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Formation of phthalic anhydride from nighttime oxidation of various heterocyclic volatile organic compounds: implications for wildfire smoke

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Wildfires impact global climate and public health by releasing gases and aerosols. Phthalic anhydride, a toxic chemical detected in wildfire smoke, has been primarily linked to the daytime oxidation of naphthalene and methylnaphthalenes. The recent report of phthalic anhydride in the nighttime oxidation of furan and furfural suggests that other heterocyclic volatile organic compounds (VOCs) may also act as potential precursors of phthalic anhydride through previously unrecognized pathways. This study presents the production of phthalic anhydride derived from the nighttime chemistry of 2-methylfuran, thiophenes, and methylpyrroles, with its mass fraction comprising ~0.1–0.4% of the secondary organic aerosols (SOAs) derived from these heterocyclic VOCs. Phthalic anhydride is proposed to be produced *via* the cycloaddition of heterocyclic backbones. We estimate that the nighttime oxidation of heterocyclic VOCs may contribute variably to phthalic anhydride production across different fuel types, with a ~30% contribution during wiregrass combustion. Overall, our findings highlight the need to further investigate the production of phthalic anhydride from these previously unrecognized precursors and pathways in wildfire smoke to better understand their atmospheric implications.

Environmental significance

Wildfires significantly impact the environment and public health by releasing harmful chemicals like phthalic anhydride. Phthalic anhydride is traditionally linked to the daytime oxidation of naphthalene and methylnaphthalenes. This study shows that the nighttime oxidation of heterocyclic volatile organic compounds (VOCs), including furans, thiophenes, and methylpyrroles, contributes to its production. Cycloaddition is crucial for producing phthalic anhydride from heterocyclic VOCs through the nighttime chemistry. Considering the fuel types, secondary organic aerosol yields, and mass fractions of phthalic anhydride reported in this study, the nighttime oxidation of heterocyclic VOCs may contribute to ~30% of phthalic anhydride production from wiregrass combustion. Further research is needed to fully understand the extent of these reactions and their effects on air quality and human health.

1 Introduction

Wildfires have become a rising concern of global climate and public health.[1–4] Climate change has significantly increased the frequency of heatwaves and droughts worldwide, driving the ignition and spread of wildfires.[5] The smoke emissions from wildfires can in turn exacerbate heatwaves and droughts by altering atmospheric processes, which is the "climate-fire feedback."[5,6] The smoke emissions involve a variety of gases and aerosols; once emitted into the atmosphere, these gases and aerosols can undergo atmospheric physicochemical processes so that new components, such as secondary organic aerosols (SOAs),

can be formed. The spread of wildfire smoke into urban areas is a concern of public health, since the exposure to smoke components can increase the risk of respiratory infections by aggravating bronchitis and lung disease.[7–9] To date, the assessment of wildfire climate impact and smoke-mediated health effects remains limited, partially due to an incomplete understanding of the smoke chemicals and their fate and transport.

Phthalic anhydride (2-benzofuran-1,3-dione) is a compound that can contribute to both radiative effects of wildfire aerosols[10–14] and wildfire-mediated diseases.[15,16] This compound has been observed in ambient aerosols worldwide (~200–400 ng m^{-3}),[17–21] with wildfires as one of the long-recognized emission sources.[22,23] The emission factor of phthalic anhydride in biomass burning (~20 mg kg^{-1}) is comparable with those of the typical tracers such as syringol (~20 mg kg^{-1}) and vanillin (~10 mg kg^{-1}).[24] Phthalic anhydride can undergo hydrolysis (*e.g.*, half-life of ~27 min with aerosol liquid water content of ~40%) to generate phthalic acid,[25–27] which has been used as one of the SOA surrogate species in wildfire smoke.[28] The well-known precursors of phthalic anhydride are naphthalene and methylnaphthalenes.[21,29–36]

In wildfire smoke, naphthalene and methylnaphthalenes are only small subsets of VOCs, while heterocyclic VOCs have

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a higher contribution to SOA formation.[37] Heterocyclic VOCs may account for ~30% of nitrate radical (NO_3) reactivity in wildfire plumes during the nighttime.[38] The total emission factor of heterocyclic VOCs is typically 10 times higher than that of naphthalene and methylnaphthalenes.[39] While phthalic anhydride is known to be produced *via* the daytime oxidation of naphthalene and methylnaphthalenes,[29,35,36,40] the nighttime oxidation of these naphthalene-type precursors that contain two fused benzene rings may not produce phthalic anhydride.[36,41–46] So far, only furan and furfural have been identified as nighttime precursors of phthalic anhydride.[12–14] Although wildfires can emit a broader range of heterocyclic VOCs, other heterocyclic VOCs such as methylfurans, pyrroles, and thiophenes have not been investigated for their potential to form phthalic anhydride.

In this study, we explore the potential formation of phthalic anhydride from the nighttime oxidation of a variety of heterocyclic VOCs, including pyrrole, 1-methylpyrrole, 2-methylpyrrole, thiophene, 2-methylthiophene, and 2-methylfuran (Scheme 1). The cycloaddition of heterocyclic backbones is proposed as a plausible mechanism leading to the formation of phthalic anhydride from the nighttime oxidation of heterocyclic VOCs. The contribution of heterocyclic VOCs to phthalic anhydride production during different fuel combustion scenarios was quantified and compared with that of naphthalene and methylnaphthalenes. Our findings indicated that the nighttime oxidation of heterocyclic VOCs can be a potentially important contributor to phthalic anhydride production in wildfire smoke.

2 Methods

2.1 Experimental setup

Experiments were conducted in a 10 m³ chamber made of the Teflon fluorinated ethylene propylene (FEP) film, maintained at room temperature (20–25 °C) and low relative humidity (RH <20%), and under dark conditions. Nitrogen dioxide (NO_2) and ozone (O_3) were introduced into the chamber, with the initial concentrations of ~450 ppb and ~1500 ppb, respectively. The concentration ratio of NO_2 to O_3 has been typically observed in

wildfire plumes.[47] Following the NO_2–O_3 reactions over a period of one hour, NO_3 radicals were generated at a concentration of ~22 ppb, as estimated using a kinetic model (Fig. S1).[48] For each studied VOC and NO_2/O_3 condition, 3 repeated experiments were performed.

The studied heterocyclic VOCs include pyrrole (TCI America, >99%), 1-methylpyrrole (TCI America, >99%), 2-methylpyrrole (AA Blocks, 98%), thiophene (Alfa Aesar, 99%), 2-methylthiophene (Alfa Aesar, 98%), and 2-methylfuran (Acros Organics, 99%). In each experiment, only one heterocyclic VOC was introduced into the chamber with a ~15 lpm zero gas flow through a heated jar following the NO_2–O_3 reactions. The initial concentration of heterocyclic VOCs was ~200 ppb. In each experiment, the SOA mass concentration reached a stable plateau within 3 hours. Post the plateau, the generated SOAs were collected onto the polytetrafluoroethylene (PTFE) membrane filters (46.2 mm, 2.0 μm, Tisch Scientific) with a flow rate of 20 lpm for 1.5 hours. The SOA filter samples were then extracted with acetonitrile (ACN), an aprotic polar solvent, to minimize potential solvent artifacts that might alter the SOA chemical composition during the extraction processes.[12] The extraction efficiency of ACN may vary across different compounds; for example, by measuring 2-nitropyrrole, 2-nitrothiophene, and phthalic anhydride, which are representative compounds found in pyrrole-, thiophene-, and furan-derived SOA, respectively,[12,49] we found different ACN-extraction recoveries of 98.4%, 73.0%, and 60.2%, respectively. While the chamber experiments may have certain limitations compared to the actual atmosphere,[50] our chamber conditions can systematically generate SOA samples from the nighttime oxidation of heterocyclic VOCs and facilitate the characterization of phthalic anhydride. A more detailed description of the experimental procedure has been provided in our previous work.[12,13,48]

2.2 Instrumentation

Phthalic anhydride was identified using gas chromatography-electron ionization mass spectrometry (GC/EI-MS) on an Agilent 6890 GC with a Restek Rtx-VMS polar column (30 m ×
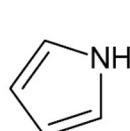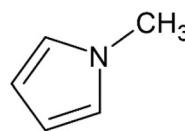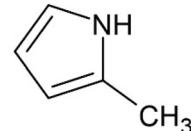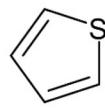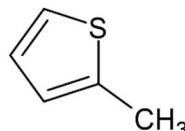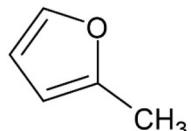
Scheme 1 The structures of six heterocyclic VOCs examined in this study for phthalic anhydride formation.

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0.25 mm i.d., 1.4 μm film thickness) and a 5975 Inert XL MSD. Helium was used as the carrier gas at a constant flow rate of 2.0 mL min^{-1}. The GC temperature program started at 35 °C for 1 minute, then increased to 250 °C at a rate of 11 °C min^{-1}, and was held at 250 °C for 4 minutes. Full scans of mass spectrometric detection were performed over a range of m/z 15–400, with the ion source and mass quadrupole set at 230 °C and 150 °C, respectively. The injection was performed in splitless mode with 1 μL of the sample solution at 250 °C. The identification was based on a spectral match with the NIST library. We used an authentic chemical standard (Sigma-Aldrich, ≥99%) to verify the chemical identity of phthalic anhydride in the SOA samples.

During the experiments, we avoided using plastic containers due to the widespread presence of phthalic acid esters (*i.e.*, phthalates) in plastics, as their thermal decomposition in the GC/EI-MS system could potentially generate phthalic anhydride. While accidental contamination with phthalates could still occur, phthalic anhydride was not detected in the blank samples, since the temperature in our GC/EI-MS system was insufficient to effectively decompose phthalic acid esters.[51,52]

Quantification of phthalic anhydride was performed using the extracted ion chromatogram (EIC) of m/z 148. The mass fractions (MFs) of phthalic anhydride were calculated using eqn (1):

$$MF = \frac{m_{\text{phthalic anhydride}}}{m_{\text{SOA}}} \tag{1}$$

Here, $m_{\text{phthalic anhydride}}$ is the estimated mass of phthalic anhydride in the ACN-extracted samples, and m_{SOA} is the total SOA mass of the ACN-extracted samples. The values of MF for the investigated VOCs as well as those for naphthalene and methylnaphthalenes are shown in Fig. S2. The production factor (PF) of phthalic anhydride for a specific VOC from wildfire emissions was further calculated from eqn (2):

$$PF = EF_{\text{VOC}} \times Y_{\text{SOA}} \times MF \tag{2}$$

EF_{VOC} is the emission factor of a VOC, and Y_{SOA} is the SOA yield of the VOC. The values of EF_{VOC} and Y_{SOA} have been reported previously.[12,31,39,48] Notably, owing to the potential presence of trace amounts of water in both the dry-condition SOA and the ACN-extracted samples, hydrolysis of phthalic anhydride could occur and affect the PF of phthalic anhydride.[53] The high concentration of VOCs and NO$_3$ radicals in chamber experiments may also potentially influence the PF of phthalic anhydride. Thus, the PF estimated in this study may serve as a semi-quantitative approach to clarify the relative importance of naphthalene, methylnaphthalenes, and heterocyclic VOCs in the production of phthalic anhydride during wildfire scenarios.

The number concentration and size distribution of the generated SOA were measured by using a scanning electrical mobility spectrometer (SEMS, Brechtel Manufacturing Inc.). SOA mass was estimated by using a mini-aerosol mass spectrometer coupled with a compact time-of-flight mass spectrometer (mAMS, Aerodyne Research Inc.). The gas-phase intermediates were measured by high-resolution time-of-flight chemical ion mass spectrometry (HR-ToF-CIMS, Aerodyne

Research Inc.) with protonated water clusters (H$_2$O)$_n$H$^+$ as the reagent ions. The ion-molecule collisions transfer the proton from (H$_2$O)$_n$H$^+$ to analyte molecules (M), forming proton-adduct ions [M + H]$^+$. Details of the instrumental parameters and the measured SOA size distribution were reported previously.[12]

3 Results and discussion

3.1 Characterization of phthalic anhydride

This study identified the presence of phthalic anhydride in SOA samples derived from both 1-methylpyrrole and 2-methyl-pyrrole (Fig. 1A and B) but not in the pyrrole-derived SOA. Real-time chemical analysis of C$_6$H$_4$$^+$ by the mAMS (the surrogate ion tracer of phthalic anhydride)[54] also showed this phenomenon (Fig. S3). These observations suggest that the methyl groups may play a critical role in the production of phthalic anhydride from methylpyrroles. Previous studies have reported that methylpyrroles can produce nitrogen-containing carbonyl compounds,[14,48] where the heteroatom (nitrogen) is preserved. However, since phthalic anhydride is a nitrogen-free product, its production would require the heteroatom of methylpyrroles to be released during nighttime oxidation processes.

Our results may also support the release of the heteroatom from the thiophenes, since phthalic anhydride was detected in both thiophene- and 2-methylthiophene-derived SOAs (Fig. 1C and D). The release of sulfur may account for ∼29% of thiophene decay during nighttime oxidation,[55] while the rest may transform into backbone-preserved products (*e.g.*, nitrothiophenes) and sulfur-containing oxygenated products (*e.g.*, organosulfates and sulfonates).[49,56] Our results also revealed that 2-methylfuran, in addition to furan and furfural,[12] can produce phthalic anhydride *via* nighttime oxidation (Fig. 1E). The aerosol-phase mass fraction of phthalic anhydride in all the heterocyclic VOC-derived SOAs is ∼0.1–0.4%, which is lower than that of the naphthalene- and methylnaphthalene-derived SOAs from OH oxidation (∼0.4–1.8%) (Fig. S2).[12,31] The identity of phthalic anhydride was confirmed with the authentic chemical standard (Fig. 1F) with identical EI mass spectra compared to the SOA samples.

3.2 Cycloaddition mechanisms of phthalic anhydride formation

The heterocyclic backbones likely undergo a cycloaddition reaction to form the bicyclic structure of phthalic anhydride. In general, the cycloaddition occurs between a diene and a dienophile. In the case of the heterocyclic VOCs, the furan backbone can act as dienes due to its weak aromaticity,[57] while its oxidation product, maleic anhydride, can act as a strong dienophile. While the cycloaddition of furan and maleic anhydride is known to proceed at room temperature in the condensed phase,[58–60] analogous reactions may also occur in wildfire-affected atmospheres. When vaporized under elevated temperatures, these molecules could undergo cycloaddition upon collision and contribute to the formation of phthalic anhydride in wildfire emissions.
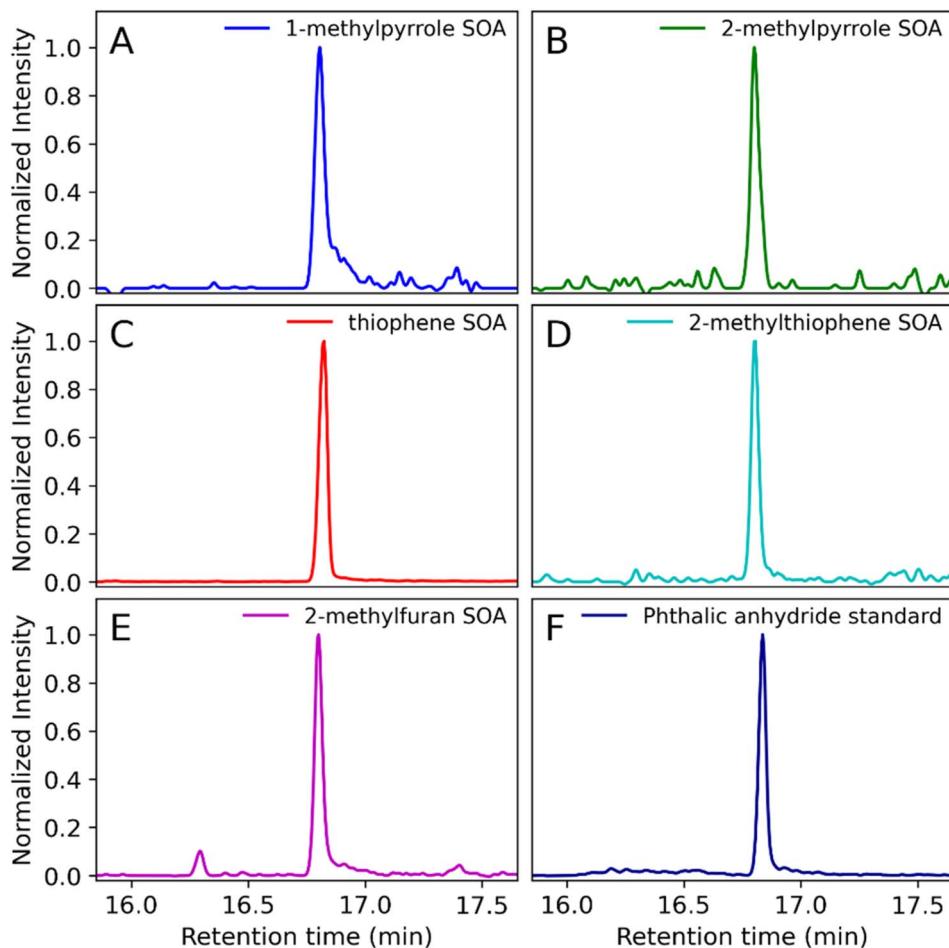
Fig. 1 EICs of m/z 148 from GC/EI-MS analysis of phthalic anhydride in (A) 1-methylpyrrole SOA, (B) 2-methylpyrrole SOA, (C) thiophene SOA, (D) 2-methylthiophene SOA, (E) 2-methylfuran SOA, and (F) the authentic standard of phthalic anhydride.

Similarly, the nighttime oxidation of 2-methylfuran and furfural may produce phthalic anhydride through the cycloaddition between the 2-furyl radical and maleic anhydride. The NO_3-initiated oxidation of 2-methylfuran can first produce furfural (Fig. S4),[61] with subsequent reactions including NO_3-induced hydrogen abstraction at the aldehyde group or NO_3–O_2 addition to the furfural backbone. Al Ali *et al.* reported that the NO_3-induced hydrogen abstraction can lead to 2-furyl radical formation (Fig. 2A),[61] while Colmenar *et al.* proposed that the NO_3–O_2 addition to the furfural backbone can lead to its decomposition into maleic anhydride (Fig. 2A and S4).[62] The cycloaddition between the 2-furyl radical and maleic anhydride may proceed with hydrogen atom migration,[63] generating a bicyclic alkoxy radical. The bicyclic alkoxy radical could undergo hydrogen abstraction by molecular oxygen, allowing the two isolated C=C double bonds on the ring to form a more stable conjugated system. Subsequently, the alkoxy group may react with a NO_2 molecule, forming a nitrate group (ONO_2) on the ring. This ONO_2 group can then be eliminated as a NO_3 radical, ultimately yielding phthalic anhydride (Fig. 2B). This proposed pathway is similar to the decomposition of the NO_3-naphthalene adduct, wherein the NO_3 radical can add to the aromatic ring to form an ONO_2 group, and conversely, the ONO_2

group can be eliminated to regenerate a NO_3 radical.[41,44] Since both naphthalene and phthalic anhydride are bicyclic aromatic compounds, NO_2 addition followed by NO_3 elimination may serve as a plausible mechanism for oxygen elimination and the formation of phthalic anhydride.

Cycloaddition reactions may also plausibly occur in the aerosol phase, as suggested by collective evidence in previous studies.[61,63–65] The SOA constituents derived from the nighttime oxidation of 2-methylfuran involve a variety of dimers and oligomers.[61] Many of these dimers and oligomers retain multiple furan backbones, and some may also exist as organic peroxides.[61] The unstable organic peroxides may decompose to generate the organic hydroperoxide and a furyl cation.[64,65] The organic hydroperoxide may further decompose to generate carbonyls or hemiacetals,[53,66] while the furyl cation may subsequently react with another furan backbone on a neighboring oligomer molecule, leading to the formation of phthalic anhydride (Fig. S5). Although the detailed stepwise mechanism remains unclear, the abundance of furan backbones in SOA constituents may play a considerable role in phthalic anhydride production.

The cycloaddition pathway in nighttime chemistry is overall different from the formation mechanisms of phthalic anhydride in the daytime. Since the naphthalene backbone is already
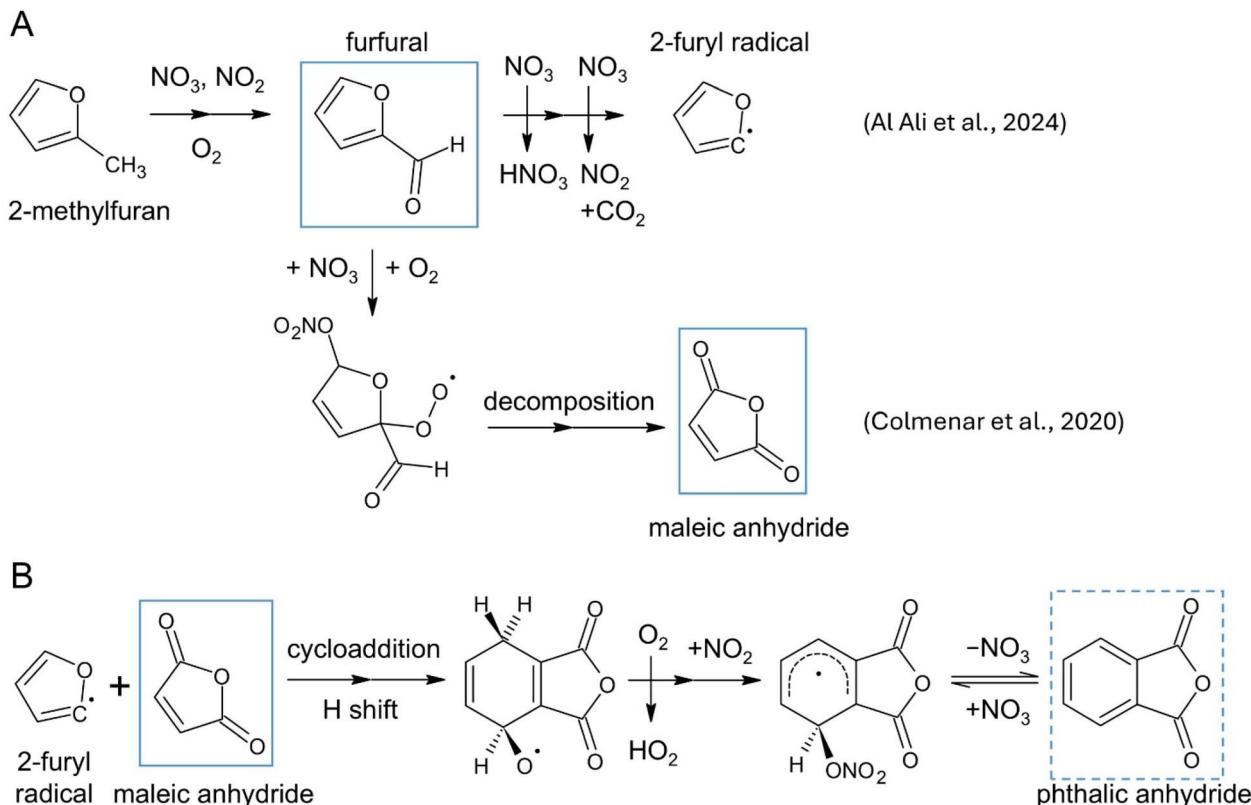
Fig. 2 Proposed formation mechanism of (A) gas–phase intermediates and (B) phthalic anhydride formed through the cycloaddition of the 2-furyl radical with maleic anhydride. The boxed species shown in the reactions were detected in the gas phase by protonated water cluster CIMS (with solid lines) and in the aerosol phase by GC/EI-MS (with dashed lines) in this study.

a bicyclic structure, photooxidation of naphthalene and methylnaphthalenes can directly produce phthalic anhydride without the collision of any organic backbones.[29,35,36,40] However, this process was not reported in NO_3-initiated oxidation of naphthalene and methylnaphthalenes,[36,41–46] suggesting that the NO_3-initiated oxidation may not effectively transform the naphthalene backbones into phthalic anhydride.

In addition, the cycloaddition pathways of methylpyrroles, thiophene, and 2-methylthiophene may not proceed from the furan-type cycloaddition at room temperature.[58] In this case, the formation of phthalic anhydride could proceed from other cycloaddition mechanisms at room temperature without catalysis.[67–70] It is also worth noting that although nighttime oxidation of pyrrole may not generate phthalic anhydride, it can produce phthalimide derivatives,[71] which share the same backbone as phthalic anhydride but differ in the heteroatom. While more in-depth studies are required to clarify the detailed mechanisms of bicyclic product formation, our study demonstrates that heterocyclic VOCs are precursors for nighttime production of phthalic anhydride.

3.3 Phthalic anhydride production in daytime and nighttime

Phthalic anhydride formation has been well demonstrated in the OH-initiated oxidation of naphthalene and

methylnaphthalenes.[29,35,36,40] We compared the production of phthalic anhydride from heterocyclic VOCs with this well-known pathway to highlight the potential significance of the nighttime oxidation processes. In our calculations, we assumed that the SOA yields and phthalic anhydride mass fractions measured in chamber experiments are reasonably representative of real wildfire smoke conditions. We also assumed that SOA formation from individual VOCs may occur independently and thus did not account for interactions involving multiple VOCs. Rather than providing a comprehensive assessment of all oxidation pathways, our goal is to demonstrate that the nighttime oxidation of heterocyclic VOCs makes non-negligible contributions to phthalic anhydride formation, which opens new perspectives on analyzing SOA formation from wildfire emissions.

The PFs of phthalic anhydride from different VOCs with different fuel types are shown in Table 1. Naphthalene is the largest contributor to phthalic anhydride production across all the fuel types, while methylnaphthalenes are major contributors in most fuels, except for wiregrass. Furans, including furan, furfural, and 2-methylfuran, generally contribute similarly to phthalic anhydride production across different fuels. In the combustion of rice straw and wiregrass, furfural is the primary contributor among heterocyclic VOCs, whereas 2-methylfuran dominates as the main contributor for other fuels (Fig. S6). While the contribution of 1-methylpyrrole to phthalic anhydride

Table 1 The estimated production factors of phthalic anhydride from the NO_3-initiated oxidation of heterocyclic VOCs and the OH-initiated oxidation of naphthalene and methylnaphthalenes among different types of fuels in wildfires

| VOCs | Production factors ($\times 10^{-4}$ g kg^{-1}) | | | | | |
	Black spruce	Ponderosa pine	Giant cutgrass	Wiregrass	Rice straw	Indonesian peat
Furan	10.79	14.55	1.03	3.05	3.99	14.55
Furfural	9.69	20.30	0.97	7.38	9.23	16.14
2-Methylfuran	14.80	23.90	0.98	5.12	7.51	26.18
1-Methylpyrrole	7.42	14.16	1.55	2.76	3.84	20.90
2-Methylpyrrole	2.33	7.14	1.10	0.00	3.24	8.57
Thiophene	1.13	1.45	2.17	0.00	0.82	3.15
2-Methylthiophene	0.00	0.68	0.00	0.00	0.28	2.39
Naphthalene	527.38	565.51	444.78	30.50	165.20	292.28
1-Methylnaphthalene	39.71	48.87	15.27	0.00	16.80	103.85
2-Methylnaphthalene	33.60	38.40	13.20	5.76	16.56	84.00
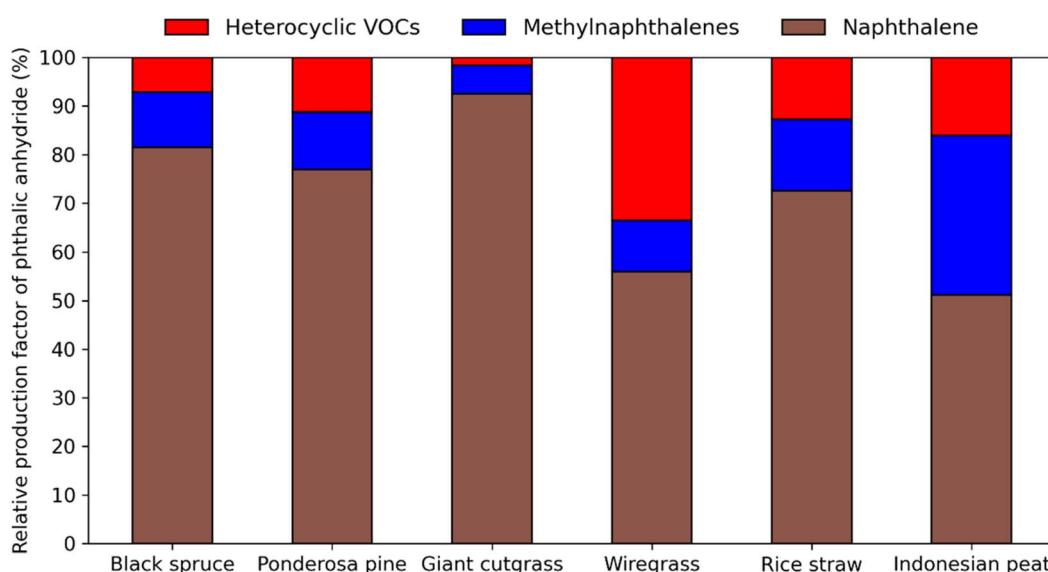
Fig. 3 Relative production factor of phthalic anhydride from daytime and nighttime oxidation of various VOCs emitted by different fuels in wildfires.

production is comparable to that of furan or furfural, thiophene, 2-methylthiophene, and 2-methylpyrrole, however, typically contribute less to the production of phthalic anhydride. The relative production factor is primarily driven by naphthalene oxidation pathways, while the contribution of methylnaphthalenes and heterocyclic VOCs can vary depending on the biomass source (Fig. 3). These results emphasize the large influence of fuel types on the variability of phthalic anhydride production.

Wiregrass combustion plays a crucial role in phthalic anhydride production through the nighttime oxidation of heterocyclic VOCs. Heterocyclic VOCs contribute approximately 30% to the total phthalic anhydride production during wiregrass combustion (Fig. 3). The combined contribution of furans (i.e., furan, furfural, and 2-methylfuran) to phthalic anhydride production is about three times greater than that of methylnaphthalenes in wiregrass combustion. In contrast, other fuels predominantly show the production of phthalic anhydride driven by naphthalene. For instance, in rice straw combustion,

the contributions from heterocyclic VOCs and methylnaphthalenes to phthalic anhydride production are comparable, with naphthalene accounting for over 70% of the total production. These differences suggest the unique pattern of phthalic anhydride formation in the smoke from wiregrass combustion. Our findings highlight the importance of considering the fuel-specific production behavior of phthalic anhydride for better constraining its role in wildfire smoke.

4 Conclusions

Our study demonstrates that heterocyclic VOCs are precursors for the formation of phthalic anhydride under nighttime conditions, with the process likely mediated via the cycloaddition mechanism and influenced by fuel types. Since previous studies have shown that the NO_3-initiated oxidation of naphthalene and methylnaphthalenes does not produce phthalic anhydride,[36,41–46] our study introduces new mechanistic insights

into phthalic anhydride formation in biomass burning plumes. Specifically, wiregrass combustion produces phthalic anhydride through pathways that heavily rely on both daytime oxidation of naphthalene and nighttime oxidation of heterocyclic VOCs. The growing frequency of wildfires driven by climate change may lead to a rise in wiregrass abundance, which in turn increases the risk of more intense wildfires.[72] This positive feedback loop could reduce tree populations and alter the composition of wildfire smoke, with a greater contribution from wiregrass combustion. In this context, the role of nighttime oxidation of heterocyclic VOCs in phthalic anhydride production could become increasingly important.

In addition, the cycloaddition mechanism is likely to be prevalent in wildfire smoke, as the 2-furyl radical and maleic anhydride can be derived from various VOCs. The 2-furyl radical can be produced from furan decomposition at high temperatures,[61,73–75] while maleic anhydride can be produced from conjugated dicarbonyls (*e.g.*, 2-butenedial and 4-oxo-2-pentenal[76,77]), which are the products from toluene and xylenes.[78,79] Moreover, the cycloaddition of thiophene with maleic anhydride may be facilitated by the high temperature of nearby wildfires.[58,80] These mechanistic insights underscore the importance of maleic anhydride as a tentative key intermediate in the phthalic anhydride production. Given that maleic anhydride can persist in wildfire plumes for several days[81] and is produced at a significant rate (~50 mg per kg of fuel),[24] the cycloaddition mechanism could play a substantial role in the formation of phthalic anhydride in wildfire smoke.

Furthermore, the new precursors of phthalic anhydride may interfere with the source apportionment of its hydrolysis product, phthalic acid. Phthalic acid has been extensively used as a molecular marker of anthropogenic SOAs,[17,82–87] and highlighted as a critical component in atmospheric aerosols that require better understanding.[88] While phthalic acid in urban aerosols has been mainly attributed to anthropogenic sources,[89] wildfire events can significantly increase the phthalic acid concentration (up to 10 times) in the nearby urban atmosphere.[90] The source apportionment of phthalic acid in the wildfire smoke was solely associated with naphthalene and methylnaphthalenes,[28] which may need to be revisited to better clarify the evolution of complex air pollution and guide the strategies of improving air quality. Notably, this study does not rule out the possibility that the OH-initiated oxidation of heterocyclic VOCs may also produce key intermediates (*e.g.*, maleic anhydride) for phthalic anhydride formation,[62,91] and such processes could potentially serve as additional routes contributing to phthalic anhydride formation alongside those from the OH-initiated oxidation of naphthalene and methylnaphthalenes. Overall, our study demonstrates the importance of understanding both daytime and nighttime precursors of toxic pollutants in wildfire smoke as well as their potential impact on human health in the context of climate change.

Author contributions

Kunpeng Chen: conceptualization, formal analysis, investigation, visualization, writing – original draft. Raphael Mayorga: investigation, formal analysis, writing – review & editing. Linhui Tian: investigation, formal analysis, writing – review & editing. Roya Bahreini: funding acquisition, writing – review & editing. Haofei Zhang: funding acquisition, supervision, writing – review & editing. Ying-Hsuan Lin: conceptualization, funding acquisition, project administration, supervision, writing – review & editing.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

All data supporting this article have been included as part of the main text or SI.

Supplementary information is available. Fig. S1 shows the NO$_3$ radical profiles obtained using a kinetic box model. Fig. S2 shows the quantification of phthalic anhydride in SOA samples by GC/EI-MS. Fig. S3 and S4 show the time series data for ion signals measured by mAMS and HR-ToF-CIMS, respectively. See DOI: **https://doi.org/10.1039/d5ea00065c**.

Acknowledgements

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