Optical Properties of Secondary Organic Aerosol Produced by Photooxidation of Naphthalene under NOx Condition

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ABSTRACT: Secondary organic aerosols (SOAs) affect incoming solar radiation by interacting with light at ultraviolet and visible wavelength ranges. However, the relationship between the chemical composition and optical properties of SOA is still not well understood. In this study, the complex refractive index (RI) of SOA produced from OH oxidation of naphthalene in the presence of nitrogen oxides (NOx) was retrieved online in the wavelength range of 315–650 nm and the bulk chemical composition of the SOA was characterized by an online high-resolution time-of-flight mass spectrometer. In addition, the molecular-level composition of brown carbon chromophores was determined using high-performance liquid chromatography coupled to a photodiode array detector and a high-resolution mass spectrometer. The real part of the RI of the SOA increases with both the NOx/naphthalene ratio and aging time, likely due to the increased mean polarizability and decreased molecular weight due to fragmentation. Highly absorbing nitroaromatics (e.g., C₆H₅NO₄, C₇H₇NO₄, C₇H₅NO₅, C₈H₅NO₅) produced under higher NOx conditions contribute significantly to the light absorption of the SOA. The imaginary part of the RI linearly increases with the NOx/VOCs ratio due to the formation of nitroaromatic compounds. As a function of aging, the imaginary RI increases with the O/C ratio (slope = 0.024), mainly attributed to the achieved higher NOx/VOCs ratio, which favors the formation of light-absorbing nitroaromatics. The light-absorbing enhancement is not as significant with extensive aging as it is under a lower aging time due to the opening of aromatic rings by reactions.

KEYWORDS: optical properties, secondary organic aerosol, NOx effect during photooxidation, atmospheric aging, chromophore characterization, chemical composition

INTRODUCTION

Atmospheric aerosols play a critical role in Earth’s radiative energy balance by either warming or cooling the atmosphere through absorption and scattering of incoming solar radiation and outgoing terrestrial radiation. The aerosol radiative forcings of aerosol—radiation interaction and aerosol—cloud interactions are estimated to be −0.22 (−0.47 to −0.04) Wm⁻² and −0.84 (−1.45 to −0.25) Wm⁻², respectively.¹ On a regional scale, the forcing may be much larger. Large uncertainties in radiative and climate forcing are mostly due to organic aerosols, and their light absorption properties are not well understood. Atmospheric brown carbon (BrC) aerosols, which absorb light mostly in the near-ultraviolet to the ultraviolet region, have been recognized to play a critical role in climate forcing, accounting for ~20% of the absorption by carbonaceous aerosols.²⁻⁶ BrC is composed of light-absorbing organic compounds with a complex chemical composition and diverse wavelength-dependent light-absorbing properties.⁷ The major source of primary BrC is commonly attributed to biomass burning, which is typically treated as the only source of primary BrC in modeling studies.⁸⁻¹⁰ However, multiple field observations¹¹⁻¹³ and laboratory studies¹⁴⁻¹⁹ demonstrated that BrC can be produced by secondary processes via photooxidation and dark reactions²⁰⁻²² of volatile organic compounds (VOCs) from various sources.⁴ Due to the complexity of the chemical composition and their variable wavelength-dependent light-absorbing properties, the investigation of secondary BrC is an active area of research.

Polycyclic aromatic hydrocarbons (PAHs), formed in pyrolytic reactions during fuel-rich combustion of fossil and biomass fuels, are an important class of semivolatile anthropogenic emissions. Light-weight PAHs (<four aromatic...
The presence of NOx during aging has to be evaluated to determine the climate effect of naph-SOA more accurately. In this study, naph-SOA are produced under atmospherically relevant relative humidity either at the same aging time but with different NOx/naphthalene ratios or under varying aging times at a constant NOx/naphthalene ratio to address the effects of NOx and atmospheric aging thoroughly. Naph-SOA is chemically characterized online by a high-resolution (HR) time-of-flight (ToF) aerosol mass spectrometer (AMS). Simultaneously, the size-dependent absorption and extinction cross sections of naph-SOA are measured using an optical system consisting of a broadband cavity-enhanced spectrometer (BBCES, 315–345 and 380–650 nm), a photoacoustic absorption spectrometer (PAS, 404 nm), and a cavity-ring-down spectrometer (CRDs, 404 nm). The chemical composition and molecular-specific light-absorbing properties of naph-SOA are further assessed offline utilizing a high-performance liquid chromatography (HPLC) separation coupled to a photodiode array (PDA) detector for UV–vis absorption measurement and high-resolution mass spectrometry (HRMS) for molecular characterization. Hence, this study comprehensively investigated the chemical composition, molecular-specific light absorption properties, and online aerosol optical properties of naph-SOA produced by the OH-initiated oxidation and the first time to quantitatively assess the impact of the NOx/naphthalene ratio and aging time, which provides experimental insights into the effect of anthropogenic SOA on climate forcing.

### Table 1. Initial Conditions and Physical–Chemical Properties of naph-SOA Generation by PAM

| experiment ID | naphthalene (ppmv) | N2O (%) | NOx (ppmv) | O3 (ppm) | RH (%) | aging time (days) | H/C | O/C | fSOA | density (g cm⁻³) |
|---------------|--------------------|---------|------------|----------|--------|------------------|-----|-----|------|-------------|
| A08           | 345                | 2       | 109        | 48.3     | 38.8   | 0.8              | 1.03| 0.67| 0.05| 1.34       |
| A14           | 345                | 2       | 124        | 48.3     | 38.9   | 1.4              | 1.03| 0.68| 0.05| 1.32       |
| A22           | 345                | 2       | 188        | 48.3     | 38.9   | 2.2              | 1.04| 0.74| 0.06| 1.32       |
| A37           | 345                | 2       | 303        | 48.3     | 38.8   | 3.7              | 1.08| 0.86| 0.06| 1.34       |
| A39           | 345                | 2       | 511        | 48.3     | 39.0   | 3.9              | 1.09| 0.88| 0.07| 1.35       |
| A49           | 345                | 2       | 1111       | 48.3     | 39.0   | 4.9              | 1.12| 0.92| 0.08| 1.33       |
| N00           | 493                | 0       | 0          | 38.4     | 38.3   | 3.2              | 1.05| 0.94| 0.03| 1.37       |
| N05           | 493                | 0.5     | 85         | 38.4     | 38.3   | 3.2              | 1.06| 0.91| 0.04| 1.34       |
| N10           | 493                | 1       | 209        | 38.4     | 38.5   | 3.2              | 1.08| 0.96| 0.05| 1.34       |
| N20           | 493                | 2       | 592        | 38.4     | 38.2   | 3.2              | 1.10| 0.96| 0.07| 1.35       |
| N40           | 493                | 4       | 1352       | 38.4     | 38.4   | 2.4              | 1.16| 0.72| 0.13| 1.36       |

- SOA Generation by the OFR. Naphthalene (Sigma-Aldrich) was used as a proxy for anthropogenic SOA precursors. Naph-SOA particles were generated by homogeneous nucleation and condensation of oxidized products from OH oxidation of naphthalene in the potential aerosol mass (PAM) oxidation flow reactor (OFR) in the absence of seed particles. The details of the PAM reactor have been described previously. A total flow of 4.3 L min⁻¹ of a N₂ + N₂O mixture and a 0.2 L min⁻¹ O₂ + O₃ mixture with a final RH of 36–39% was used, with a corresponding residence time of 184 s. The initial SOA conditions for naph-SOA production are listed in the Supporting Information (Table S1), including the initial naphthalene and O₃ concentrations, RH, and measured NOx concentrations. The NOx/naphthalene ratios varied between 0 and 3.2, as shown in the Supporting Information (Table S1), which are within the typical range of NOx/VOC ratios in the ambient conditions.

### EXPERIMENTAL METHODS

#### Naph-SOA Generation by the OFR

- Naphthalene (Sigma-Aldrich) was used as a proxy for anthropogenic SOA precursors. Naph-SOA particles were generated by homogeneous nucleation and condensation of oxidized products from OH oxidation of naphthalene in the potential aerosol mass (PAM) oxidation flow reactor (OFR) in the absence of seed particles. The details of the PAM reactor have been described previously. A total flow of 4.3 L min⁻¹ of a N₂ + N₂O mixture and a 0.2 L min⁻¹ O₂ + O₃ mixture with a final RH of 36–39% was used, with a corresponding residence time of 184 s. The initial SOA conditions for naph-SOA production are listed in the Supporting Information (Table S1), including the initial naphthalene and O₃ concentrations, RH, and measured NOx concentrations. The NOx/naphthalene ratios varied between 0 and 3.2, as shown in the Supporting Information (Table S1), which are within the typical range of NOx/VOC ratios in the ambient conditions.
OH radicals were produced through the reaction of O(1D) with water, whereas O(3P) radicals were formed from the photolysis of O3 by UV light (λ = 254 nm). N2O (99.999%) was introduced to the PAM reactor as the source of NO and NO2 generated by the reactions of O(1D) + N2O → NO2 and NO + O3 → NO2 + O2. This method provides a more homogeneous NOx environment and can achieve a much higher NO concentration in the reactor than adding NOx directly. The OH concentration in the PAM was controlled by adjusting the UV light intensity. The OH exposures in this study were within the range of (1.04–5.05) × 1014 molecules cm−2 s−1 determined by measuring the decay of coincjected SO2 (Thermo Fisher Scientific, Model 43i). By assuming a daily average radical concentration of [OH] = 1.5 × 106 molecules cm−3, the equivalent aging time in this study ranged from 0.8 to 4.9 days. Due to the fast conversion of NO to NO2 in the sampling line by the high O3 concentration, we cannot measure the NO concentration directly. Therefore, only the total NOx concentration after the PAM reactor is recorded (SERINUS 40, Ecotech, Australia).

To investigate the influence of NOx and aging on the optical properties of naph-SOA, two sets of experiments were conducted. Five experiments (Table 1, N00–N40) were performed under the same aging time (3.2 days for N00–N20, 2.4 days for N40, which was limited by the reactor), but with different N2O inputs (0–4%), to achieve different NOx/naphthalene ratios to test the influence of NOx. Another six experiments (Table 1, A08–A49) were carried out with 2.0% N2O, but with different aging times (0.8–4.9 days). This set of experiments was designed to probe the combined effect of NOx and aging time.

The Aerodyne photochemical model implemented in MATLAB (Mathworks) was used to simulate the photochemical reactions in the PAM reactor. Due to limited knowledge of the reaction mechanism and reaction rate constants of OH oxidation of naphthalene, only a simplified RO2 chemical is included in the model, as described previously. By considering the reaction rate constants of naphthalene with OH, O3 and NOx, we estimated that more than 98% of the naphthalene was consumed by OH radicals in all of the experiments. More details about the box model are provided in Text S1, and the model output results are shown in Table S1.

**Online Measurement of SOA Chemical Composition and Density.** The size distributions of SOAs were monitored by a scanning mobility particle sizer (SMPS, TSI Incorporated, classifier model 3080, CPC model 3775). The chemical composition of naph-SOA was characterized by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., Billerica, MA, more details in Text S1), which was operated alternatively in V and W modes. More details about the data processing and instrument calibration can be found in the Supporting Information (Text S1). The effective density (ρe) of naph-SOA particles was derived from measurement of the aerodynamic diameter (d_a) obtained by an aerodynamic aerosol classifier (AAC, Cambustion) and the mode mobility diameter (d_m), which was measured by the SMPS after the AAC.

**Light Extinction and Absorption Measurement.** The aerosol extinction cross section, σ_ex(λ, D_p, m), which depends on the light wavelength (λ), the particle mode diameter (D_p), and the complex refractive index (RI, m = n + ki, where n and k are the real part and imaginary part, respectively) of the material, is described by the expression shown in eq 1

$$\sigma_{\text{ex}}(\lambda, D_p, m) = \frac{\alpha_{\text{ex}}(\lambda, D_p, m)}{N(D_p)}$$

where $\alpha_{\text{ex}}$ is the extinction coefficient of the measured particles and $N(D_p)$ is the particle number concentration (cm−3). Size-dependent absorption and extinction cross sections are measured using a photoacoustic absorption spectrometer (PAS), a cavity-ring-down spectrometer (CRDS), and a broadband cavity-enhanced spectrometer, which consists of two channels (BBCESUV, 315–345 nm; and BBCESvis, 380–650 nm). Briefly, aerosols from the ORF pass through an ozone scrubber and then are dried with a diffusion dryer (RH < 20%). The dried aerosols are then passed through a denuder filled with activated charcoal to remove NOx in the gas phase. The outcome particles are size-selected (175–325 nm with 25 nm step) with an AAC and then directed into our optical system for optical property characterization. Meanwhile, the particle number concentration and the mobility size distribution are measured by a parallel CPC and an SMPS, respectively. The experimental setup is shown in the SI (Figure S1), and the operational details of the instruments can be found in our previous studies.

By assuming homogeneous chemical composition of the particles across the different sizes, the complex RI of the aerosols was retrieved by fitting a theoretical Mie curve to the size-dependent extinction cross-section data at each specific wavelength. The retrieval algorithm was limited to searching for $n \geq 1$ and $k \geq 0$.

**Offline Characterization of naph-SOA Using the HPLC-PDA-HRMS Platform.** All details for the offline characterization of naph-SOA using HPLC-PDA-HRMS have been published elsewhere by Siemens et al. Briefly, naph-SOA was collected on Teflon filters (poly(tetrafluoroethylene) PTFE, 0.45 μm pore size, 47 mm diameter, Whatman) for offline analysis. The filters were extracted with acetonitrile (Optima LC/MS grade, Fisher Chemical) under sonication and then analyzed using a high-performance liquid chromatography (HPLC) system coupled with a photodiode array detector (PDA), both from Thermo Vanquish, and a high-resolution (HR) Q-Exactive HF-X hybrid quadrupole Orbitrap mass spectrometer equipped with an electrospray ionization (ESI) source (HPLC-PDA-ESI/HRMS, Thermo Scientific, Inc.). About ~3 μg of dissolved organic matter (OM) was injected into the HPLC for each sample. Analytes were separated on a reversed-phase column (Luna C18, 150 × 2 mm, 5 μm particles, 100 Å pores, Phenomenex, Inc.) using a 200 μL min−1 binary solvent mixture containing water (A) and acetonitrile (B), with both solvents containing 0.1% (v/v) formic acid. A 90 min LC gradient was programmed as follows: 0–3 min at 10% of B, 3–63 min at a linear gradient to 100% of B, 63–70 min B held at 100%, 70–71 min decreased to 10% of B, and 71–90 min held at 10% of B to re-equilibrate the column. UV–vis absorption spectra were recorded using the PDA detector over the wavelength range of 200–680 nm. Mass spectra were acquired for the m/z range of 80–1200 Da at a mass resolution of m/Δm = 240 000 (at m/z 200). The raw data were acquired using Xcalibur software (Thermo Scientific) and were further processed using MZmine-2.
RESULTS AND DISCUSSION

Online Chemical–Physical Characterization of naph-SOA. Despite the changes in the NOx/naphthalene ratio and aging time, the particle effective density did not change significantly (1.32–1.37 g cm$^{-3}$). The particle size distributions of naph-SOA are shown in Figure S2. For experiments conducted to study the NOx addition effect (N00–N40), the particle mode diameter of naph-SOA was about 97 nm. It decreased to $\sim$75 nm upon NOx addition, and the particle number concentration decreased when the NOx/naphthalene increased from 0.17 to 1.2. The addition of NOx in the PAM reactor favors the formation of organic nitrates through the RO$_2$ + NO channel (Table S1). These organic nitrates have lower volatility that may lead to more efficient new particle formation, thus increasing the particle number concentration and decreasing the particle mode diameter. At the highest NOx/naphthalene ratio, the particle number decreased significantly although the particle mode diameter increased to 90 nm. Overall, the total particle mass decreased when the NOx/naphthalene ratio increased from 0.17 to 2.7, indicating a suppression effect of NOx on naph-SOA formation, which is in line with previous studies.$^{23,24,35}$ For naph-SOA produced with a fixed initial N$_2$O concentration (A08–A49), the particle mode diameter increased from 68 to 81 nm when the equivalent aging time increased from 0.8 to 4.9 days, while the particle number concentration kept increasing except for the experiment with the highest aging time (A49). This caused the total mass of naph-SOA to keep increasing with aging time. At low aging time conditions, the SOA formation was characterized by the addition of oxygenated functional groups to gas-phase molecules, which can further partition into the particle phase; therefore, the SOA yield increased with aging time. However, with further aging, cleavage of C–C bonds of intermediate products became more prominent, thus decreasing the SOA yield.$^{49–61}$

AMS mass spectra of selected naph-SOA experiments are presented in Figure S3 for low and high NOx/naphthalene (0.17 vs 1.2) and aging time (0.8 vs 4.9 days) conditions. Characteristic fragments of aromatics such as m/z 50–51 (C$_2$H$_3^+$, C$_4$H$_7^+$), m/z 65 (C$_5$H$_4^+$), and m/z 76–77 (C$_6$H$_5^+$, C$_7$H$_8^+$) were detected as the major hydrocarbon-like fragments (C$_x$H$_y^+$) in all of the mass spectra. All of the mass spectra show a high intensity of m/z 44 (CO$_2^+$, indicative of carboxylic acids) and a low intensity of m/z 43 (C$_2$H$_3$O$^+$, indicative of carbonyls). All of these features are different from typical mass spectra of SOAs from biogenic VOCs (high m/z 43, C$_2$H$_4$O$^+$; m/z 27, C$_3$H$_3^+$; m/z 41, C$_5$H$_5^+$; m/z 55, C$_6$H$_5$O$^+$).$^{21,36,41}$ Under NOx conditions, high intensities of nitrogen-containing fragments (e.g., C$_2$H$_3$N,N$^+$, NO$_2^+$, and NO$_3^+$) are also observed, indicating intensive formation of nitro-organics. The fragment intensity ratio of NO$_3^+$/NO$^+$ can be used to identify nitro-organics in the particles, as this ratio is much lower for nitro-organics ($\sim$ 0.1) than that of inorganic nitrates ($\sim$ 0.5, determined from NH$_3$NO$_3$).$^{62–65}$ For naph-SOA produced with NOx, the NO$_3^+$/NO$^+$ ratios in the mass spectra vary between 0.09 and 0.16 (Figure S4). This ratio is very close to that of nitro-organics, further supporting the generation of nitrated naph-SOA in the presence of NOx.

At high NOx/naphthalene conditions, the C$_4$H$_5^+$ shows a lower intensity (23% vs 26%), while the signal intensity of nitrogen-containing fragments (NO$_2^+$ and C$_4$H$_4$O,N$^+$) is much higher (12% vs 7%) as compared to that of naph-SOA produced under a low NOx/naphthalene condition (Figure S3a). However, under a higher aging time, the intensities of CO$_2^+$ (14% vs 11%) and nitrogen-containing fragments (10% vs 8%) were much higher, while the intensities of hydrocarbon-like fragments were lower (25% vs 35%), indicating an increased carbon oxidation level and a more pronounced formation of nitrogen-containing species.

The H/C and O/C ratios extracted from the AMS mass spectra data without considering the NO$_3^+$ ions are plotted in a Van Krevelen diagram (Figure 1). This plot provides an insight into the major functional groups of SOAs. For experiments conducted to test the effect of the NOx/naphthalene ratio (N00–N40), when the NOx/naphthalene ratio is below 1.2 (N00–N20), the H/C and O/C ratios do not change significantly. This is consistent with the same equivalent aging time of naph-SOA. When the NOx/naphthalene ratio is 2.7, the equivalent aging time of naph-SOA is 2.4 days. The H/C ratio is significantly higher due to a lower oxidation level of SOAs as inferred by the lower O/C. When naph-SOA was produced with the same initial N$_2$O (A08–A49), both the H/C and O/C ratios increased with aging time (Figure 1 and S4), indicating OH addition to the aromatic rings and carboxylic acid group formation. The changes in the O/C and H/C ratios of naph-SOA can be well described by a linear fit. The $\Delta$(H/C)/$\Delta$(O/C) slope obtained in this study is 0.32 ± 0.03 ($R^2 = 0.96$), indicating the addition of hydrogen atoms and the production of alcohol or peroxide. This ratio is dramatically different from that obtained for naph-SOA produced in the absence of NOx (slope $\approx$ −0.09 ± 0.03),$^{36}$ which implies the formation of alcohol or peroxide.$^{66}$

Complex Refractive Index of SOA. Figure 2 shows the RI of naph-SOA across the wavelength range of 315–650 nm as obtained by the BBCES system. This is the first wavelength-dependent RI result for naph-SOA in a continuous UV–vis range based on online characterization. The real part of the RI ($n$) slightly decreases with increasing wavelength, which is similar to that observed for SOA produced from biogenic and anthropogenic VOCs.$^{21,43,67}$ For example, the $n$ for naph-SOA produced with the aging time of 3.9 days decreased from 1.63 ± 0.02 at 315 nm to 1.53 ± 0.01 at 650 nm, with a $\Delta n$ of 0.1 (Figure 2b). As the aging time increases, $n$ first increases until
the aging time reaches 2.2 days and then is almost constant with the change in aging time. The differences are within the uncertainty of \( n \). PAS-CRD measurements are more precise to differentiate small changes in the RI, and the results are shown in Figure 2c,d. There is a slight change in \( n \) (1.554 ± 0.001 to 1.606 ± 0.001) as the aging time increases (Figure 2d). An increase of \( n \) (1.542 ± 0.001 to 1.643 ± 0.001) is also observed when the NOx/naphthalene ratio increased from 0 to 2.7 (Figure 2c). A previous study by Lambe et al.\(^3\) reported the RI of naph-SOA from OH oxidation of naphthalene in the absence of NOx. The observed \( n \) values varied from 1.58 ± 0.06 to 1.66 ± 0.04 at 405 nm, comparable with our results.

The imaginary part of the RI (\( k \)) shows a strong spectral dependence, with \( k \) decreasing toward longer wavelengths (Figure 2a) as obtained from the BBCES system. For example, \( k \) decreases from 0.034 ± 0.004 at 315 nm to 0 at longer wavelengths. \( k \) increases with increasing aging time in the wavelength range where absorption is measured. \( k \) increased from 0.001 ± 0.002 to 0.061 ± 0.006 at 315 nm on increasing the aging time from 0.8 to 4.9 days (Figure 2a). This is also confirmed by the PAS measured at 404 nm, where \( k \) increased from 0.001 ± 0.001 to 0.008 ± 0.001 (Figure 2d). \( k \) values obtained by the PAS and BBCES agree with each other within the measurement uncertainty. The retrieved \( k \) values for naph-SOA are comparable to those measured for SOA produced from the OH oxidation of toluene and m-xylene\(^1\) but are substantially higher than those measured for SOA from the NOx/OH oxidation of biogenic VOCs.\(^2\) Without considering the aging time of SOA, results from the PAS measurements in this study are comparable to those reported for naph-SOA produced from OH oxidation in the absence of NOx (at 405 nm, \( k = 0.8–3.6 \times 10^{-3} \)).\(^3\)

The mass absorption coefficient (MAC) is frequently used to describe the absorbing properties of aerosols. Figure S5 displays the MAC values obtained for naph-SOA produced from OH oxidation under different NOx/naphthalene ratios and aging times. Overall, the MAC values measured here have a strong spectral dependence between 300 and 500 nm, and the MAC values span a wide range under different oxidation conditions. At 405 nm, the MAC values range from 0.22 to 0.38 m\(^2\) g\(^{-1}\) for the samples analyzed (N00, N40, A37, A49). These values are substantially higher than those reported for naph-SOA produced in the absence of NOx (0.025–0.088 m\(^2\) g\(^{-1}\))\(^3\) but comparable to the value reported for naph-SOA generated in the presence of NOx (0.31 m\(^2\) g\(^{-1}\)).\(^3\) Xie et al. also measured the MAC value for naph-SOA produced under the initial NOx/naphthalene ratio of 3.0.\(^3\) Their results at 405 nm (0.72 m\(^2\) g\(^{-1}\)) agree well with that of naph-SOA produced under the NOx/naphthalene ratio of 20 by Metcalf et al. (0.81 m\(^2\) g\(^{-1}\))\(^3\) but are much higher than our measurements. This may be a result of the different oxidation conditions and experimental setups. Higher RH in this study (40% vs <15%) favors the condensation of semivolatile species that may have a lower light absorption.\(^6\) The XAD4-coated annular denuder upstream of the filter used by Xie et al. can also remove the semivolatile species from the particles and then increase the light absorption of the remaining less-volatile SOA. Moreover, the much higher NOx/VOC ratio (~20) in the study by Metcalf et al.\(^3\) promotes the formation of stronger light-absorbing chromophores. All of these could explain the lower MAC values measured in this study as compared to the literature results.

**Formation of Chromophores in naph-SOA.** Bulk optical measurements from PAS and UV–vis absorbance have confirmed the formation of BrC chromophores in naph-SOA. Figure 3 shows the HPLC-PDA chromatograms (panels a and b) of naph-SOA generated under NOx/naphthalene ratios of 0 and 2.7 with comparable aging times (3.2 vs 2.4...
days). Many strong-absorbing chromophores are observed in the HPLC elution time of 3−25 min. The chemical formulas are assigned based on accurate mass measurements, and the tentative structures are proposed based on these chemical compositions, LC retention times, UV−vis absorption spectra, and literature reports, taking into account the ring-retaining, cyclization, and ring-opening reactions of naphthalene and its oxidized intermediates. Oxygenated aromatic hydrocarbons (CHO, e.g., C8H6O6, C6H6O3, C11H12O5, C8H6O2, C8H6O4, and C11H12O7) are the major chromophores in naph-SOA produced without NOx (Figure 3a,c). This is different from the result by Xie et al., who claimed a nitroaromatic compound (C10H7NO3) was the major absorbing species for naph-SOA produced without NOx. It seems that there was a NOx contamination in Xie et al.’s chamber experiment or an artifact during the filter analysis. These CHO chromophores in naph-SOA produced without NOx also contribute to the light absorption of naph-SOA produced with NOx. However, strong light-absorbing nitroaromatics (CHON, e.g., C9H9NO6, C6H5NO4, C7H7NO4, C7H5NO5, C8H5NO5, C8H5NO6, C9H9NO6, C10H9NO4) are produced when NOx is involved in SOA formation (Figure 3b,c), and these species contribute significantly to the absorption of the SOA (~45% of the MAC at 350−450 nm for the A49 experiment, Figure S6d). Quantitative contributions of the identified BrC chromophores to the total MAC values of the solvent-extractable BrC were calculated using the method described by Hettiyadura et al.71 The major absorbing CHO species, which contain hydroxy, carbonyl, and carboxylic functional groups, elute faster than the CHON species, which contain additional nitro groups, probably due to the low polarity of the −NO2 group, which reduces the overall polarity of CHON compounds. Xie et al. detected eight nitroaromatic species in the SOA produced with an initial NOx/naphthalene ratio of 3.35 Among them, four species (C10H7NO3, C10H7NO4, C8H9NO5, C6H5NO4) contribute significantly to the light absorption at 365 (~18%), 400 (47%), and 450 (~18%) nm. The two most absorbing species (C10H7NO3 and C10H7NO4) found by Xie et al. are not identified as major absorbing species in our study probably due to the different RH between these two studies, which can change the gas-particle partitioning. Moreover, the application of surrogate standards by Xie et al. for quantification may also introduce large uncertainties in the determination of major chromophores. In this study, these two species elute at 28.12 and 31.26 min. Light absorption by chromophores eluting after 25 min is negligible; thus, the HPLC-PDA-HRMS analysis here is only performed within an
elution time of 25 min. In contrast, C6H5NO4, which was found to be a minor chromophore by Xie et al., is the primary contributor to light absorption of naph-SOA produced in this study (Figure 3b), especially in the long-wavelength range. This is consistent with its broad UV−vis absorption spectra55 and higher abundance in the SOA (0.94% of the total SOA).25 In our study, C6H5NO3 and C7H5NO5, which elute between 19.5 and 19.8 min in our HPLC, are also detected as major products of naph-SOA produced under NOx conditions (1.1% and 0.5% of the total SOA) in a previous study.25 These two species have strong absorption in the UV−vis wavelength range and contribute significantly to the total light absorption of naph-SOA in this study.

Figure 4. Evolution of optical properties of naph-SOA due to aging, as indicated by increasing H/C and O/C ratios, in the presence of NOx. The upper and lower panels show the change of the imaginary part and the real part as a function of nitrate fraction ($f_{NOx}$), H/C ratio, and O/C ratio measured with HR-ToF-AMS. The dashed lines show the RI values at 330 nm (purple), 404 nm (cyan), and 532 nm (green).

Figure 5. RI (404 nm) changes as a function of the NOx/VOC ratio (a, b) and aging time, which is represented by O/C (c, d). Blue markers indicate the results from experiments N00−N40, which are conducted with a fixed aging time but with different NOx/VOC ratios. Red markers indicate results from experiments A08−A49, which were performed with different aging times and NOx/VOC ratios. Brown markers represent literature results at 405 nm for naph-SOA produced without NOx under different aging times.36 $k$ obtained from experiment N40 was not included in the fitting (panel b) due to the shorter aging time than N00−N20. To constrain similar NOx/VOCs and O/C ratios for comparison, only part of the results is included in the fitting, as shown in panels (b)−(d).

Influence of Aging Time and NOx on the Complex Refractive Index. The elemental ratios (H/C, O/C) obtained from HR-ToF-AMS are commonly used to indicate the aging process. Moreover, the NOx observed by the HR-ToF-AMS (inorganic nitrogen-containing ions) are fragments of nitro-organic compounds (e.g., nitroaromatics), as confirmed by the NO$_3^-$/NO$^+$ ratio; thus, the nitrate fraction ($f_{NOx}= NO_3^-/(NO_3^- + organic)$) can be used to indicate the fraction of nitroaromatics in naph-SOA. As shown in Figures 1 and S4, H/C and O/C ratios, as well as $f_{NOx}$, NO$_3^-$/NO$^+$ ratios, increase with aging time in the presence of NOx, respectively. Figure 4 plots the RI of naph-SOA against the $f_{NOx}$, H/C ratio, and O/C ratio. The imaginary part increases...
significantly with the $f_{NOx}$, H/C ratio, and O/C ratio, indicating important roles of nitro-organic compounds and aging time on the absorbing properties of naph-SOA. The real part of the RI increases until the aging time of naph-SOA reaches 3.7 days (with $f_{NOx} = 0.06$, H/C = 1.08, and O/C = 0.86). Then, it remains almost constant as the aging time increases from 3.7 to 4.9 days.

Previous studies have reported an increase of RI when the SOA is produced from aromatic precursors in the presence of NOx than under low NOx conditions.4,35,72,73 The OH oxidation of naphthalene occurs through hydrogen abstraction from the aromatic ring. In the presence of NOx, this intermediate then undergoes ring-retaining reactions to produce 2-nitronaphthalene.25,40 In addition, cyclization and ring-opening reactions of intermediates can generate formyl-benzoic acid, terephthalaldehyde, formyl-benzoic acid, 2-formyl-cinnamaldehyde, and 2-hydroxy-4-nitrobenzoic acid,25,37,39,40,74 which absorb light in the UV–vis wavelength range (Figure 3). Therefore, during the aging of naph-SOA, ring-retaining reactions introduce more oxygenated and nitro functional groups, while ring-opening reactions break the aromatic rings. In the PAM reactor, the NOx/VOC ratio increased with the aging time (Figure 1); thus, changes in the chemical composition and optical properties of naph-SOA are affected by both the NOx/VOC ratio and the aging time.

**Effect of NOx/Naphthalene Ratio on the RI.** As the aging time for generation of naph-SOA is fixed (N00–N40), the $f_{NOx}$ increases with increasing NOx/naphthalene ratio (Figure S4a), indicating that the reactions produce an increasing amount of CHON products (Figure S7) by adding nitro groups to the oxidized intermediates.40 The imaginary part of the RI for naph-SOA linearly increases with the NOx/naphthalene ratio with a slope of 0.004 at 404 nm (Figure 5b). As the NOx/VOC ratio increases, more RO$_2$ will react with NO to produce nitro-organic compounds (Table S1) that are highly absorbing. A higher nitro-organic compound content under higher NOx/naphthalene ratios was observed by HR-ToF-AMS (Figures S3 and S4) and HPLC-HRMS (Figure S7). Siemens et al.55 have analyzed the double-bond equivalent value (DBE) of the assigned species. They suggest that the high DBE values of the CHON compounds retain the aromaticity and are likely nitroaromatics. These nitroaromatic compounds have an extended network of π bonds, and they possess additional oxygenated functional groups, resulting in feasible light-absorbing properties toward the longer wavelength range.25–77 The real part of the RI increases with increasing aging time and NOx/naphthalene ratio, especially in the lower ranges (Figure 5a). An empirical expression relates the real part of RI ($\alpha$) positively to the molecular volume (density $\rho$) divided by the molecular weight (MW)) mean polarizability ($\alpha$) as follows

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\alpha}{3MW}$$

The mean polarizability can be estimated using elemental composition.78–79 It is positively correlated with the number of atoms in a molecule. As the NOx/VOC increases, the mean polarizability of naph-SOA increases and the density remains constant, while the MW decreases, as indicated by the significant decay of large molecules observed by Siemens et al.55 Therefore, an increase of the real part of RI is expected with the increase of the NOx/VOC ratio. At higher NOx/naphthalene ratios, the increased prevalence of NOx promotes RO$_2$ to react more with NOx to form nitro-organic compounds than reacting with another RO$_2$ to produce larger molecules (e.g., ROOR).

**Effect of Aging on the RI.** As the aging process proceeds in the presence of NOx, more oxygenated functional groups are formed and NOx participates in the reactions, leading to the production of CHON compounds.80 While the functionalization can increase the light-absorbing ability of naph-SOA, further oxidation causes ring-opening, leading to loss of aromacity and eventual loss of functional groups (fragmentation). Loss of aromacity is also going to contribute to the change in RI. Therefore, the overall change of the chemical composition and optical properties of naph-SOA is a combined effect of functionalization and fragmentation.

Figure 5 shows the RI measured by the PAS-CRD at 404 nm. As the aging time increases (indicated by the O/C ratio), both the real part and the imaginary part increase (Figure 5d). The n values show a linear dependence on the O/C ratio of naph-SOA, with a slope of $\Delta(n)/\Delta(O/C) = 0.17$ ($R^2 = 0.92$). This is consistent with the finding for the heterogeneous OH aging of squalene and azelaic acid aerosols.81 These results suggest a dominant role of functionalization, leading to an increase in the mean polarizability, which results in higher $n$ values. However, an opposite trend was observed by Lambe et al., who found that $n$ values decrease with an increase in the O/C ratio of naph-SOA produced without NOx.80 Lambe et al. observed a significant decrease in the H/C ratio of naph-SOA although the O/C ratio increased with aging time, suggesting that a significant fragmentation process dominated in their experiments.

The $k$ values at 404 nm linearly increase with the O/C ratio of naph-SOA produced under different aging times (Figure 5d). The magnitude of this increase is $\Delta(k)/\Delta(O/C) = 0.024$. This increase is much more significant than that observed for naph-SOA produced without NOx with similar O/C ratios (slope of $\Delta(k)/\Delta(O/C) = 0.0065$ for SOA with the O/C ratio below 1.0), indicating the dominant role of NOx in the absorption enhancement during aging. This is further confirmed by the results shown in Figure 5b. For experiments performed with varying aging times (A08–A49), the NOx/VOCs ratio also increased. The magnitude of this increase is $\Delta(k)/\Delta(NOx/VOC) = 0.0043$, which is similar to that of naph-SOA produced with the same aging time but with different NOx/VOCs ratios (N00–N40, $\Delta(k)/\Delta(NOx/VOC) = 0.0041$). This significant absorption enhancement is governed by a strong-absorbing CHON chromophore production under higher NOx/VOCs conditions, which promotes the RO$_2$ + NO reactions (Table S1, Figures S3 and S7).

**Atmospheric Implications.** The broadband refractive index across the UV–vis wavelength range was obtained for the first time for naph-SOA produced under atmospheric relevant conditions. The imaginary parts of RI for naph-SOA are comparable to those measured for SOA produced from OH oxidation of typical anthropogenic VOCs and are substantially higher than those measured for biogenic SOA. Since naphthalene is the most abundant PAH in urban atmospheres and can produce SOA with high yields, naph-SOA has been identified as one of the major SOA sources in urban areas by both model simulations and ambient observations.28 Considering the prominent absorbing properties of naph-SOA...
and its ubiquitous occurrence, we expect napht-SOA to be a potential BrC source in urban atmospheres and also downwind from such areas. Our lab results also provide valuable information that napht-SOA might help explain the previously observed prominent secondary BrC in urban areas not affected by strong biomass burning emissions. Therefore, napht-SOA should be incorporated in models to better understand the atmospheric BrC burden and its climate effects.

MAC values obtained in this study differ from those obtained for napht-SOA produced under dry conditions, suggesting that relevant RH conditions are critical for laboratory BrC studies. The broad range of MAC values also highlights the important role of the NOx/VOC ratio and aging time on the SOA optical properties. Chromophores typically assigned as biomass burning markers (e.g., nitroaromatics, oxygenated PAHs) were also found in napht-SOA, demonstrating the need for comprehensive molecular-level analysis for source apportionment and predictive understanding of BrC in the atmosphere.

We conclude that within the studied ranges, both longer aging time and a higher NOx/VOC ratio during napht-SOA formation yield more light-absorbing nitroaromatic species, emphasizing the influence of NOx emissions and photochemical aging on the evolution of chemical and optical properties of aerosols from real-world anthropogenic emissions. Our results indicate that elevated light absorption of the SOA downwind cities can be observed due to napht-SOA aging under NOx conditions during the first few days of atmospheric transport. This phenomenon was observed by Qin et al. at a suburban site downwind of Guangzhou, China, where the light absorption of fresh SOA was negligible, while aged SOA showed strong absorbing properties. Unlike previous studies that tested the NOx effect on the optical properties of SOA qualitatively using “high NOx” and “low NOx/NOx-free” conditions, this study provides a quantitative analysis of the impact of the NOx/VOC ratio on the absorption of SOA. The imaginary part of RI increases with the NOx/VOC ratio with a slope of 0.004 at 404 nm. We also quantified the aging effect and found that the k of napht-SOA linearly increases with the O/C ratio with a slope of 0.024. These quantitative results are useful for models to accurately capture the evolution of BrC in the ambient environment, therefore contributing to an accurate description of the potential impacts of anthropogenic emissions on the global radiative budget, air quality, and cloud feedbacks.

[PDF]

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c07328.

Experimental setup of this study (Figure S1); particle size distribution of napht-SOA and the chemical composition information obtained by HR-ToF-AMS (Figures S2–S4); contributions of CHO and CHON compounds to the total cumulative intensities and the MAC (Figures S5–S7); contribution of OH, O3, and NO3 in the naphthalene oxidation (Table S1); and the refractive index of various types of SOA at 404 nm (Table S2)

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**Notes**

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