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Haoyu Jiang and Luca Carena contributed equally to this work.

Key Points:

- Laser flash photolysis demonstrate that excited triplets of polycyclic aromatic hydrocarbons initiate degradation of dimethylsulfoxide
- A number of organic sulfur (OS) compounds that are known secondary organic aerosol precursors are formed
- Theoretical calculations support the mechanistic pathways describing the formation of OS compounds

Supporting Information:

Supporting Information may be found in the online version of this article.

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Photosensitized Degradation of DMSO Initiated by PAHs at the Air-Water Interface, as an Alternative Source of Organic Sulfur Compounds to the Atmosphere

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Abstract The photochemical reactions of organic compounds at the water surface lead to the formation of gas-phase molecules that may contribute to new particle formation in the atmosphere. Here, we observe the formation of organic sulfur (OS) compounds that are known secondary organic aerosol (SOA) precursors, upon irradiation of aqueous solutions containing typical polycyclic aromatic hydrocarbons (PAHs) such as pyrene, fluoranthene, and phenanthrene as well as dimethylsulfoxide (DMSO). The reactivity between the excited triplet states of PAHs (³PAHs*) and DMSO was determined by transient absorption spectroscopy and a tentative reaction mechanism for DMSO degradation was proposed, supported by theoretical calculations of the reaction Gibbs energies. In all cases, we observe rapid formation of methanesulfonic acid, methanesulfinic acid, methylsulfonylmethane, ethyl methanesulfonate, hydroxymethanesulfonic acid, and 2-hydroxyethanesulfonic acid by use of novel membrane inlet-single photon ionization-time of flight mass spectrometry. These results suggest that ubiquitous PAHs and DMSO at the sea surface may represent an alternative source of OS compounds during daytime, through photochemical processes that should be considered in future models to better represent the SOA formation processes in the atmosphere.

1. Introduction

As an important interfacial region between the atmosphere and the sea, the sea surface microlayer (SML) is enriched with organic and inorganic compounds compared to bulk water. Although SML has a thickness of only 1 μm to 1 mm at the sea's uppermost surface, which persists at wind speeds of up to 10 m s^{-1} (Wurl et al., 2011), it plays a crucial role in the enhanced photodegradation of substances because it is illuminated by an intense Ultraviolet-Visible (UV-VIS) fraction of sunlight (Vasilkov et al., 2001). Pollutants released from anthropogenic activities will influence the photochemical processes at the SML, and thereby change the air-sea interaction, with still poorly known consequences for coastal air pollution and biogeochemical cycle systems.

Polycyclic aromatic hydrocarbons (PAHs), a typical group of primary pollutants produced by biomass burning, coal combustion, and petroleum combustion are enriched at the surface of both seawater and freshwater via atmospheric deposition (Lammel, 2015). Two to five-ring PAHs at the sea surface mainly come from the interfacial diffusive exchange between the upper sea level and lower marine atmosphere (González-Gaya et al., 2019). Substantial concentrations of PAHs have been detected to accumulate at the SML, with even 200–400 times enhanced concentrations compared to the water bulk (Chen et al., 2006; Cincinelli et al., 2001; Hardy et al., 1990; Lohmann et al., 2009; Seidel et al., 2017; Vácha et al., 2006). At the sea surface, phenanthrene (PHE), fluoranthene (FLA), and pyrene (PYR) are the most commonly detected PAHs,

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which accounted for 14%–96% of the total amount of detected PAHs at the water surface (Li et al., 2017; Ma et al., 2013; Pérez-Carrera et al., 2007; Valavanidis et al., 2008). PAH concentrations at the water surface varied in different global areas, being up to $55 \mu\text{g L}^{-1}$ (300 nM) in the surface water of some creeks and ranging between 9 and $15 \mu\text{g L}^{-1}$ (47–81 nM) in SML in Nigeria (Benson et al., 2014; Nwineewii & Marcus, 2015).

Dimethylsulfoxide (DMSO) is a ubiquitous organic sulfur (OS) compound in the ocean, and it is one of the main compounds of the marine sulfur cycle (Lee et al., 1999). The main sources of DMSO in the ocean are the degradation of phytoplankton (Andreae, 1980), photo-induced oxidation of dimethyl sulfide (DMS; Barnes et al., 2006; Brimblecombe & Shooter, 1986), microbial oxidation of DMS (Zhang et al., 1991), and deposition from the atmosphere due to DMSO's high Henry's Law coefficient ($\approx 10^7 \text{ M atm}^{-1}$) and mass accommodation coefficient (0.10) (Davidovits et al., 2006; González-Gaya et al., 2016; Legrand et al., 2001). Surface tension measurements of aqueous DMSO solutions have indicated that the number densities of this compound at the air-water interface are higher than the concentrations in the water bulk, suggesting surface partitioning effects (Allen et al., 1999). Because sunlight intensity is also strongest in the water surface microlayer, the photosensitized chemistry of PAHs/DMSO should be enhanced at the air-water interface compared to the bulk. In the aqueous phase of marine aerosol deliquescent particles, 78% of DMS is oxidized by ozone (O_3) to DMSO. Moreover, DMSO exhibits concentrations varying in the range of $1.5\text{--}532 \text{ nmol L}^{-1}$ from the open ocean to the coastal zones. Although it mostly occurs in the ocean, DMSO has also been detected in rivers ($<2.5\text{--}210 \text{ nmol L}^{-1}$) (Andreae, 1980), lakes (up to 180 nmol L^{-1}) (Richards et al., 1994), rainwater ($2\text{--}4 \text{ nmol L}^{-1}$) (Ridgeway et al., 1992), and in aerosols ($69\text{--}125 \text{ nmol L}^{-1}$) (Harvey & Lang, 1986).

One of the main degradation pathways of DMSO is considered to be the microbial consumption or reduction to DMS (Lee et al., 1999), as well as the reaction with hydroxyl radicals (OH). The latter reaction yields methanesulfonic acid ($\text{CH}_3\text{SO}_2\text{H}$), which in turn may react again with OH radicals to form methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) (Librando et al., 2004). Considering the presence of OH radicals in lakes and sea-surface water, and the occurrence of DMSO at concentrations that are 1–2 orders of magnitude higher than those of DMS, the photochemical oxidation of DMSO may be a relatively more important process than the photooxidation of DMS (Lee et al., 1999).

Detailed studies, focused on the photochemical processes that occur at the water surface are necessary to improve our understanding of the interactions between the air-water interface and the atmosphere. The reactions of ozone (O_3) and hydroxyl radicals (OH) with aromatic compounds at the air-water interface can be a competitive chemical process to the photosensitized reactions of aromatic compounds (Alvarez et al., 2012; Jammoul et al., 2009; Rana & Guzman, 2020; Reeser et al., 2009; Wang et al., 2021). The heterogeneous oxidation of PAHs of atmospheric relevance has been extensively investigated in past years (Donaldson et al., 2009; Monge et al., 2010; Styler et al., 2011; Zhou et al., 2019). However, the structure of gas-phase compounds formed during PAH photodegradation and the reaction pathways leading to their formation are still unclear. Recently, it has been shown that the excited triplet state of fluorene can initiate the degradation of DMSO at the air-water interface and produce OS compounds in the atmosphere (Mekic et al., 2020a, 2020b).

In this study, to our best knowledge, for the first time we found that the detected OS compounds formed by the photochemical degradation of DMSO initiated by sunlight-excited PAH molecules (PHE, FLA, and PYR) are known precursors of secondary organic aerosols (SOAs) in the atmosphere. The gas-phase products formed by light-induced degradation of PAHs/DMSO were assessed by membrane inlet single photon ionization (SPI) time of flight mass spectrometry (MI-SPI-TOFMS) (Mekic et al., 2020a; Zhang et al., 2019). We suggest a tentative reaction pathway of the formed OS compounds during photosensitized degradation of DMSO initiated by excited triplets of PAHs, which is supported by theoretical calculations of the reaction Gibbs energies.

2. Experimental

2.1. Photoreactor

A jacketed double-wall rectangular ($5 \times 5 \times 2 \text{ cm}$) photoreactor made up of borosilicate glass was designed to simulate calm water covered by an organic film made up of DMSO and PAHs. The photoreactor was thermostated ($T = 293 \text{ K}$) by a thermostatic bath (LAUDA ECO RE 630 GECO, Germany). Details of the

reactor were provided in our previous papers (Mekic et al., 2020a, 2020b); hence, only a brief description is given here. An air flow of 150 mL min^{-1} ($0\text{--}500 \text{ mL min}^{-1}$ HORIBA METRON mass flow controller; accuracy, $\pm 1\%$) was drifting through the photoreactor above the water surface, to carry the gas-phase product compounds through a 0.5-m long Teflon tube (4 mm I.D.) into the MI-SPI-TOFMS. At the exit of the reactor, air flow of 750 mL min^{-1} ($0\text{--}1 \text{ L min}^{-1}$ HORIBA METRON mass flow controller; accuracy, $\pm 1\%$) was added to obtain the required 0.9 L min^{-1} flow for MI-SPI-TOFMS.

The three compounds considered in this study, PHE, FLA, and PYR (Sigma-Aldrich, China) with concentrations of $1 \times 10^{-4} \text{ mol L}^{-1}$ were dissolved separately in mixtures of DMSO and ultrapure water (10:90 v/v), corresponding to a DMSO concentration of 1.4 mol L^{-1} (Mekic et al., 2020b). Such high concentrations of the organic cosolvent have been used previously to evaluate the influence of the solvent on PAHs photolysis (Donaldson et al., 2009; Grossman et al., 2016; Librando et al., 2014). The reactor was filled with 10 mL of freshly prepared solution. A Xenon lamp (Xe, 500 W) was used to irradiate the solutions containing PAHs and DMSO. The spectral irradiance of the Xe lamp was measured with a calibrated spectroradiometer (Ocean Optics, USA) equipped with a linear-array CCD detector and compared to sunlight radiation (Mekic et al., 2020a, 2020b). All experiments were performed in duplicate.

2.2. Triplet State Formation and Reactivity With DMSO

The triplet state formation of selected PAHs and reactivity with DMSO in the solution was investigated using transient absorption spectroscopy. A nanosecond laser flash photolysis setup and absorption equipment were used as previously reported (Mekic et al., 2020a). For this work, a $2 \times 10^{-3} \text{ mol L}^{-1}$ stock solution of each PAH was prepared in pure DMSO and mixed with an appropriate amount of DMSO and water just before the experiment. The triplet state reactivity was investigated by selecting one specific wavelength for each PAH and following the decay of triplet absorption as a function of time. The fit of data with a mono-exponential decay gives the pseudo-first order decay constant at the preselected wavelength (k' (s^{-1})). The second-order rate constant between $^3\text{PAH}^*$ and DMSO (k'' ($\text{M}^{-1} \text{ s}^{-1}$)) was determined from the slope of the linear fit of k' versus DMSO concentration. The error was determined as 95% confidence interval of this fit.

2.3. Membrane Inlet Single Photon Ionization Time of Flight Mass Spectrometry

An MI-SPI-TOFMS instrument (SPIMS 3000, Guangzhou Hexin Instrument Co., Ltd., China) was used to detect the gas-phase compounds formed during the photodegradation of DMSO, initiated by irradiated PAHs. A polydimethylsiloxane (thickness 0.61 mm, Technical Products Inc., USA) membrane was used in the injector of the TOF-MS (Zhang et al., 2019). The ionization of the compounds was performed by vacuum ultraviolet (VUV) light emitted by a deuterium (D_2) lamp (Hamamatsu, Japan). SPI, with energy of 10.8 eV was used as a “soft” ionization method to detect the gas-phase compounds.

The sampled VOCs are exposed to VUV radiation in the SPI source, where they get efficiently ionized if their ionization energy is lower than the VUV photon energy. Due to the low transfer of excess energy, SPI is a soft ionization technique that is characterized by high molecular ion yield and low degree of fragmentation (Hanley & Zimmermann, 2009; Hua et al., 2011; Wurl et al., 2011). The mass of the product ion equals the analyte mass, greatly facilitating the interpretation of the mass spectrum of complex VOCs mixtures (Deng et al., 2021; Mekic et al., 2020b).

The TOF mass analyzer consists of a double-pulsed acceleration region, a field-free drift tube, a reflector, and an ion detector. The length of the double-pulsed acceleration region is 52 mm. The field-free drift region is 300 mm long and held at an electric field potential of 2,200 V, where the ions drift at a constant speed. The reflector is separated into two stages with different field strengths by a grid at earth electric potential. The first and second stages are 90 and 35 mm long, respectively. Two micro channel plates assembled with chevron-type are used as an ion detector. A 350 MHz Analog to Digital Converter is used for measuring and recording the output current signal from micro channel plates. The detection limit of TOF-MS is around 1 ppb for most trace gases. Here, the time resolution of SPI-MS was set to 5 s.

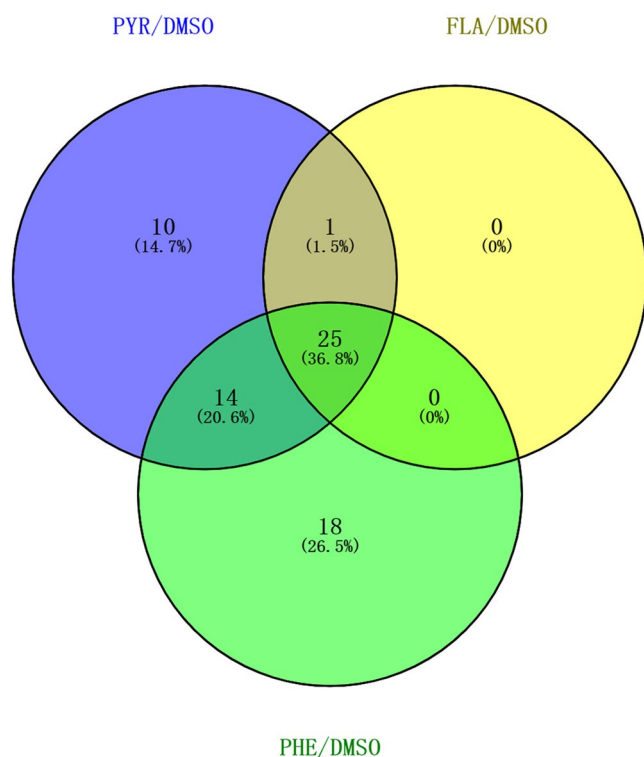


Figure 1. Venn diagram of the detected molecular formulas for the photodegradation of polycyclic aromatic hydrocarbons/dimethylsulfoxide.

The raw data were processed with commercial software (SPI-MS 3000 V1.0.1.2.0, Guangzhou Hexin Instrument Co., Ltd., China), where the selected Gauss peaks above a preset threshold are smoothed with a given average number.

2.4. Theoretical Calculations

The proposed structures of all the tentatively identified gaseous compounds are based on reasonable inferred elemental compositions for a single mass, based on assumptions made by using NIST Chemistry Web-Book (<https://webbook.nist.gov/chemistry/mw-ser/>) and the database of MI-SPI-TOFMS. The possibilities should be considered for the existence of isomers and of different molecular formulas with the same molecular weight. Theoretical calculations were performed to gain some insights into the transformation pathways of ³PHE*, ³PYR*, ³FLA*, and DMSO in the gas phase.

All calculations presented in this work were performed with Gaussian 16W package (Frisch et al., 2016). The level of B3LYP/6-311G (d,p) was applied for geometry optimizations and frequency calculations for all molecules involved and proposed in the reaction scheme (Binning & Curtiss, 1990; McLean & Chandler, 1980). There were no imaginary frequencies for all molecules optimized. Single-point energy calculations were performed at a more expensive level, the M06-2X/Def2-TZVP level (Weigend, 2006; Weigend & Ahlrichs, 2005; Zhao & Truhlar, 2008). The existence of possible geometric isomers and conformers for each species was considered and investigated, and those with lowest calculated Gibbs free energies were selected. Molecular oxygen (O₂), carbon dioxide (CO₂), and water molecules (H₂O) were placed as reactants or products (if need-

ed) to balance reactions in the schemes. Detailed Gibbs free energies for all molecules are presented in Tables S1–S3 in Supporting Information S1, and the corresponding Gibbs reaction energies are shown in Scheme 1 and Scheme 2.

3. Results and Discussion

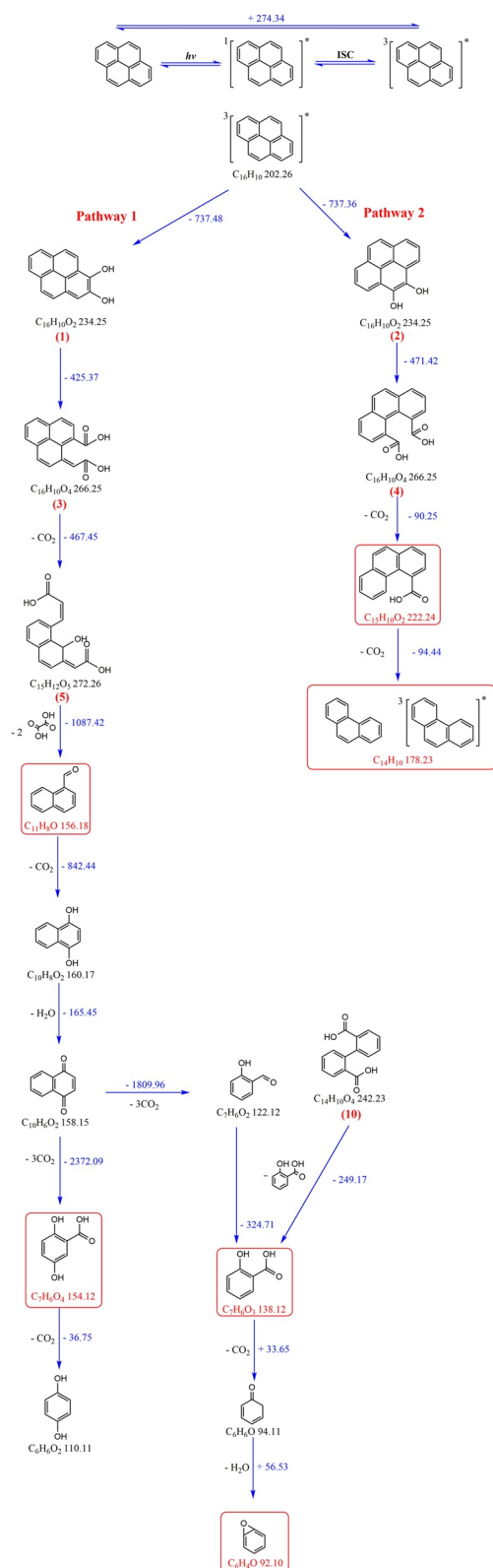
3.1. Organic Sulfur Compounds Detected by MI-SPI-TOFMS

To detect the gas-phase compounds formed by degradation of PAHs/DMSO in the dark and under irradiation, we applied MI-SPI-TOFMS as a novel promising technology for the online and continuous monitoring of VOCs (Mekic et al., 2020a; Zhang et al., 2019).

Figure 1 shows the Venn diagrams of the observed secondary gas-phase products of the degradation of PAHs/DMSO under light irradiation. It reveals that most of the gas-phase compounds were formed by degradation of PHE/DMSO, and that many of them were the same as the degradation products generated by PYR/DMSO and FLA/DMSO. The Venn diagrams showing the comparison of the formed products under different conditions are presented in Figure S1 in Supporting Information S1.

Among all detected compounds, we tentatively identified many unsaturated multifunctional molecules and OS compounds that are summarized in Tables S4 and S5 in Supporting Information S1.

Within the studied systems, PHE/DMSO and PYR/DMSO were major contributors to the individually formed gas-phase compounds (Figure 1). Among all detected gas-phase products, we highlight the formation of OS compounds, which enables a comparison with the corresponding OS compounds identified in ambient aerosol particles (see below).



3.2. Comparison of the Identified OS Compounds With Data From Field Measurements

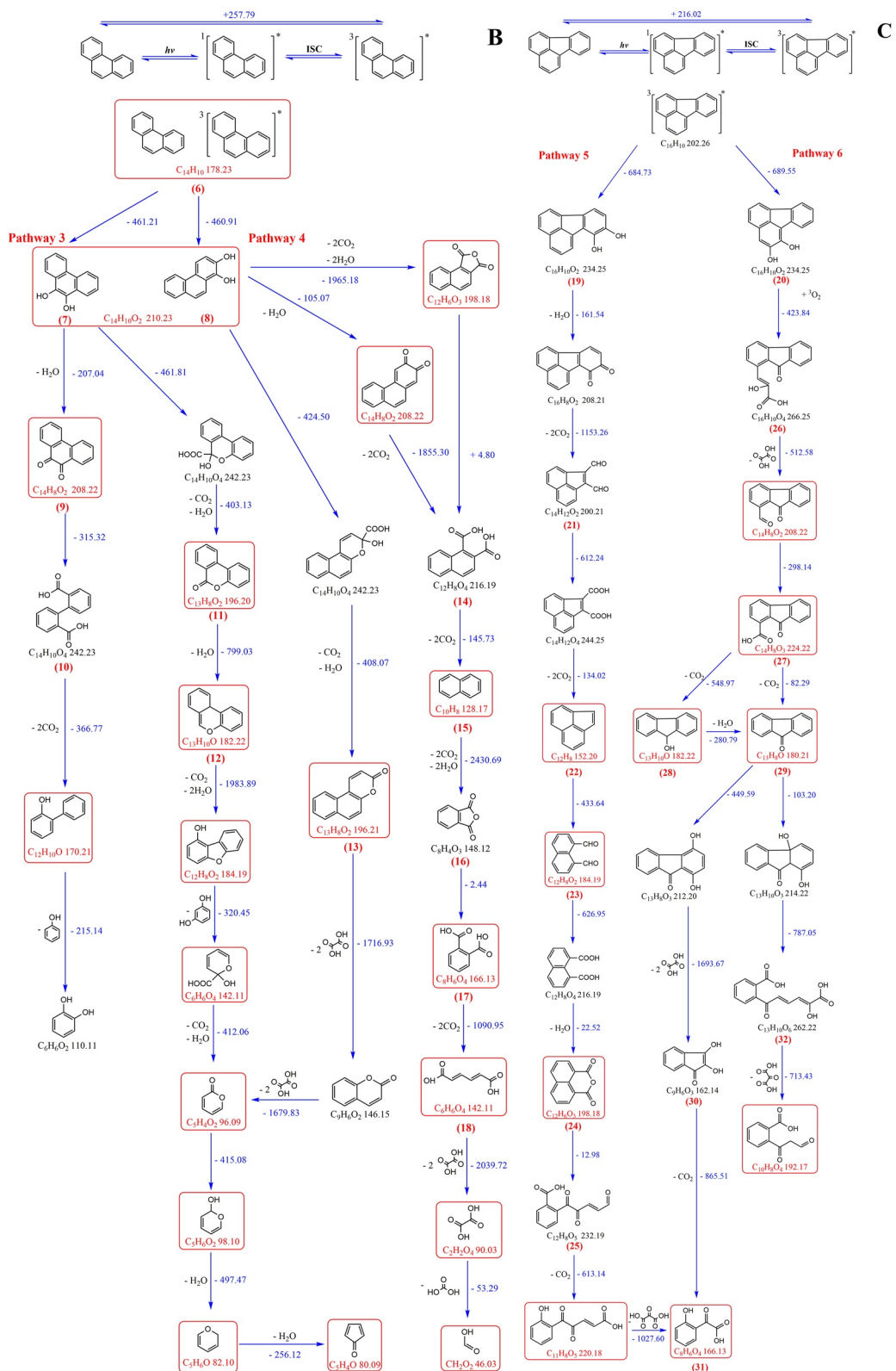
Table 1 shows the comparison of the identified OS compounds under irradiation, with those detected during different field campaigns. It has to be noted that the agreement between the chemical formulas detected in this study and those from field measurements does not necessarily imply the same molecular structure, because multiple structural isomers are possible for each formula (Mekic et al., 2020a; Nizkorodov et al., 2011). There are 1 and 11 unique tentative OS formulas that emerged upon light irradiation of PYR/DMSO and PHE/DMSO, respectively. There are also six shared OS formulas that are released upon light irradiation of both, PYR/DMSO and PHE/DMSO, and eight shared OS formulas that are generated by all PAHs/DMSO, that is, PYR/DMSO, PHE/DMSO, and FLA/DMSO, in the presence of light irradiation.

In our previous study (Mekic et al., 2020a, 2020b), we have identified the OS compounds formed during the photodegradation of a mixture of fluorene and DMSO. Here, we confirm that in addition to fluorene, the photodegradation of other light-weight PAHs (PYR, FLA, and PHE) mixed with DMSO represents a source of OS compounds that have been detected in field measurements. Among the detected OS formulas, six of them (highlighted in bold font in Table 1) have additionally been identified as SOA precursors (Berresheim & Eisele, 1998; Berresheim et al., 1993; Dawson et al., 2012; Gaston et al., 2010; Hopkins et al., 2008; Karl et al., 2007; Ning et al., 2020). These OS compounds can form surfactant films on the aerosol particles in the marine boundary layer, by which means they influence the surface tension and hygroscopicity of the particles (Decesari et al., 2011; Tao et al., 2014a).

3.3. Time Evolution of OS Compounds

The photochemical degradation of PAHs/DMSO releases a number of OS compounds in the gas phase. We observed rapid formation of methylsulfonylmethane ((CH₃)₂SO₂, MSM), ethyl methanesulfonate (CH₃SO₃C₂H₅, EMS), methanesulfonic acid (CH₃SO₃H, MSA), methanesulfinic acid (CH₃SO₂H, MSIA), hydroxymethanesulfonic acid (CH₄O₄S, MSAOH), and 2-hydroxyethanesulfonic acid (C₂H₅O₄SH, ESAOH). All these compounds have been found in particles in coastal as well as inland regions and identified as SOA precursors (Berresheim & Eisele, 1998; Berresheim et al., 1993; Dawson et al., 2012; Gaston et al., 2010; Hopkins et al., 2008; Karl et al., 2007; Ning et al., 2020). Although, in the past years, the formation chemistry of sulfuric acid in the marine atmosphere has been extensively studied, our knowledge of the formation of other sulfur-containing organic compounds such as MSIA, MSA, MSM, EMS, and ESAOH is still in its infancy. The gaseous MSA and MSIA are particularly important species participating in the initial stage of new particle formation (NPF; Chen et al., 2016; Schobesberger et al., 2013; Zhao et al., 2017). MSIA can be formed via OH radical addition to DMSO with the removal of a CH₃ radical, while MSA as the simplest organosulfate is mainly formed through gas-phase SO₂ oxidation of DMS and heterogeneous oxidation of DMSO (Barnes et al., 2006; Glasow & Crutzen, 2004). The discrepancy between modeled and measured vertical profiles of MSA suggested a missing source close to the ocean surface, which is much stronger than the estimated chemical production from DMS oxidation (Zhang et al., 2014). The comparison between daytime and before-dawn measurements indicated that this strong source of

Scheme 1. Detailed reaction mechanism describing the formation of gas-phase products initiated by ³PAHs* and dimethylsulfoxide. Numbers in brackets, written below each molecule, are compound designations to follow the discussion better with Scheme 1. All identified products are framed into red rectangles (see Tables S3 and S4 in Supporting Information S1 for additional details on their detection). The numbers near each reaction arrow represent Gibbs energies arising from quantum chemistry calculations.



Scheme 1. Continued

Table 1
Tentative Organic Sulfur (OS) Formulas Detected in the Present Study That Were Identified in Ambient Atmospheric Aerosols

Reaction system	m/z	Tentative chemical formulas	References ^a
PYR/DMSO	202	$C_7H_6O_5S$	Kuang et al. (2016)
		$C_8H_{10}O_4S$	Wang et al. (2016)
PHE/DMSO	168	$C_5H_{12}O_4S$	Kuang et al. (2016)
		$C_3H_6O_6S$	Kuang et al. (2016)
	170	$C_4H_{10}O_5S$	Kuang et al. (2016)
		$C_4H_6O_6S$	Kuang et al. (2016)
	182	$C_5H_{10}O_5S$	Kuang et al. (2016), Tao et al. (2014b), Wang et al. (2016), and Zhu et al. (2019)
		$C_6H_{14}O_4S$	Kuang et al. (2016) and Wang et al. (2016)
	192	$C_6H_8O_5S$	Wang et al. (2016)
	194	$C_6H_{10}O_5S$	Kuang et al. (2016)
	196	$C_7H_{14}O_4S$	Kuang et al. (2016) and Wang et al. (2016)
		$C_5H_8O_6S$	Kuang et al. (2016), Tao et al. (2014b), and Wang et al. (2016)
	198	$C_6H_{12}O_5S$	Kuang et al. (2016), Tao et al. (2014b), and Wang et al. (2016)
		$C_7H_{16}O_4S$	Kuang et al. (2016) and Wang et al. (2016)
	204	$C_5H_{10}O_6S$	Kuang et al. (2016), Tao et al. (2014b), Wang et al. (2016), and Zhu et al. (2019)
		$C_6H_{14}O_5S$	Kuang et al. (2016) and Wang et al. (2016)
	206	$C_7H_8O_5S$	Wang et al. (2016)
	208	$C_7H_{10}O_5S$	Kuang et al. (2016) and Wang et al. (2016)
		$C_8H_{14}O_4S$	Kuang et al. (2016)
210	$C_6H_8O_6S$	Kuang et al. (2016) and Wang et al. (2016)	
	$C_7H_{12}O_5S$	Kuang et al. (2016)	
PYR/DMSO and PHE/DMSO	112	$CH_4O_4S^b$ (MSAOH)	
	124	$C_3H_8O_3S^b$ (EMS)	
	152	$C_2H_4O_4S$	Kuang et al. (2016)
PAHs/DMSO	80	$CH_4O_2S^b$ (MSIA)	
	94	$C_2H_6O_2S^b$ (MSM)	
	96	$CH_4O_3S^b$ (MSA)	
	126	$C_2H_6O_4S^b$ (ESAOH)	
PAHs/DMSO	140	$C_3H_8O_4S$	Kuang et al. (2016)
	154	$C_4H_{10}O_4S$	Kuang et al. (2016)
		$C_3H_6O_5S$	Kuang et al. (2016)

Table 1
Continued

Reaction system	m/z	Tentative chemical formulas	References ^a
	166	$C_4H_6O_5S$	Kuang et al. (2016)
		$C_5H_{10}O_4S$	Kuang et al. (2016) and Wang et al. (2016)
	178	$C_5H_6O_5S$	Wang et al. (2016)

^aReferences related to the chemical formulas of OS compounds identified in ambient aerosols. ^bBold chemical formulas correspond to the OS compounds that are known SOA precursors.

MSA is photolytically enhanced in daytime; it has been suggested that gaseous DMSO could be the potential precursor of MSA (Zhang et al., 2014). Here, we show that the reactions of DMSO photosensitized by light-excited PAHs enriched at the water surface could represent an important source of gaseous MSA and MSIA formation near the ocean surface. Figures 2a and 2b show typical time evolution profiles of MSIA and MSA, formed upon irradiation of PAHs/DMSO. The formation profiles of MSM, EMS, MSAOH, and ESAOH are shown in Figure S2 in Supporting Information S1.

Figure 2a shows that gas-phase MSIA is promptly formed upon light irradiation of FLA/DMSO, PYR/DMSO, and PHE/DMSO: in about 15–20 min, its signal intensity increases in all three cases. In the case of PHE/DMSO, the signal intensity of MSIA promptly decreases after the maximum, presumably due to its consumption and the formation of other products. During the photodegradation of FLA/DMSO and PYR/DMSO, the intensity of formed MSIA remains approximately stable during a period of ca. 1 hr (most likely because the formation of MSIA balances its consumption), before decreasing in these cases as well. Similar behavior was observed for the formation profiles of MSA upon photodegradation of FLA/DMSO, PYR/DMSO, and PHE/DMSO (Figure 2B).

3.4. Photodegradation Pathway of DMSO Initiated by Excited Triplets of FLA, PYR, and PHE

In addition to OS compounds, a number of unsaturated multifunctional compounds were also detected. A reaction mechanism of FLA/DMSO, PYR/DMSO, and PHE/DMSO degradation is suggested here, based on the information obtained from the detected tentative products in the gas phase and on quantum chemistry calculations. Because the three PAHs are the only light-absorbing compounds that can act as photosensitizers,

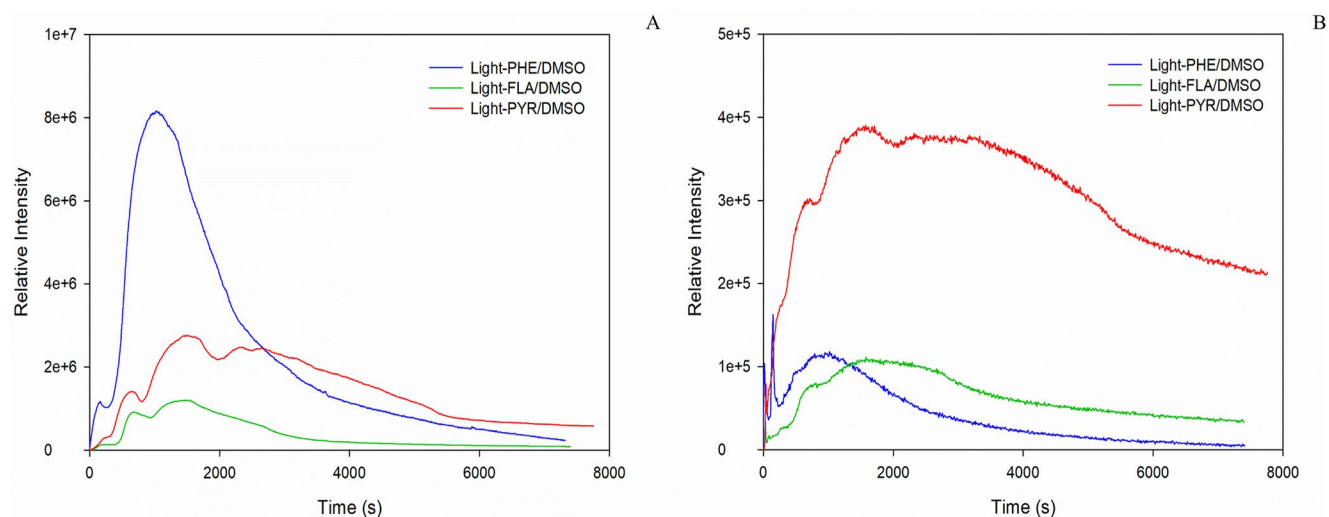


Figure 2. Formation profiles of MSIA ($m/z = 80$) upon photodegradation of polycyclic aromatic hydrocarbons (PAHs)/dimethylsulfoxide (DMSO) (a). Formation profiles of MSA ($m/z = 96$) upon photodegradation of PAHs/DMSO (b).

the initial step we propose is the photoexcitation of PAHs through a $\pi \rightarrow \pi^*$ electronic transition, followed by intersystem crossing to produce the excited triplet states ($^3\text{PAHs}^*$) (Barbas et al., 1996, 1997; Fasnacht & Blough, 2002, 2003).

To verify the actual involvement of $^3\text{PAHs}^*$ in the photosensitized process, the reactivity of the excited triplet states of FLA, PYR, and PHE was investigated by laser flash photolysis, and the transient absorption spectra are reported in Figure S3 in Supporting Information S1.

The triplet reactivity of FLA and PHE was monitored at, respectively, 400 and 480 nm corresponding to the absorption maxima of $^3\text{FLA}^*$ and $^3\text{PHE}^*$. For PYR, the wavelength of 420 nm was selected in order to avoid the interference of long-lived species absorbing around 440 nm (Figure S3 in Supporting Information S1). The correlation between the pseudo-first order decay of $^3\text{PAHs}^*$ and DMSO concentration gives the second order rate constants $k_{3\text{FLA}^*, \text{DMSO}} = 4.09 \pm 0.36 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $k_{3\text{PYR}^*, \text{DMSO}} = 5.25 \pm 0.78 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{3\text{PHE}^*, \text{DMSO}} = 6.18 \pm 0.76 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 3). These values are similar to the reactivity determined between the excited state of fluorene and DMSO in water (Mekic et al., 2020a). They suggest that the triplet states of FLA, PYR, and PHE are all able to react with DMSO, and that the process likely accounts for the observed DMSO phototransformation.

It has also been demonstrated that $^3\text{PAHs}^*$ can react with DMSO in water/DMSO solution (Mekic et al., 2020a), including the pathway leading to the formation of singlet oxygen ($^1\text{O}_2$) through energy transfer to triplet-state oxygen ($^3\text{O}_2$) (Wilkinson et al., 1995), the pathway yielding hydroxyl (OH) radicals through

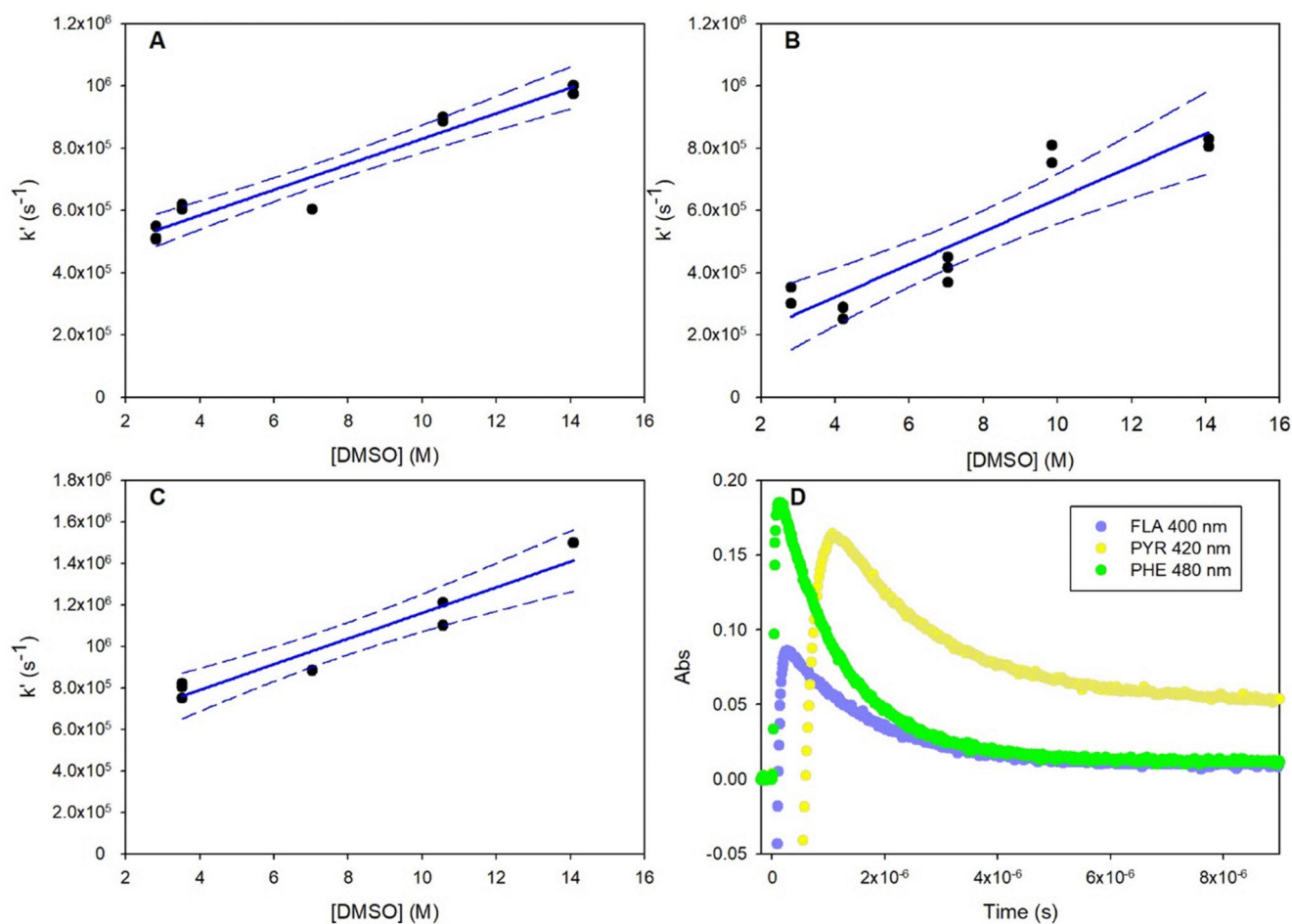
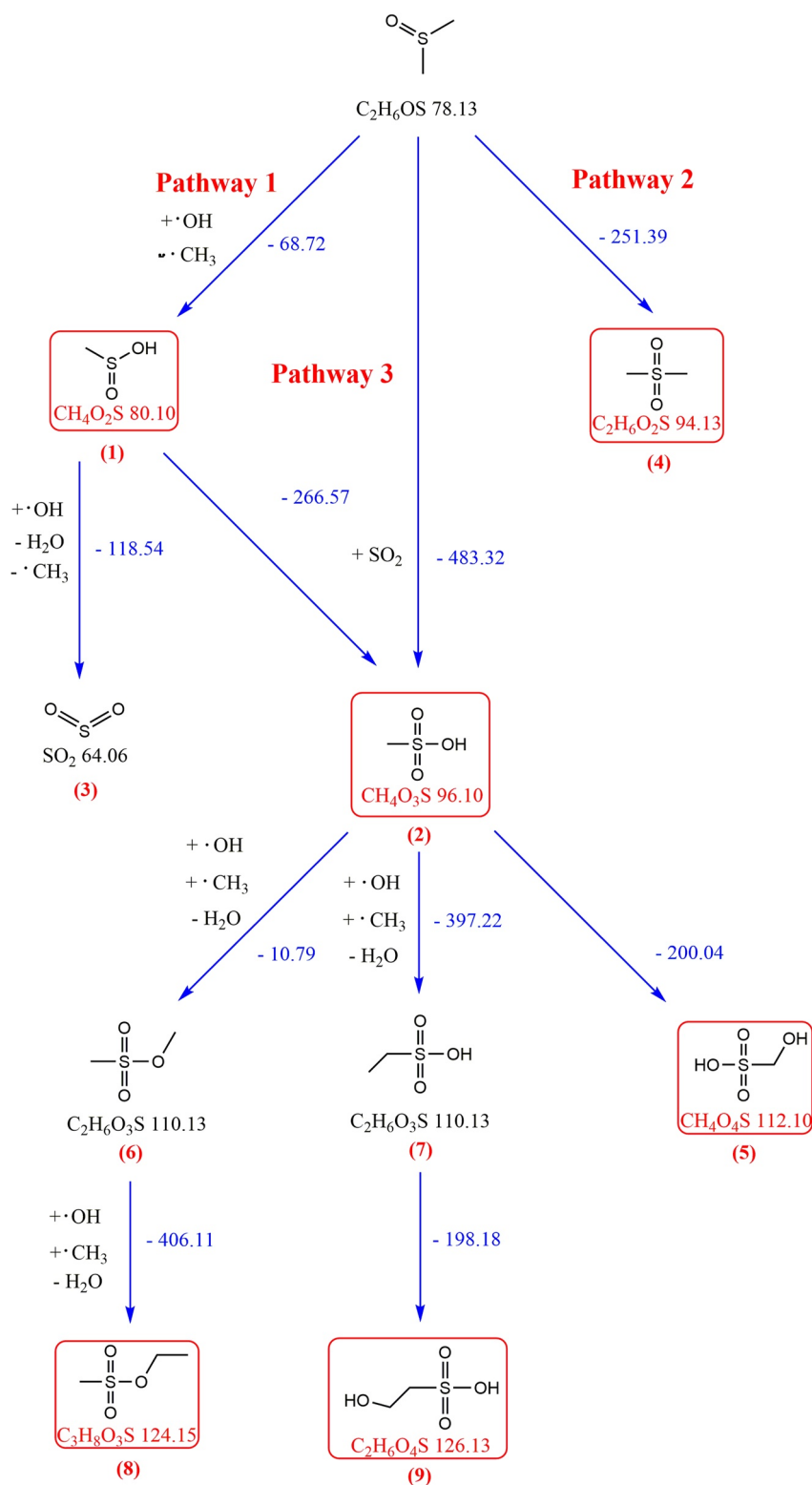


Figure 3. Plots of the pseudo-first order rate constant of fluoranthene (FLA) (a), pyrene (PYR) (b), and phenanthrene (PHE) (c) triplet state signals as a function of dimethylsulfoxide (DMSO) concentration. The solid line represents the linear fit and the dashed line the 95% confidence interval of this fit. Panel (d) shows the time trend of the absorbance at different pre-selected wavelengths of the excited states of FLA, PYR, and PHE in the presence of 7.04 M DMSO.



Scheme 2. Reaction mechanism describing the formation of gas phase products initiated by OH radical oxidation of dimethylsulfoxide. Numbers in brackets, written below each molecule, represent compound designations to follow the discussion better with Scheme 2. The identified organic sulfur products as secondary organic aerosol precursors are framed into red rectangles. The numbers near each reaction arrow represent Gibbs energies arising from quantum chemistry calculations.

water oxidation by $^3\text{PAHs}^*$ (Brigante et al., 2010), and the pathway leading to the formation of radicals through electron transfer. The formation of unsaturated compounds is accompanied with free radicals and reactive oxygen, which could favor the generation of OS products.

In this context, it has to be noted that the steady state production of $^1\text{O}_2$ by carbonyl compounds can be in the order of 2–11 pM (Eugene & Guzman, 2019), suggesting it as a competitive pathway at the air-water interface.

In this study, the comprehensive reaction schemes we propose account for the majority of the detected unsaturated multifunctional compounds and the above-mentioned OS compounds in the gas phase, which emerge from the photosensitized processing of DMSO by light-excited PAHs ($^3\text{PYR}^*$, $^3\text{FLA}^*$, and $^3\text{PHE}^*$) at the air-water interface. As shown in Scheme 1, the general photodegradation mechanism initiated by $^3\text{PAH}^*$ could be divided into six proposed pathways initiated by $^3\text{PYR}^*$, $^3\text{FLA}^*$, and $^3\text{PHE}^*$, which are complementary to the reaction mechanisms suggested by previous studies (Cao et al., 2015; Liang et al., 2006; Rehmann et al., 2001; van Herwijnen et al., 2003). During the photodegradation of PYR, PHE could also be one of the intermediate products participating in oxidation reactions. Pathways 1 and 2 describe the reactions of $^3\text{PYR}^*$ in the presence of O_2 to yield 1,2-pyrenediol (1) and 4,5-dihydroxy-pyrene (2). The degradation of the latter compounds could involve O_2 attack to the aromatic ring (at positions corresponding to the 1/2 and 4/5 of PYR, see Figure S4 in Supporting Information S1), allowing the ring to open and yielding dicarboxylic acids (3 and 4). In Pathway 1, further degradation could be initiated at positions corresponding to 8a/10a of PYR, triggering another phenyl ring opening (5) and generating smaller degradation products with aromatic ring structures. In pathway 2, by the cleavage of carboxyl groups, PHE (6) could be formed after a decarboxylation pathway.

Pathways 3 and 4 describe the degradation of PHE (6), yielding 9,10-dihydroxy-phenanthrene (7), and 1,2-dihydroxy-phenanthrene (8). In pathway 3, the photooxidation of 9,10-phenanthraquinone (9) might yield the biphenyl compound (10) by a ring opening at the position that corresponds to the 8a/10a of PHE (Figure S4 in Supporting Information S1). The substituted biphenyl is subsequently decomposed into a single aromatic structure after photooxidation. Additionally, O_2 attack might also afford a ring expanded lactone and further transformation into xanthone (11) and xanthene (12). In pathway 4, the photodegradation of 1,2-anthraquinone could yield naphthopyrone (13), which could be subsequently converted into smaller molecules by cleavage of the aromatic ring. Meanwhile, phenyl ring opening at the positions corresponding to the 4a/10a or 8a/4b of PHE would yield in succession 1,2-naphthalenedicarboxylic acid (14), naphthalene (NAP) (15), phthalic anhydride (16), and phthalic acid (17). Subsequently, with a last phenyl ring opening followed by oxidative transformation, one could account for the generation of an acyclic structure (muconic acid (18)), which might then be degraded into smaller molecules upon photooxidation and decarboxylation.

Pathways 5 and 6 describe the reaction of $^3\text{FLA}^*$ in the presence of O_2 to yield 9,10-dihydroxy-fluoranthene (19) and 1,2-dihydroxy-fluoranthene (20). In pathway 5, degradation of (19) could involve O_2 attack to the saturated phenyl ring to form $\text{C}_{14}\text{H}_{12}\text{O}_2$ (21) and acenaphthylene (22). Activation of the saturated five-member ring of (22) at the 6b/10a position could give naphthalene-2,3-dicarbaldehyde (23), which could then be converted into 1,8-naphthalic anhydride (24) and the compound $\text{C}_{12}\text{H}_8\text{O}_5$ (25) having a single aromatic ring.

In pathway 6, a ring opening following O_2 attack to (20) to give (26), would enable further formation of 9-fluorenone-1-carboxylic acid (27), followed by the production of 9-fluorenone (28) and 9-fluorenone (29). Further degradation would occur upon oxidation, at positions corresponding to the 6b/10a and 6a/6b of FLA, with ring cleavage and production of 1,2-dihydroxy-indanone (30), 2-hydroxyphenylglyoxylic acid (31), and $\text{C}_{13}\text{H}_{10}\text{O}_6$ (32).

Moreover, DMSO can be oxidized by oxygen and OH radical formed during the reaction of DMSO and $^3\text{PAH}^*$, yielding further radical species and OS compounds (Scheme 2). The formation mechanisms of OS compounds from $\text{DMSO} + ^3\text{PAH}^*$ were suggested to be generally divided into three possible pathways, all starting from DMSO. Pathway 1 describes the reaction between DMSO and the OH radical that yields MSIA (1) and a methyl radical (CH_3), followed by the formation of MSA (2) and SO_2 (3) (Arsene et al., 2002; Falbe-Hansen et al., 2000; González-García et al., 2006; Urbanski et al., 1998).

It has been reported that the OH-addition route in the gas-phase atmospheric oxidation of DMSO would result in high yields of SO₂ (3), which is a precursor of H₂SO₄. In contrast, MSA (2) would be produced by a liquid-phase reaction involving MSIA (Allen et al., 1999; Arsene et al., 2002; Kukui et al., 2003; Urbanski et al., 1998). In pathway 2, an overall addition of oxygen (e.g., following OH attack plus H-atom abstraction by O₂) allows the transformation of DMSO into MSM (4). Pathway 3 describes the formation of MSA (2) via the oxidation of DMSO in the presence of SO₂. Further transformation would occur upon oxidation of MSA (2) and yield MSAOH (5). The OH and CH₃ radicals could further oxidize MSA (2) into C₂H₆O₃S (6 and 7), followed by the formation of EMS (8), and ESAOH (9), respectively.

4. Conclusions and Implications

In the present study, it was shown that the photochemistry of PAHs with DMSO at the sea surface may initiate the formation of many gas-phase OS compounds, some of which are well-known SOA precursors. In all cases, the formation of MSM, EMS, MSIA, MSAOH, and ESAOH was observed. The obtained results may better explain field observations of NPF events in the atmosphere above the ocean surface, which are different from the primary emitted aerosol particles from biological processes occurring in the ocean (O'Dowd et al., 2004).

The photosensitized transformation of DMSO by the excited triplet states of PAHs suggested in this study can contribute to the sulfur cycle in the SML, and it could be an important process controlling the volatility and efflux of sulfur from the oceans into the atmosphere (Mopper & David, 2002). We found that DMSO was oxidized to photochemically stable species, including MSIA and MSA, a process that results in the formation of cloud condensation nuclei (CCN), which in turn affects the Earth's radiative balance (Mopper & David, 2002).

In a very recent paper, a small difference has been observed in product formation (Stirchak et al., 2019), implying differences in the photochemical pathways that are operational in freshwater compared to sea-water—surface. The phenomenon was ascribed to the presence of halide ions, metals, and pH differences between the two aqueous environments (Stirchak et al., 2019). Indeed, it has been shown that excited triplet states of aromatic ketones such as benzophenone (BP) can interact with halide ions. Jammoul et al. (2009) have shown that the excited triplet state of BP reacts slowly with chloride ions ($k < 10^6 \text{ M}^{-1} \text{ s}^{-1}$) compared to its reactions with bromide and iodide. In fact, the reaction between ³BP* and iodide proceeds very fast, close to the diffusion limit. The photodegradation of fluorene was enhanced in the presence of bromide and chloride ions at ionic strengths up to 0.3 M, with a tendency to decrease at higher ionic strength values (Mekic et al., 2020b). In the presence of iodide ions, a sharp increase of the pseudo-first order rate constant of fluorene degradation was observed at ionic strength values up to 0.01 M, followed by slow increase at higher ionic strength (Mekic et al., 2020b).

These observations suggest that in the future, the effect of halide ions and metals on the photosensitized chemistry of PAHs/DMSO should be explored in order to better understand the formation of secondary product compounds above the sea surface compared to that above the surface of freshwaters.

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Data Availability Statement

All data in this manuscript are freely available upon request through the corresponding author (gligorovski@gig.ac.cn and davide.vione@unito.it). Data sets for this research are available in the in-text data citation reference: Jiang (2021).

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