Aqueous-Phase Production of Secondary Organic Aerosols from Oxidation of Dibenzothiophene (DBT)

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Abstract: Intermediate-volatility organic compounds (IVOCs) have been recognized as an important contributor to the secondary organic aerosol (SOA) formation via gas-phase reactions. However, it is unclear whether or not IVOCs-SOA can be produced in the aqueous phase. This work investigated aqueous oxidation of one model compound of IVOCs, dibenzothiophene (DBT). Results show that DBT can be degraded by both hydroxyl radical and the triplet excited states of organic light chromophores ($^3\text{C}^*$). Aqueous dark oxidation of DBT was also possible. SOA yields of 32% and 15% were found for hydroxyl radical (OH)-mediated photo-oxidation and dark oxidation, respectively. A continuous and significant increase of oxidation degree of SOA was observed during OH photo-oxidation, but not during the dark oxidation. Factor analyses revealed that there was a persistent production of highly oxygenated compounds from the less oxygenated species. OH-initiated photochemical reactions can also produce species with a relatively large light-absorbing ability, while such photo-enhancement due to direct light irradiation and $^3\text{C}^*$-initiated oxidation could occur, but is much less important. In the future, studies on the second-order rate constants, molecular characterization of the oxidation products from this and other IVOCs precursors are needed to better understand the role of this reaction pathway in SOA budget, air quality and climate change.

Keywords: dibenzothiophene; intermediate-volatility organic compounds; secondary organic aerosol; aqueous phase; brown carbon

1. Introduction

Secondary organic species or aerosols (SOA) are important yet highly complicated constituents of atmospheric particles, and their formation mechanism is much less clear compared to their inorganic companions [1,2]. Traditionally, SOA is thought to be generated mostly via gas-phase oxidation reactions, but in recent decades, it is well established that SOA can also be produced in atmospheric aqueous phases (e.g., fog and cloud droplets, aqueous aerosols) effectively [3,4]. This SOA from aqueous-phase reactions, termed as “aqSOA”, may contribute as much mass as the gas-phase reactions [3]. On the other hand, intermediate-volatility organic compounds (IVOCs) with effective saturation concentrations ($C^*$) in the range of $10^3$–$10^6$ µg m$^{-3}$ [5] are proved to be an important group of precursors of SOA. These species have been observed in vehicle [6,7], ship [8], aircraft emissions [9], as well as biogenic emissions [10]. Most studies regarding SOA formation from IVOCs, however, focus on the gas-phase reactions and production yields [11–13], while the possibility and importance
of IVOCs-aqSOA remain unclear. This is largely due to that IVOCs may have low water solubility or Henry’s law coefficient, making it an unlikely effective aqSOA precursor in a theoretical view. Nevertheless, some phenolic carboxyls [14] or polycyclic aromatic hydrocarbon (PAH) compounds [15], which actually belong to the IVOCs category, are found to be effective in producing aqSOA. Very recently, our group also shows that 4-ethylphenol (with a C* in the high-end of IVOCs) [16], naphthoquinone and phenanthrene (both with C* values in the low-end of IVOCs) [17] all have significant aqSOA yields. These findings call more investigations on a wider coverage of IVOCs species to understand its role in the SOA budget.

In this work, we chose dibenzothiophene (DBT) as one example compound to investigate the possible role of aqueous processing on IVOCs. DBT is one of the PAH compounds, and has been detected in ambient air [10]. DBT is also linked with crude oil and petroleum from which it is removed before further use [18,19], as well as wood-burning [20]. In some cases, DBT is of interest in monitoring marine biota, water and sediments [21]. DBT has a vapor pressure of $2.05 \times 10^{-4}$ mm Hg [22] and a C* of $2.2 \times 10^3$ µg m$^{-3}$, falling into the low-end of IVOCs. The goal of this work is to study the degradation of DBT, production yields, chemical and optical properties of SOA derived from aqueous oxidation of DBT, highlighting the probability of IVOCs-aqSOA formation and providing parameters likely useful for atmospheric model simulations.

2. Experiments

2.1. Aqueous Oxidation Experiments

In this work, we investigated aqueous oxidation of DBT (99%, Shanghai Macklin) with two types of oxidants. One is hydroxyl radical (OH), introduced by the photolysis of hydrogen peroxide ($\text{H}_2\text{O}_2$, 30%, Sinopharm Chemical Reagent). Another oxidant is organic triplet excited state ($^3\text{C}^*$), which is a specific oxidant that only exists in condensed phases and is generated via light absorption by organic chromophores [23]. In this work, we used 3,4-dimethoxybenzaldehyde (DMB) (99%, Sigma-Aldrich) as the photosensitizer to generate $^3\text{C}^*$. The reaction solutions were 10 µM DBT with 300 µM $\text{H}_2\text{O}_2$ or with 15 µM DMB. A 10 µM amount is higher than the real concentration of DBT in ambient air, and the choice of this concentration is mainly due to the SP-AMS measurement limitations. DBT-aqSOA characterization would be heavily influenced by the background organic impurities in purified water if a lower concentration is used, while if we use a higher concentration, it may be not dissolved completely. A high $\text{H}_2\text{O}_2$ concentration was used to speed up the oxidation (in the order of hours), while a low concentration of DMB (relative to $\text{H}_2\text{O}_2$ concentration) was to make the degradation rate by $^3\text{C}^*$ comparable to that by OH. In addition, 10.0 mg L$^{-1}$ ammonium sulfate was added into the reaction solution as an internal standard [24–26]. Sulfuric acid (96%, Sinopharm Chemical Reagent) was used to adjust the solution pH to ~5 (close to real values in fog and cloud waters [27]). The pH of the starting solution was checked with a pH meter before each experiment.

Oxidation experiments were conducted in a photo-reactor (BILON, Shanghai, China) equipped with a 1000 W Xe lamp as the light source [17]. The Xe lamp emits a broad UV−Vis light spectrum and those with wavelengths <290 nm were filtered out by Pyrex glass to mimic tropospheric sunlit conditions. Six 150 mL glass vials, each containing 100 mL of solution, were placed equidistantly around the lamp in a circular manner. The temperature of the reaction vessel was controlled at ~25 °C during measurements. The vials were well sealed; therefore, evaporation of precursor/product was expected to be negligible. The vials were wrapped in alumina foils and lights were turned off during dark aging experiments.

2.2. Kinetic Analysis

The concentration of DBT in each sampled solution during oxidation was immediately determined by using a high-performance liquid chromatograph (HPLC) (Waters, USA) with a UV−Vis detector (wavelength of 254 nm was selected) and a C18-WP column (4.6 × 250 mm, 5 µm). The mobile phase
was a mixture of methanol and water (w/w, 9:1; isocratic method) with a flow rate of 1 mL/min. The decay of DBT typically obeys apparent pseudo-first-order kinetics, therefore follows the equation below:

$$\frac{(\text{DBT})_t}{(\text{DBT})_0} = \exp(-kt)$$  \hspace{1cm} (1)

Here, $(\text{DBT})_0$ and $(\text{DBT})_t$ are the initial concentrations of DBT (time $= 0$) and that during oxidation (time $= t$). The rate constant ($k$) can be obtained by fitting the experimental data to Equation (1). Half-lifetimes of DBT oxidations ($t_{1/2}$) under different scenarios can then be estimated.

2.3. Optical Analysis

Organic carbon (OC) contents of reacted solutions were determined by a total organic carbon (TOC) analyzer (TOC-LCPH, Shimadzu, Japan), and the light absorption spectra were then analyzed by an ultraviolet–visible (UV–Vis) spectrophotometer (8453, Agilent, USA). The light absorption can be converted into an absorption coefficient at a wavelength $\lambda$ ($\text{Abs}_\lambda$) according to Equation (2), $A_\lambda$ refers to absorbance at wavelength $\lambda$, $A_{700}$ is used to correct the baseline shift (average value of 695 nm–705 nm) and $L$ is the optical path length of the quartz tube (1 cm). Furthermore, we calculated the mass absorption efficiency at 365 nm (MAE$_{365}$, in m$^2$ g$^{-1}$ C), as an indicator of the light-absorbing ability of the organic species (“brown carbon” (BrC)) generated during aqueous oxidation. The calculation of MAE$_{365}$ is described in Equation (3). Here, $C_{\text{mass}}$ is the OC concentration measured by the TOC analyzer.

$$\text{Abs}_\lambda = (A_\lambda - A_{700}) \cdot \frac{\ln(10)}{L}$$ \hspace{1cm} (2)

$$\text{MAE}_{365} = \frac{\text{Abs}_{365}}{C_{\text{mass}}}$$ \hspace{1cm} (3)

2.4. Chemical and Factor Analysis

Another series of OH-mediated experiments (as well as the dark control experiment) was conducted by connecting the photo-reactor with an Aerodyne soot particle aerosol mass spectrometer (SP-AMS) [30,31]. The SP-AMS enables us to monitor changes of aqSOA bulk composition in the form of 70 eV electron impact (EI) ionized mass spectrum, and concentration in near real-time (1.5 min time resolution in this work). Experimental setup, SP-AMS operation and data analysis were similar to those described previously in our work [17,32]. Briefly, the reaction vial was connected to a thin line to continuously deliver solution into a clean vial for SP-AMS measurements, and another line allowing the solution to flow back. The reacted solution was then nebulized by using an atomizer. The mist was dehumidified by a diffusion dryer, and the remaining particles were sent to the SP-AMS for analyses. The nebulization mimicked the evaporation of cloud/fog droplets in real atmosphere. Non-refractory species in the particles were evaporated at 600 °C, ionized by 70 eV EI and their mass spectra were recorded by the SP-AMS. The AMS data was processed by using the Igor-based software toolkit SQUIRREL (version 1.56D) and PIKA (version 1.15D).

The mass yields of aqSOA ($Y_{\text{SOA}}$) were estimated by using Equation (4) below:

$$Y_{\text{SOA}} = \frac{(\text{aqOrg})_{t,\text{AMS}} - (\text{aqOrg})_{0,\text{AMS}}}{(\text{Precursor})_{\text{reacted}}}$$ \hspace{1cm} (4)

Here, $(\text{aqOrg})_{t,\text{AMS}}$ and $(\text{aqOrg})_{0,\text{AMS}}$ refer to the concentrations of organic matter detected by AMS (converted to mg L$^{-1}$ with reference to known sulfate concentration) at time $t$ and time $0$, respectively. $(\text{Precursor})_{\text{reacted}}$ is the amount of consumed precursor, which can be estimated by the rate expressions determined in Section 2.2.

Moreover, we employed the positive matrix factorization (PMF) model [33] to deconvolve the mass spectral matrix of aqOrg measured by the SP-AMS. The PMF analyses aim to resolve a few
3. Results and Discussion

3.1. Precursor Degradation and Mass Yields of aqSOA

Concentrations of DBT during aqueous oxidations under different conditions are shown in Figure 1. Based on Figure 1, we calculated the pseudo-first-order rate constants (and uncertainties) and half-lives, as shown in Table 1. The OH-mediated photochemical degradation of DBT appeared to be the fastest, with a ~60% decay in 420 min, corresponding to a rate constant of $2.03 \times 10^{-3}$ min$^{-1}$ and a half-life of 342 min. Photo-oxidation by $^3\text{C*}$ was also significant, but the rate was slower (~32% degradation in 420 min, with a rate constant of $2.03 \times 10^{-3}$ min$^{-1}$ and half-life of 668 min). However, this was due to that a much smaller concentration of $^3\text{C*}$ source of DMB (15 μM) than OH source of H$_2$O$_2$ (300 μM) was used here. Direct oxidant-free photolysis was comparatively slow (~12% degradation in 420 min, with a rate constant of $0.532 \times 10^{-3}$ min$^{-1}$ and half-life of 1601 min). It is worthy to mention that aqueous oxidation of DBT could also occur under dark conditions. Two dark experiments had similar decay rates ($0.532 \times 10^{-3}$ min$^{-1}$ with DMB, and $0.602 \times 10^{-3}$ min$^{-1}$ with H$_2$O$_2$), slightly quicker than the direct photolysis rate. Such dark reaction rates were close to those determined for another PAH compound phenanthrene under the same experimental conditions in our previous work [17]. Dark reactions might be caused by oxidation with dissolved O$_2$. In the future, we will bubble the solution before dark aging experiments to remove potential oxidation by O$_2$, and investigate again the dark reactions.

![Figure 1](image_url)  
Figure 1. Concentrations of the precursor (dibenzothiophene, DBT) during aqueous oxidation under different conditions.
In Figure 2a, we present the aqSOA mass yields during photochemical oxidation of DBT by OH based on online SP-AMS measurements. The experiment lasted about 9 h, thus about two-thirds of the precursor was degraded according to the rate constant in Table 1. The mass yield was found to increase consistently during oxidation and reached ~32% till the end of illumination. It should be noted that the SP-AMS measured mass of organics at the starting point, namely (aqOrg)$_0$, was significantly larger than zero. This was due to the precursor DBT might not evaporate completely during nebulization, and some background organic impurities could remain in particle-phase as well. The initial organic mass was subtracted to calculate the aqSOA yield according to Equation (4) and it was ~20% at the precursor’s half-life. As a comparison, we also determined the corresponding aqSOA yields under dark experiment and showed the results in Figure 2b. It seemed that there was no observable increase during the first 250 min (note we prepared the solution and placed it into the reaction vessel as quickly as possible to avoid dark reactions before the test); however, the aqSOA yield increased to ~15% at the end of oxidation, when ~28% DBT was degraded based on the rate expression in Table 1. The measured yields under both light irradiation and dark conditions highlight the significance of SOA formed in aqueous phase from DBT.

![Figure 2](image_url)

**Figure 2.** Mass yields of the aqSOA formed during hydroxyl radical (OH)-mediated photochemical oxidation (a) and dark oxidation (b) (note in each plot, the first pink point is zero; the first black circle is the average of the first 7 pink points, namely the 10.5 min average value; other black circles are average values of every 12 pink points, namely the 18 min average; the error bar is one standard deviation).

### 3.2. Chemical Properties and Evolution of aqSOA

During the OH-initiated oxidation experiment, we added ammonium sulfate as an internal standard. It is necessary to check whether or not ammonium sulfate can influence the aqueous oxidation. In this work, we found that sulfate concentration remained the same throughout the course of oxidation, and no significant N-containing fragment ions were found in the aqSOA mass spectra, indicating that both ammonium and sulfate influences were negligible. In fact, ammonium sulfate was used as an internal standard in a number of previous studies [14, 24–26], and reactions between ammonium sulfate and the precursors were also not found. However, some organic precursors, such as isoprene epoxydiol [34], glycolaldehyde [37], methylglyoxal [38,39], aldehydes [40] and glyoxal [41,42],

| Precursor | Oxidant | Oxidant Concentration | Illumination | $k$ ($10^{-3}$ min$^{-1}$) | $t_{1/2}$ (min) |
|-----------|---------|-----------------------|--------------|-----------------------------|----------------|
| DBT (10µM)| H$_2$O$_2$ | 300 µM | √ | 2.03 (±0.08) | 342 |
| DBT (10µM)| H$_2$O$_2$ | 300 µM | – | 0.602 (±0.06) | 1152 |
| DBT (10µM)| DMB | 15 µM | √ | 1.03 (±0.1) | 668 |
| DBT (10µM)| DMB | 15 µM | – | 0.532 (±0.08) | 1303 |
| DBT (10µM)| – | – | √ | 0.433 (±0.04) | 1601 |

**Table 1.** Experimental conditions and the decay parameters of DBT.
could react with ammonium. Therefore, interactions between ammonium salts and different organic species in aqueous phases and influences on the SOA are yet to be investigated.

With the SP-AMS, we could obtain an ion-speciated mass spectrum of the organic species from nebulized solution (aqOrg) every 1.5 min. Examples of such mass spectra at 60 min, 300 min and 480 min are shown in Figure 3. Ion fragments with m/z up to 300 amu were fitted. Based on the mass spectra, elemental ratios of the aqOrg measured at each time step were calculated by using the method of Aiken et al [43]. It should be noted that the aqOrg mass at the starting point of reaction (time 0) was not zero; therefore, the SP-AMS determined aqOrg composition might be influenced by unevaporated precursor and background organic impurities. In this case, relative changes rather than absolute values of bulk properties of aqOrg can better reflect the evolution of aqSOA. The relative values were calculated by subtracting the absolute value at time 0 from the corresponding value at time t.

![Figure 3](image_url)

**Figure 3.** Examples of high-resolution mass spectra of the organics determined by the soot particle aerosol mass spectrometer (SP-AMS) during OH-mediated aqueous oxidation at different times: (a) 60 min, (b) 300 min, and (c) 480 min.

We illustrated the relative changes of the oxygen-to-carbon (O/C) ratio (ΔO/C) and the hydrogen-to-carbon (H/C) ratio (ΔH/C) for both photochemical and dark oxidations in Figure 4. Note the absolute O/C and H/C values of the starting aqOrg were 0.14 and 1.38, respectively; while O/C and H/C of pure DBT were 0 and 0.73 (if adjusted by the AMS calibration ratio). Therefore, the starting aqOrg did contain background organics. Nevertheless, during the course of photo-oxidation, we observed a generally continuous increase of O/C and a decrease of H/C. In the end, the increment of O/C was ~0.21, while the decrease of H/C was about -0.3. This result suggests significant oxygen-addition reactions as well as a loss of species with high H/C ratios during photochemical aging. During dark oxidation, the data was largely scattered. In general, no significant changes in O/C were found. Corresponding ΔH/C ratio showed no obvious changes on average in the first 250 min but decreased to about -0.04 in the end. Note the changes of H/C matched with those of aqSOA yield, suggesting the formation of products with relatively low H/C ratios after 250 min. The oxidation state, calculated as 2 × O/C − H/C [44], is often used as a metric of the oxidation state of OA. The relative changes of OS_C (ΔOS_C, also calculated by subtraction of absolute OS_C value at time 0 from that at time t) were presented in Figure 5 for both photochemical and dark aged aqSOA as well. In general, ΔOS_C rose significantly to ~0.8 till the end of oxidation, while during the dark aging process it had very large uncertainties, and there was no very clear change after 250 min as those in Figures 1b and 4d. Nevertheless, degradation of DBT did occur in the first 250 min (Figure 2b), yet led to no changes in aqSOA yields, O/C, H/C and
The underlying mechanism of the dark aging process cannot be well resolved by current SP-AMS measurements and should be investigated in the future.

Figure 4. Time series of changes of oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) during OH-mediated photochemical oxidation (a,b) and dark oxidation (c,d) (note in each plot, the first pink point is zero; the first black circle is the average of the first 7 pink points, namely the 10.5 min average value; other black circles are average values of every 12 pink points, namely the 18 min average; the error bar is one standard deviation).

Figure 5. Temporal variations the oxidation states (OS_c) during OH-mediated photochemical oxidation (a) and dark oxidation (b) (note in each plot, the first pink point is zero; the first black circle is the average of the first 7 pink points, namely the 10.5 min average value; other black circles are average values of every 12 pink points, namely the 18 min average; the error bar is one standard deviation).

To further elaborate the aqueous oxidation mechanisms, we performed PMF analyses on the aqOrg data matrix. Similar to our and some other previous works [14,17,36], a three-factor solution was resolved. The temporal variations of different factors during the course of photochemical oxidation are shown in Figure 6, and the corresponding factor profiles are presented in Figure 7. Since the aqOrg data matrix obtained under dark had very large uncertainties as can be seen in Figure 4c,d and
Figure 5b, PMF analysis was technically impractical and the results were non-robust, therefore they are not discussed here. In fact, the results in Figure 6 had some uncertainties as well due to the very fine time resolution of the SP-AMS measurement. Factor 1, representing the first-generation products, had the smallest \( \text{OS}_c \) (−1.23). Compared with other factors, the starting concentration of Factor 1 was not zero, indicating that this factor also contained unevaporated precursor and background organics. The time series of Factor 1 increased most rapidly among three factors in the initial stage, and reached its maximum mass concentration at ~100 min, then decreased quickly and was completely depleted at ~400 min. Factor 2, with a medium \( \text{OS}_c \) (−0.97), lagged behind Factor 1, reached its peak at ~250 min, then gradually decreased to about zero till the end of oxidation (~540 min). Such behaviors suggest there was very likely a chemical transformation of Factor 1 (first-generation products) to Factor 2 (second-generation products). Factor 3 increased continuously throughout the illumination, and it has the highest \( \text{OS}_c \) (−0.70) among the three factors. Both Factor 1 and Factor 2 initially formed could contribute to Factor 3 during the oxidation. It should be noted that PMF factors can be used to describe the average particle composition during specific time periods of the experiment [45], but they may not be directly attributed to distinct chemical groups and oxidation generations. A better way to elucidate the aqSOA evolution can be fulfilled by investigating the temporal variations of tracer compounds generated from different reaction pathways. In this regard, molecular identification and quantification of the products sampled during different stages of oxidation are needed.

3.3. Optical Properties of Illuminated Solutions

To probe whether or not aqueous oxidation can enhance the light absorption of DBT, we measured light absorption spectra of the starting pure DBT solution, and the final solutions upon direct photolysis, OH-oxidation and \( ^3\text{C}^* \)-oxidation, respectively (Figure 8a). Results show that aqueous oxidation under different conditions all can increase light absorption of the precursor. Direct illuminated solution, however, mainly led to appreciable increase in the short-wavelength ultraviolet light range (<300 nm), while illuminated solution by OH also had significant enhancement over 300 nm. A very large absorption enhancement below 350 nm was observed for \( ^3\text{C}^* \)-oxidized solution, but this was mainly due to light absorption by \( ^3\text{C}^* \) itself, rather than the aqSOA products; light enhancement above 350 nm due to products was in fact small.
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4. Conclusions and Implications

This work conducted aqueous oxidation experiments on an IVOCs model compound, DBT. We showed that DBT decayed under both OH and organic triplet excited state (3C*) oxidations. Direct light irradiation could lead to photo-degradation too but to a much lesser extent. Based on our experimental condition, DBT could degrade under dark, with rate constants even higher than that of direct photolysis, yet more tests are still needed to verify the significance of dark oxidation. In the future, second-order rate constants should be investigated for a better evaluation of the decay kinetics. The aqSOA yields of OH-initiated photo-oxidation and dark oxidation were determined to be ~32% and ~15%, respectively. The oxidation degree of aqSOA increased remarkably during OH-mediated oxidation, but insignificantly during dark aging. However, the dark oxidation might be influenced by the presence of molecular O2, and control experiments where oxygen is removed from the system...
should be investigated to reveal the detailed mechanism of dark oxidation. PMF analyses resolved three factors of the aqSOA from OH photo-oxidation. It was found that there was an initial formation of relatively less oxygenated first- and second-generation products, and they could chemically transform into highly oxygenated third-generation products in different stages of oxidation. In addition, light absorption measurements showed OH-mediated aqueous oxidation was a significant source of BrC.

Overall, our findings in this work demonstrate that aqueous oxidation of IVOCs (photochemical or dark aging) can be a source of SOA, pointing out a likely additional SOA source not previously considered. Our experiments mimicked the cloudy/foggy conditions. Similar processes may occur in wet aerosols but require further investigations. Of course, studies on more IVOCs with diverse saturation vapor pressures, water solubility as well as molecular structures, are highly needed to obtain a full understanding of the probabilities and significances of IVOCs-aqSOA. If it is important, aqueous processing of IVOCs should be implemented in atmospheric models to facilitate accurate simulation of SOA. In addition, our work shows that IVOCs-aqSOA (especially from OH-oxidation) is a source of BrC, therefore this process may play a role in aerosol light absorption, radiative forcing, as well as climate change.

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