESULTS AND DISCUSSIONS

Distribution of chromophores in the LC-DAD heatmaps. The LC-DAD heatmaps provide a snapshot of BrC chromophore distributions for all the SOA samples (Fig. 1 and Figs. S3-5), where the hotspots illustrate the retention time (RT) and wavelengths of light absorption. Fig. 1 shows the LC-DAD heatmap of pyrrole SOA, which is divided into two panels, corresponding to the RT ranges of 0-2 min and 2-21 min, respectively (Fig. 1A-B).

Compositional analysis revealed that the major hotspots detected at RT of 1.6-1.7 min may be attributed to mono-nitrogen chromophores (Fig. 1C), while those detected at RT of 8.7-12.3 min may be ascribed to the di-nitrogen and tri-nitrogen chromophores (Fig. 1D). Notably, the analytes at RT of 1.6-1.7 min were comprised of many mono-nitrogen compounds, while only two products were shown at RT of 8.7-12.3 min. The mono-nitrogen chromophores (Fig. 1A) in pyrrole SOA collectively acquired much stronger light absorption compared to di-nitrogen and tri-nitrogen chromophores (Fig. 1B), which indicated the potential importance of the mono-nitrogen chromophores in BrC light absorption. The strong light absorption corresponding to mono-nitrogen chromophores is also observed in 1-MP SOA (Fig. S3) and 2-MP SOA (Fig. S4), wherein the mono-nitrogen chromophores led to much higher or similar absorption intensities compared to those of the di-nitrogen and tri-nitrogen chromophores. In a recent study, we found di-nitrogen and tri-nitrogen chromophores in pyrrole SOA and 2-MP SOA as nitro- and dinitro-substituted

chromophores.[42] This finding suggested that the mono-nitrogen chromophores would lack nitro groups, and their nitrogen may be inherited from the pyrrole backbones, as evidenced by the structural characterization in the following section. However, in contrast to electron-withdrawing groups such as nitro groups, the nitrogen atom on the pyrrole backbone cannot attract electron density toward itself and thus the light absorption of the mono-nitrogen chromophores is mostly due to the non-nitrogen electron-withdrawing groups in the molecule. Furthermore, our previous study of furan SOA revealed that nitrogen-free products were the predominant contributors to the major LC-DAD hotspots,[44] whereas the major hotspots in furfural SOA can be attributed to both nitrogen-containing and nitrogen-free products (Fig. S5). Despite this, all the LC-DAD heatmaps indicate the importance of different types of electron-withdrawing groups in BrC light absorption. Analysis of functional groups with attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy conducted in our previous study suggested that chromophores with carbonyl groups may account for a significant portion of the light absorption of SOA samples from nighttime oxidation of heterocyclic VOCs.[43]

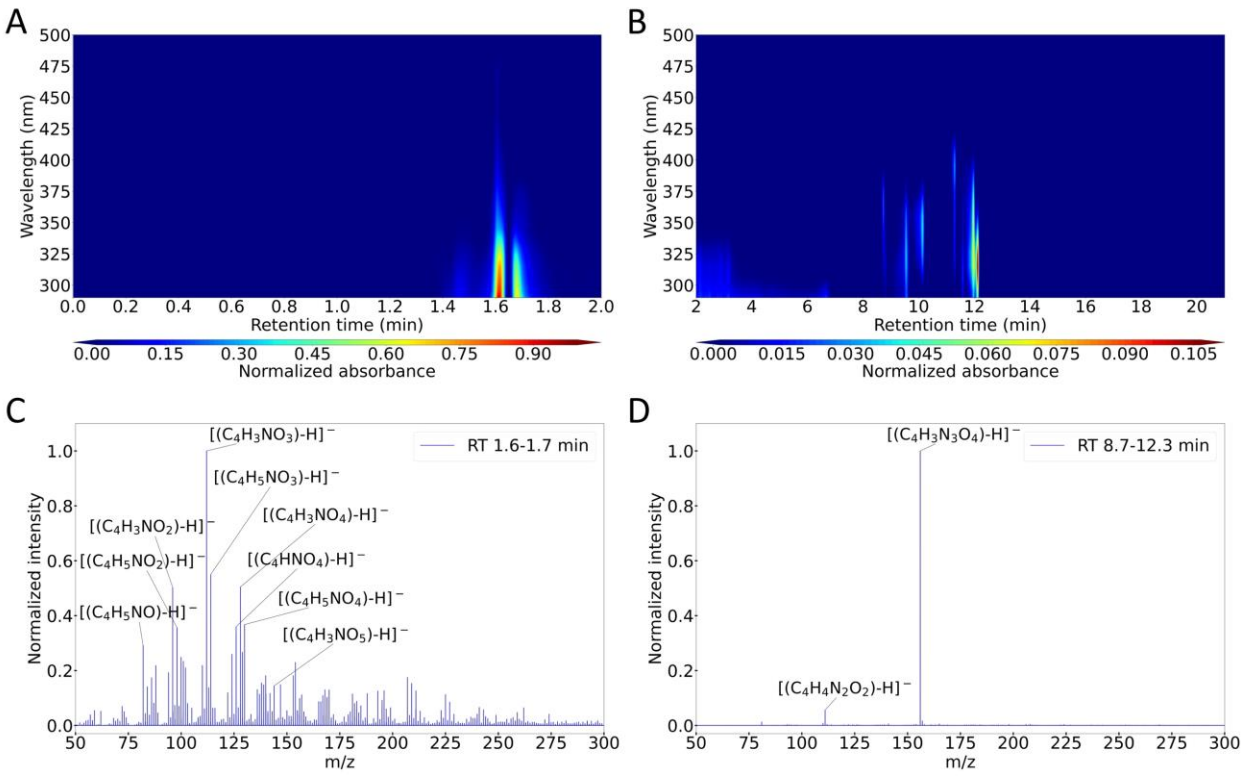


Figure 1. LC-DAD heatmaps of pyrrole SOA: (A) 0-2 min, and (B) 2-21 min, followed by the mass spectra corresponding to the major hotspots, respectively (C-D). The light absorption of chromophores was normalized to the highest value of the whole LC-DAD heatmap, with each panel having its own color scale for a clear representation of chromophore distribution. With LC mobile phase changing (Fig. S2A), the separated hotspots in two unique RT zones represent distinct chromophores with different polarities.

Even though nitroaromatic chromophores have been identified as important contributors to BrC light absorption in pyrrole SOA and 2-MP SOA,[41, 42] the LC-DAD heatmaps (Fig. 1A-B and Fig. S3A-B) disclosed that mono-nitrogen chromophores could account for the majority of the light absorption. This is because nitroaromatic chromophores and mono-nitrogen chromophores

have absorption peaks at different wavelength ranges and, as a result, have wavelength-dependent light absorption contributions, which will be discussed further in the following sections.

Molecular characterization of carbonyl chromophores. In the current study, the molecular composition of carbonyl chromophores was determined by complementary analytical instrumentation, and their UV-Vis spectra were simulated using quantum chemical approaches (Figs. 2 and 3). Following the identification of the molecular formula in Fig. 1C, we performed tandem MS experiments to elucidate their structures. Here, $C_4H_4NO_4^-$, a deprotonated ion of $C_4H_5NO_4$, is selected as an example. The LC-ESI-Q-ToFMS measurements showed a single peak in the EIC of this ion as well as its fragmentation pattern (Fig. 2A), which can help derive the tentative molecular structures and thus support the theoretical computation of UV-Vis spectra. The IMS-TOF measurements also confirmed the presence of $C_4H_4NO_4^-$ in ESI (-) and indicated two major isomers for this ion (Fig. 2B). To rule out the potential interference from solvent and LC electrospray ionization efficiency,[43, 44] the presence of $C_4H_5NO_4$ was supplementally verified by *in situ* characterization with FIGAERO-ToF-CIMS (Fig. 2C). Plausible fragmentation pathways were derived based on the tandem MS data (Fig. S6A), wherein $C_4H_5NO_4$ can be characterized as formyl carbonyl amino acetic acid and its imidic acid isomer. Both compounds are chain-structural carbonyl chromophores, as confirmed by the theoretical computation of their UV-Vis spectra (Fig. 2D). Using the same approaches, the ring-retaining carbonyl chromophores in pyrrole SOA were also characterized, including 2-hydroxy-2-pyrroline-4,5-dione ($C_4H_3NO_3$), 5-hydroxy-2,3,4-pyrrolidinetrione ($C_4H_3NO_4$), and 5-hydroxy-2,3-pyrrolidinedione ($C_4H_5NO_3$) (Figs. S7-10). Similar to pyrrole, nighttime oxidation of furan can generate light-absorbing diones. As one of the major products in furan SOA, $C_4H_2O_4$ was characterized as 4-hydroxyfuran-2,3-dione and 5-

hydroxyfuran-2,3-dione (Figs. 2E-G and Fig. S6B).[44] These products exhibit distinct UV-Vis spectra with different central wavelengths and peak absorptivity (Fig. 2H).

Given that both LC-ESI-Q-TOFMS and IMS-TOF in this study could only detect deprotonated ions (because of the nature and limitations of ESI(-)) and may not characterize all carbonyls generated, GC/EI-MS was used to investigate more diverse carbonyl chromophores. Previous GC/EI-MS analysis of secondary BrC samples revealed a number of light-absorbing heterocyclic diones, including maleimide (from pyrrole and its derivatives), maleic anhydride, and phthalic anhydride (from furan and furfural).[43] In the current study, N-methylmaleimide was discovered by GC/EI-MS (RT =10.5 min) in 1-MP SOA samples (Fig. 3A). The presence of this compound was confirmed by its authentic chemical standard (Fig. 3B) and also supported by the tentative fragmentation pathways (Fig. S11A) as well as the *in situ* FIGAERO-ToF-CIMS measurement (Fig. 3C). Also, the presence of 2-methyl-2-pyrroline-4,5-dione, an isomer of N-methylmaleimide, in 2-MP SOA was confirmed by multi-instrumental measurements (Figs. 3E-G) and the tentative fragmentation pathways (Fig. S11B). The calculated UV-Vis spectra showed that both diones can contribute to light absorption above 290 nm (Figs. 3D and 3H).

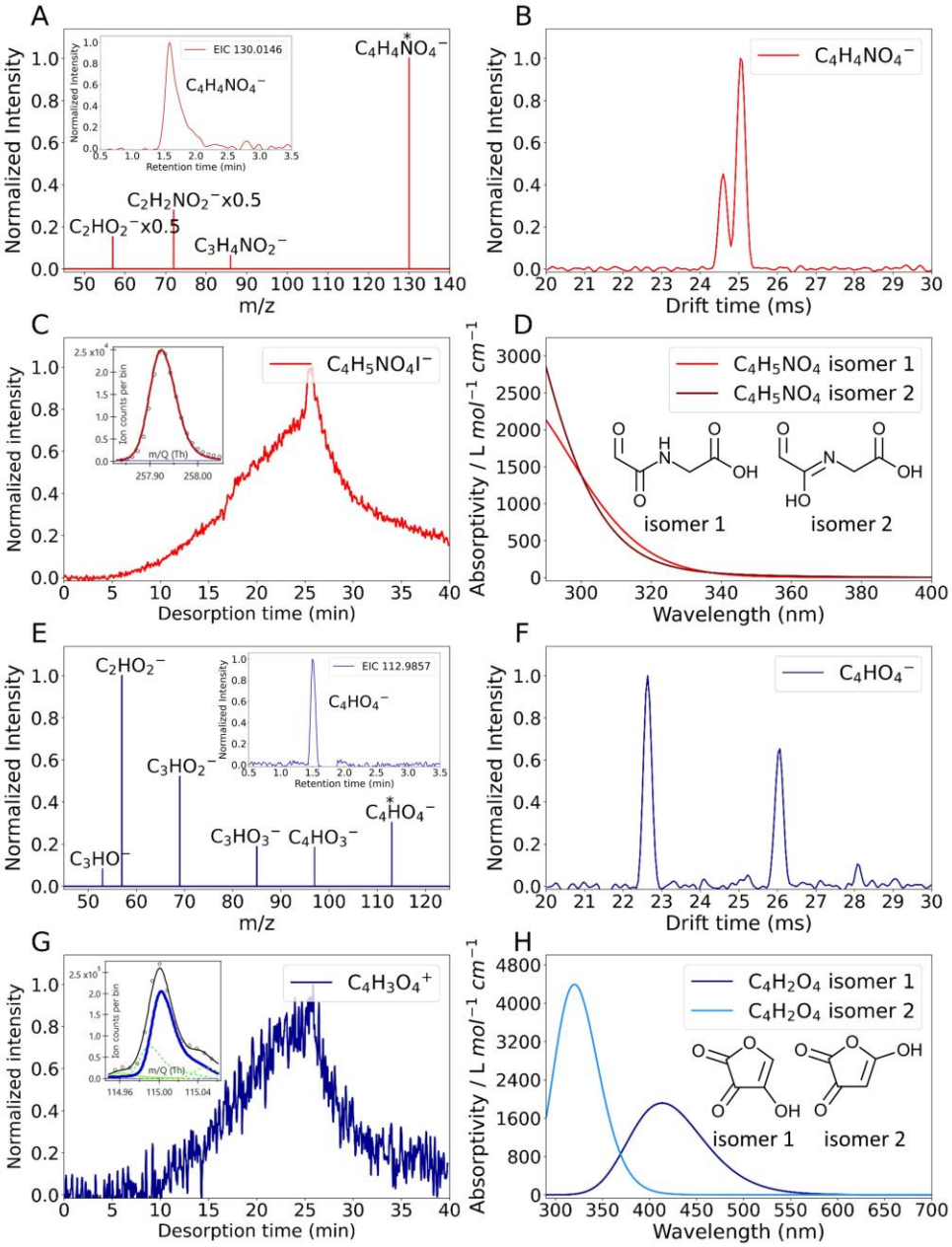
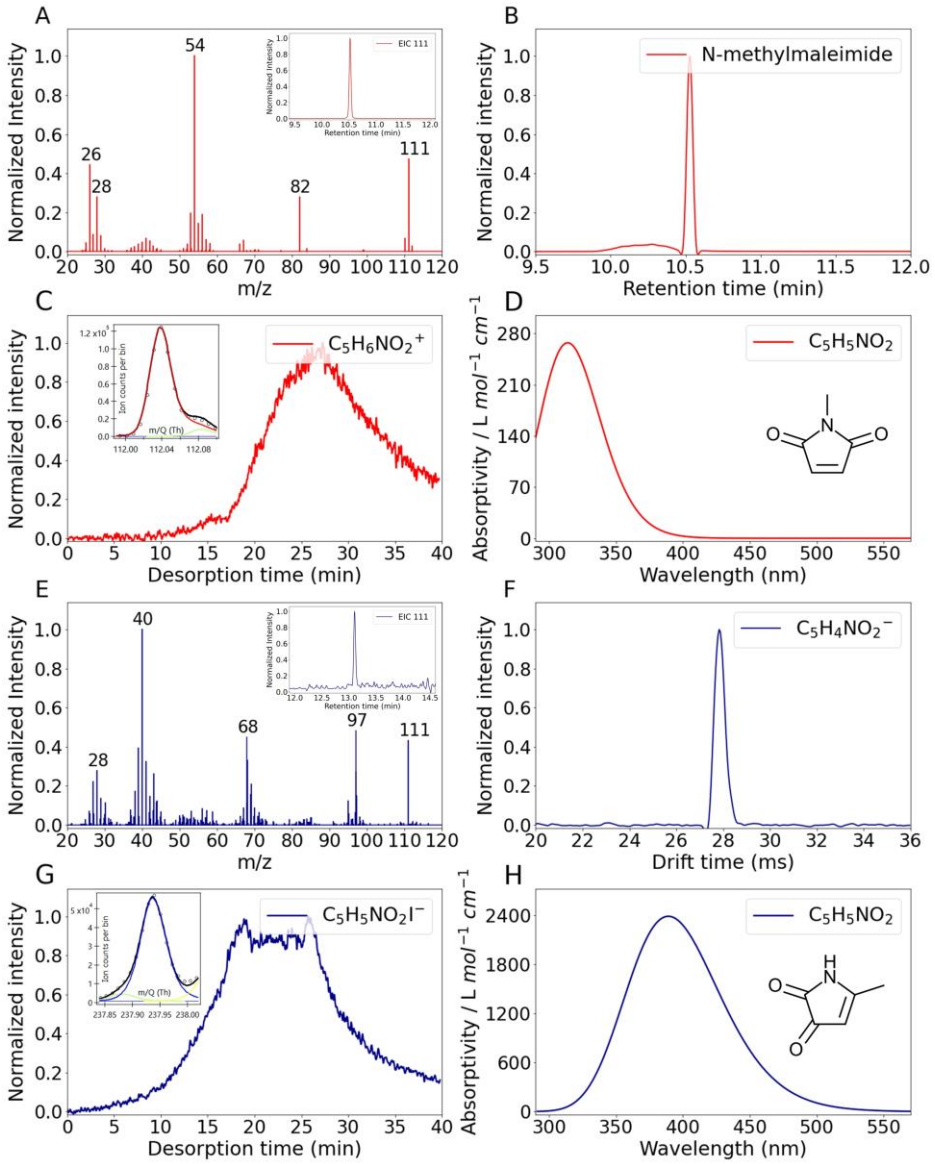


Figure 2. Characterization of carbonyl chromophores in pyrrole SOA and furan SOA: (A) EICs and tandem mass spectra of $C_4H_5NO_4$; (B) IMS-TOF drift grams of $C_4H_5NO_4$; (C) FIGAERO-ToF-CIMS peak fitting and thermograms of $C_4H_5NO_4$; (D) theoretical UV-Vis spectra of isomers of $C_4H_5NO_4$; (E) EICs and tandem mass spectra of $C_4H_2O_4$; (F) IMS-TOF drift grams of $C_4H_2O_4$; (G) FIGAERO-ToF-CIMS peak fitting and thermograms of $C_4H_2O_4$; (H) theoretical UV-Vis spectra of $C_4H_2O_4$ isomers.



281

282 **Figure 3.** Characterization of carbonyl chromophores in 1-MP SOA and 2-MP SOA: (A) GC/EI-
283 MS characterization of $C_5H_5NO_2$ in 1-MP SOA; (B) EIC of *m/z* 111 from the N-methylmaleimide
284 chemical standard; (C) FIGAERO-ToF-CIMS peak fitting and thermograms of $C_5H_5NO_2$ in 1-MP
285 SOA; (D) theoretical UV-Vis spectrum of $C_5H_5NO_2$ in 1-MP SOA; (E) GC/EI-MS
286 characterization of $C_5H_5NO_2$ in 2-MP SOA; (F) IMS-TOF drift gram of $C_5H_5NO_2$ in 2-MP SOA;
287 (G) FIGAERO-ToF-CIMS peak fitting and thermograms of $C_5H_5NO_2$ in 2-MP SOA; (H)
288 theoretical UV-Vis spectrum of $C_5H_5NO_2$ in 2-MP SOA.

289

290 Notably, N-containing carbonyl chromophores such as imides and amides are ubiquitous
291 in SOA samples from the N-containing heterocyclic VOC precursors (e.g., pyrrole and its
292 derivatives in this study). The lone pair electrons from the nitrogen atom in imides and amides can
293 conjugate with the unsaturated bonds (e.g., carbonyl groups), which facilitate the n-π^* excitation
294 of delocalized electrons and hence support the formation of BrC chromophores. However,
295 different N-containing carbonyl chromophores may lead to different contributions to BrC light
296 absorption, depending on their mass ratio in SOA samples, spectral wavelengths, and absorptivity.
297 For example, $C_4H_5NO_4$ and $C_4H_3NO_3$ have similar mass ratios in pyrrole SOA (3.37±0.11% and
298 2.86±0.57%, respectively) based on the semi-quantification, but the UV-Vis spectrum of $C_4H_5NO_4$
299 only covers 290-350 nm (Fig. 2D), while the UV-Vis spectrum of $C_4H_3NO_3$ can extend to 500 nm
300 (Fig. S7J). Although the UV-Vis spectra of $C_4H_3NO_3$ and $C_4H_3NO_4$ cover a similar range of
301 wavelengths, the latter possesses a higher mass ratio (8.86±1.11%) and a lower absorptivity (Fig.
302 S7K). It is also noted that the presence of nitrogen may lead to a redshift of the spectral peaks (e.g.,
303 Fig. S7J and isomer 2 in Fig. 2H), suggesting the potentially important role of N-containing
304 carbonyl chromophores in modulating BrC light absorption.

305

306 **Light absorption contribution of carbonyl and nitroaromatic chromophores.** The light
307 absorption contributions of identified carbonyl and nitroaromatic chromophores can be estimated
308 by comparing their integrated LC-DAD absorbance within the corresponding RT ranges to the
309 overall LC-DAD absorbance, which are similar to those described in the literature.[16, 17] Although
310 the estimated light absorption contributions may not be rigorously accurate due to the incomplete
311 elution of chromophores that can strongly interact with the stationary phase of the LC column,[17]

this approach has successfully revealed the indispensable role of nitroaromatic chromophores in BrC aerosols from biomass burning events.[16, 17] Similarly, the relative importance of carbonyl chromophores and nitroaromatic chromophores at different wavelengths can thus be evaluated by this approach. Here, C_4 carbonyls and C_4 nitroaromatics in pyrrole SOA, which may predominantly contribute to the major hotspots in the LC-DAD heatmaps (Fig. 1), were categorized as two groups of chromophores, while other chromophores, which may comprise oxidation products with higher molecular weights and high double bond equivalence (DBE) (Fig. S12), were classified as "others." It is noted that the C_4 N-containing carbonyls (both ring-retaining and ring-opening products) and C_4 nitroaromatics are produced from the C_4 backbone of pyrrole; in other VOC systems, the carbon number of the lower-molecular-weight chromophores can be different and dependent on the VOC precursors. The light absorption contribution of each group of chromophores was visualized along with the wavelengths in both percentages (Fig. S13A-B) and mass absorption coefficient (MAC) profiles (Fig. 4). The latter was estimated by combining Fig. S13 and the MAC profiles reported in our prior study.[42]

Our results showed that, while C_4 nitroaromatics account for the majority of light absorption in the 350-430 nm range, C_4 carbonyls contribute significantly more below 350 nm and above 430 nm, accounting for over 40% of the total light absorption in both wavelength ranges (Fig. 4A and Fig. S13A). The C_5 nitroaromatics and C_5 carbonyls in 2-MP SOA, which are produced from the C_5 backbone of 2-MP (Ref. 42 and Fig. 3H), revealed comparable tendencies in the wavelength dependence of light absorption contribution (Fig. 4B and Fig. S13B). However, in the visible range, the contribution of C_4 carbonyls to light absorption was greater than the other two categories in pyrrole SOA (Fig. 4A and Fig. S13A), whereas the contributions of the three categories in 2-MP SOA were comparable (Fig. 4B and Fig. S13B). The quantitative differences

between Fig. 4A and Fig. 4B (also between Fig. S13A and Fig. S13B) reveal the vital role of VOC structures in regulating the relative contributions of carbonyl chromophores and nitroaromatic chromophores to secondary BrC light absorption, which could be due to the interference of diverse oxidation pathways (e.g., diverse pyrrolyl radical shifts).[42]

The relative impact of carbonyl chromophores on BrC light absorption is further evaluated by the ratio of their absorption cross-section emission factors (EF_{absC}), which accounts not only for the MACs but also the carbon emission factors of VOC precursors from burning sources and the SOA yields.[41] Details of the EF_{absC} calculations for pyrrole SOA and 2-MP SOA were described previously.[42] Taking biomass burning of ponderosa pine forests, which is relevant to wildfires in the western US and Canada,[57] as an example, $C_{4\text{-}5}$ carbonyl chromophores may contribute more to BrC light absorption below 350 nm and above 430 nm than $C_{4\text{-}5}$ nitroaromatic chromophores (Table S3). It is also noted that the light absorption of 1-MP SOA was mainly attributed to mono-nitrogen $C_{4\text{-}5}$ carbonyls and the "others" category instead of $C_{4\text{-}5}$ nitroaromatics (Fig. 3D, Fig. S4, Fig. S14A, and Fig. S15A). As highlighted in our prior study,[42] the absence of $C_{4\text{-}5}$ nitroaromatics may account for the inhibited nitro-substitution by the methyl group on the nitrogen atom of the 1-MP backbone, which reinforces the importance of VOC structures in the light absorption contribution of carbonyl chromophores.

In addition, the heteroatoms in heterocyclic VOCs may greatly alter the oxidation pathways and hence the light absorption contribution of carbonyl and nitroaromatic chromophores. For example, formation of pyrrole-derived nitroaromatics is initiated by the H-abstraction on the nitrogen heteroatom,[42] while formation of furan-derived carbonyls is related to the NO_3 addition and subsequent NO_2 elimination mechanisms affected by the oxygen heteroatom.[58] Our previous research and the current findings suggest that the light absorption of furan SOA can be primarily

attributed to $C_{4\text{-}5}$ carbonyls and the "others" category (Fig. S14B and Fig. S15B).[42, 44] Nonaromatic nitro-substituted carbonyl chromophores, such as $C_4H_3NO_7$ in furan SOA,[44] may also contribute to BrC light absorption. Similarly, light absorption of furfural SOA can be mainly attributed to the carbonyl chromophores (Fig. S14C and Fig. S15C), which is likely related to the carbonyl functional group in furfural. Collectively, these findings demonstrate the significance of carbonyl chromophores in the light absorption of secondary BrC.

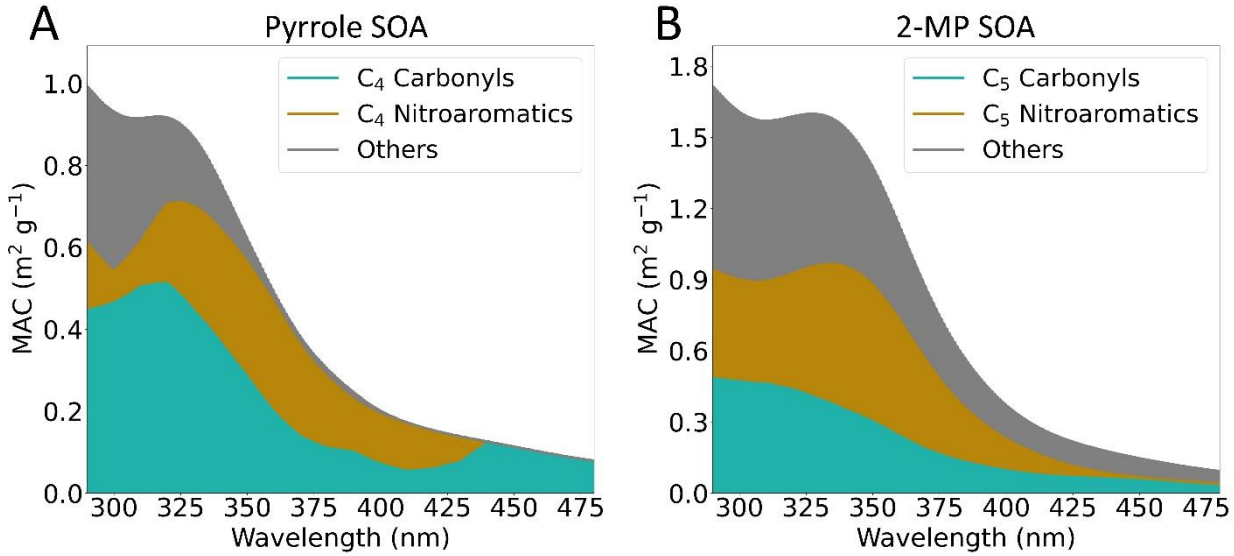


Figure 4. Light absorption contribution of chromophores to MAC profiles: (A) C_4 carbonyls, C_4 nitroaromatics and other chromophores in pyrrole SOA; (B) C_5 carbonyls, C_5 nitroaromatics and other chromophores in 2-MP SOA.

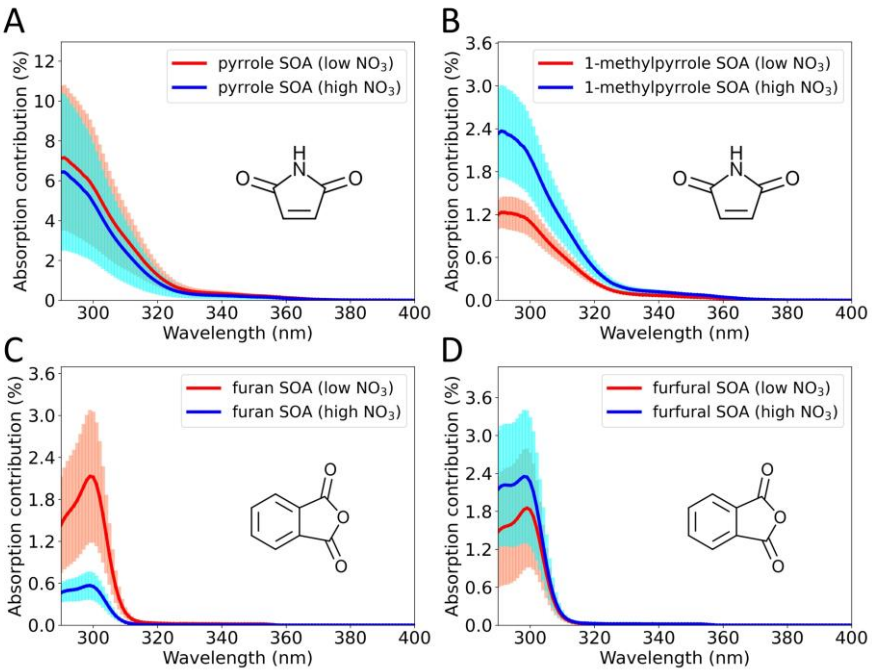


Figure 5. Light absorption contributions of maleimide to (A) pyrrole SOA and (B) 1-MP SOA, and phthalic anhydride to (C) furan SOA and (D) furfural SOA under low and high NO_3 levels. The absorption contribution is estimated by the ratio of light absorption of molecular chromophores calculated by the Beer-Lambert law and the total light absorption of BrC samples. The shadow around the lines shows the standard deviation of absorption contribution at each wavelength.

Furthermore, depending on the SOA systems, the light absorption contribution of molecular carbonyl chromophores in secondary BrC may vary under different environmental conditions. The NO_3 radical level has been reported as a critical environmental factor that affects the secondary BrC formation of pyrroles and furans.[42-44] As marker compounds of secondary BrC from the nighttime oxidation of several unsaturated heterocyclic VOC precursors, maleimide and phthalic anhydride were selected to investigate the influence of NO_3 radical levels on their light absorption contribution, and their molecular light absorptivity and mass ratio in various SOA

384 samples have been experimentally measured in prior studies.[43] Our results indicated that the light
385 absorption contribution of maleimide in pyrrole SOA remained essentially constant as the NO_3
386 radical level increased (Fig. 5A), whereas it increased significantly in 1-MP SOA as the nitrate
387 radical level increased (Fig. 5B). The light absorption contribution of phthalic anhydride exhibited
388 a divergent trend in furan SOA and in furfural SOA as the NO_3 radical level increased; specifically,
389 it reduced in furan SOA and enhanced in furfural SOA (Fig. 5C-D). The dependence of light
390 absorption contribution on the level of NO_3 radicals may be attributed to the alteration of chemical
391 kinetics and, consequently, the branching ratios of carbonyl chromophores production as the NO_3
392 concentrations change. The effects of VOC types on the contribution of molecular carbonyl
393 chromophores to light absorption should also be noted. Maleimide, for instance, may account for
394 ~7% of light absorption at 290 nm in pyrrole SOA (Fig. 5A), but a much lower value in 1-MP
395 SOA (Fig. 5B). The observed discrepancy could be attributed to the methyl group on 1-MP, which
396 could hinder the formation of maleimide and alternatively generate other chromophores (e.g., N-
397 methylmaleimide in Fig. 3D). Thus, the role of carbonyl chromophores in secondary BrC is
398 significantly influenced by complex atmospheric conditions and VOC emissions.

399 Overall, our results indicate the prevalence of carbonyl chromophores in SOA from the
400 nighttime oxidation of heterocyclic VOCs. The UV-Vis spectra of the characterized carbonyl
401 chromophores cover a wider range of wavelengths (i.e., ~290-500 nm) compared to the
402 nitroaromatic chromophores (i.e., ~290-400 nm) characterized in our previous studies,[42, 55]
403 suggesting their distinct contributions to BrC light absorption at different wavelengths.
404 Comparison between isomers also highlights that the spectral light absorptivity of carbonyl
405 chromophores in secondary BrC can be governed by the structure of VOC precursors, which is
406 consistent with our previous research on nitroaromatic chromophores.[42] The structural dependence

of UV-Vis spectra indicates the importance of structure-related information in the process-level prediction of secondary BrC formation. Moreover, the characterized carbonyl chromophores and their structural analogues, including heterocyclic diones and triones, have been widely observed in SOA systems from other VOCs, for example, those generated by photooxidation of a variety of aromatic hydrocarbons.[59-63] Heterocyclic diones have also been widely observed in field measurements of ambient aerosols from biomass burning plumes.[38, 64, 65] Although triones in ambient aerosols were less reported,[66] they have been suggested as possible contributors to BrC generated from aqueous-phase reactions.[67, 68] The collective evidence demonstrates that carbonyl chromophores are ubiquitous constituents in SOA and may play an active role in secondary BrC formation.

ATMOSPHERIC IMPLICATIONS

Molecular chromophores are the key to BrC light absorption, connecting the microscopic physicochemical processes in atmospheric aerosols with the macroscopic radiative budget in the Earth system. The newly characterized chromophores enable a more detailed process-level depiction of BrC formation, which is essential for improving the assessment of BrC's impact in the context of climate change. Our study shows that carbonyl chromophores can be important constituents of secondary BrC from nighttime oxidation of heterocyclic VOCs, with wavelengths ranging from UV to visible. While research on ambient aerosols in wildfires has suggested that nitroaromatic chromophores, such as nitrophenols, nitrocatechols, nitroguaiacols, and nitrosyringols, may predominately contribute to BrC light absorption in the visible range,[16, 17] field studies have also provided increasing evidence indicating that carbonyl chromophores could be distinct contributors to BrC light absorption in the UV range.[69] It is further noted that the carbonyl

chromophores characterized in our studies are not only found in other SOA systems but are also commonly observed in field studies.[38, 59-65] Indeed, carbonyl compounds are ubiquitous in atmospheric aerosols and have long been recognized as the key species in tropospheric chemistry[70, 71] and the critical precursors of secondary BrC formation in the aerosol phase via NH_3/amine-driven reactions[72-75] or forming charge transfer complexes with alcohols.[76, 77] Our study can complementarily provide a new perspective for evaluating the role of carbonyls in atmospheric aerosols based on their intrinsic light absorption, for example, the initiation of photosensitization which can facilitate aqueous SOA formation.[78-82]

Furthermore, carbonyl chromophores produced by nighttime oxidation of N-containing VOCs may represent a potentially important component in secondary BrC that was previously unrecognized. Our study reveals that light-absorbing imides and amides can be critical chromophores in the SOA of pyrrole and its derivatives. Given that biomass burning releases a variety of N-containing heterocyclic VOC precursors,[37-39] the formation of N-containing carbonyl chromophores could be a potentially significant contributor to the light absorption of secondary BrC. Furthermore, as widely observed in field studies of wildfire emissions,[33, 38, 83, 84] N-containing carbonyl chromophores offer another pivot in addition to the nitroaromatic chromophores for a more in-depth understanding of secondary BrC formation, particularly the wavelength-dependent change of BrC light absorption as well as the diverse physicochemical processes. Although nitroaromatic chromophores may likely possess stronger absorptivity compared to carbonyl chromophores, the former are largely related to anthropogenic emissions of NO_x,[85, 86] whereas the latter may be generated by more divergent atmospheric oxidation pathways, such as OH-driven oxidation of VOCs.[64] Broader sources of carbonyl chromophores may result in greater ubiquity in the atmosphere under different environmental conditions, implying more extensive effects. Further

research is needed to reveal the role of carbonyl chromophores in other BrC systems and to estimate the radiative forcing from carbonyl chromophores. Overall, this study expands the current understanding of chromophore formation and provides a molecular-level foundation as the basis for further investigations into the effects of secondary BrC formation on the Earth's energy budget in the context of climate change.

ASSOCIATED CONTENT

Supporting Information

ACN extraction efficiency of surrogate standards of BrC chromophores (Table S1); Cartesian coordinates for geometrical structures of carbonyl chromophores in the theoretical calculations (Table S2); Wavelength-dependent EF_{absC} of $C_{4\text{-}5}$ carbonyls and $C_{4\text{-}5}$ nitroaromatics (Table S3); First-order wall loss rate constants along with particulate diameter (Figure S1); LC mobile phase composition along with retention time and response factors of selected N-containing carbonyls (Figure S2); LC-DAD heatmap and compositional mass spectra of 2-MP SOA (Figure S3); LC-DAD heatmaps and compositional mass spectra of 1-MP SOA (Figure S4); LC-DAD heatmaps and compositional mass spectra of furfural SOA (Figure S5); Tentative fragmentation pathways of $C_4H_4NO_4^-$ and $C_4HO_4^-$ (Figure S6); Heterocyclic carbonyl chromophores in pyrrole SOA (Figure S7); Tentative fragmentation pathways of $C_4H_2NO_3^-$ (Figure S8); Tentative fragmentation pathways of $C_4H_2NO_4^-$ (Figure S9); Tentative fragmentation pathways of $C_4H_4NO_3^-$ (Figure S10); Tentative fragmentation pathways of $C_5H_5NO_2$ (Figure S11); Oxidation products with higher molecular weights and high double bond equivalence (Figure S12); Light absorption contributions of chromophores in pyrrole SOA and 2-MP SOA in percentages (Figure S13); Light absorption contributions of chromophores in 1-MP SOA, furan SOA and furfural SOA in percentages (Figure

S14); Light absorption contributions of chromophores to the MAC profiles in 1-MP SOA, furan SOA and furfural SOA (Figure S15).

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Notes

The authors declare no competing financial interest.

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