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Article

Molecular Composition of Photooxidation Products Derived from Sulfur-Containing Compounds Isolated from Petroleum Samples

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ABSTRACT: Following the Deepwater Horizon (DWH) oil spill, the limited availability of the Macondo well oil prompted the use of a more widely available surrogate oil supplied by BP, collected from a nearby well. It is chemically similar but has minor compositional differences compared to the oil spilled in DWH. Similarly, the two light sweet crude oils were shown to produce abundant sulfur-containing photoproducts upon solar irradiation, despite a low sulfur content in both parent oils (<0.5 wt %). To investigate the role of chemical functionality in photooxidation of sulfur-containing hydrocarbons, sulfides and thiophenes were isolated from DWH and surrogate parent oils and subjected to laboratory-based irradiation. Their water- and oil-soluble photoproducts were analyzed by ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry to access compositional differences between photoproducts of the two oils. The results demonstrate that DWH produces heavily oxidized water-/oil-soluble compounds (up to $O_{18}S_1$), whereas the surrogate oil yields species with only up to 14 oxygen atoms ($O_{14}S_1$). To understand the behavior of a geochemically different sample, a light distillation cut from an Arabian heavy oil was also subjected to the same preparatory workflow and analysis. The results point to the occurrence of photoinduced polymerization reactions during the production of high-molecular-weight/heavily oxidized water-soluble compounds. Furthermore, thiophene and sulfide fractions from all oils were shown to produce abundant water- and oil-soluble photoproducts upon laboratory-irradiation, confirming the importance of this process in oxidative, surface weathering of oil and in the production of petroleum-derived dissolved organic sulfur species. Sulfides from light oils were susceptible to photooxidation and matched previous reports of low-double bond equivalent O_xS_1 species from irradiated DWH and surrogate oils.

INTRODUCTION

photooxidation of petroleum following oil spills was first documented in the 1970s,[1−3] when Overton et al. suggested that petroleum degradation by sunlight likely involves three simultaneous processes: photoinduced oxidation, fragmentation, and polymerization.[4] Recent studies by high-resolution mass spectrometry have improved the understanding of the molecular changes caused by oil weathering through studies focused on the photooxidation of oil after the *Deepwater Horizon* (DWH) spill in 2010.[5−11] In particular, petroleum-derived hydrocarbons have been demonstrated to undergo photooxidation from sunlight in the environment to produce oil- and water-soluble photoproducts with an extremely high oxygen content relative to parent oils (e.g., up to O_{10} in oil and O_{20} in water).[12−15] These molecular changes can be simulated at a laboratory scale in a solar microcosm, which enables the study of specific photogenerated chemical functionalities to further understand their photo-oxidative transformation. A recent study of heavy petroleum fractions (asphaltenes and asphalt) confirms that photochemical transformations also involve polymerization and fragmentation.[13,14] These weathering processes greatly affect the solubility of hydrocarbons, because incorporation of oxygen through photooxidation reactions increases their relative polarity and enables dissolution in more polar solvents, such as water.[1,16] Photoinduced fragmentation (of alkyl chains, naphthenic rings, and/or aromatic rings) can also promote water solubility because fewer alkyl chains (higher O/C) translate into decreased hydrophobicity. However, photoproducts and reaction pathways appear to be sample-dependent. For example, asphaltenes, a subfraction of petroleum characterized by their high heteroatom content, have been shown to vary in terms of their photochemistry: asphaltenes from a Canadian bitumen were demonstrated to undergo photofragmentation and photooxidation upon laboratory irradiation that yielded abundant/compositionally diverse water-soluble species, whereas asphaltenes from a Wyoming oil did not produce detectable amounts of water-soluble species.[14] Furthermore, photooxidation of crude oil on water has been demonstrated to produce toxic water-soluble products.[17]

Little is known about the role of heteroatoms (e.g., O, N, S, and V) and chemical functionality (e.g., thiophene versus sulfide (for sulfur) and pyridine versus pyrrole (for nitrogen)) in the chemistry (e.g., solubility and toxicity) of petroleum photoproducts. For example, several types of sulfur-containing functionalities exist in crude oil: thiophenes (aromatic), sulfides/disulfides (nonaromatic), and thiols. Thiophenes

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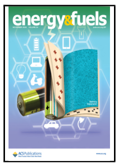

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consist of a five-membered aromatic ring with a resonant sulfur atom and are commonly fused to benzo groups in the form of benzothiophene and dibenzothiophene. Thiophenic species are the most abundant type of sulfur in petroleum and have been shown to be nonreactive/noncorrosive in refinery operations; they are extremely stable structures, which persist throughout geologic time and survive thermal/catalytic refinery processes.[18,19] Conversely, sulfides/disulfides comprise a smaller mass fraction of sulfur-containing species in crude oil, but are much more reactive and corrosive than their thiophenic counterparts.[20,21] Moreover, sulfoxides have been detected in crude oils by positive-ion (+) electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS), but were shown to comprise a very small percent of the total sulfur in petroleum.[22] Sulfur content and functionality are especially of interest to refinery/production strategies because governmental regulations limit their concentrations in commercial products to protect the environment and public health, and there are many methods to isolate sulfur species from petroleum.[23−27] In line with these concerns, sulfur chemistry is crucial for understanding the formation of water-soluble species through photooxidation of oil spills (fate), as well as environmental consequences (impact). Correspondingly, a study involving photoirradiation of various benzothiophene model compounds along with a high-sulfur crude oil demonstrated that water-soluble sulfur-containing acidic species are produced from photooxidation.[28] Another study showed that dibenzothiophene compounds photooxidize in the environment following an oil spill, as well as in laboratory irradiation.[2] Additional studies have shown that both thiophene and sulfide functionalities can undergo photooxidation upon formation of singlet oxygen from sunlight and that sulfides produce sulfoxides from photooxidation.[29,30]

Following the DWH oil spill, oil collected directly from the Macondo well could be obtained from the National Institute for Standards and Technology (NIST), standard reference material (SRM) 2779. However, because of its low availability, many studies employed a surrogate oil (available in larger quantities) from a nearby well, because its bulk chemical composition and properties, such as API gravity, are similar to those of the oil spilled in the DWH incident.[31] It is interesting to note that preliminary experiments showed that both surrogate and DWH parent oils produce abundant water-soluble SO_x species after solar irradiation, despite extremely low sulfur content in the parent oils.[15] However, the influence of sulfur functionality (e.g., sulfidic versus thiophenic) and its potential effect on the production/composition of abundant SO_x species are currently unknown.

FT-ICR MS has been employed for molecular characterization of petroleum and its photoproducts because of its high mass-resolving power and mass accuracy. Petroleum composition is inherently extremely complex and becomes even more complex through photoweathering processes, which generate new species through photooxidation (tens of thousands of new compounds).[32,33] Thus, we employ a 9.4 Tesla FT-ICR MS instrument to study differences in sulfur-containing photoproducts from DWH and surrogate oils. A previously developed solid-phase extraction (SPE) yields fractions enriched in sulfidic or thiophenic functionalities,[25] which are subsequently photoirradiated. It is important to point out that sulfur content is elevated in heavy crude oils; thus, to better understand the sulfur chemistry involved in the photoproduction of water-solubles, we also subjected a distillate from an Arabian heavy crude oil to the same analytical workflow for comparison. Following separation, each fraction was photoirradiated in a solar simulation microcosm in the laboratory, and the oil- and water-soluble photoproducts were isolated, extracted, and characterized by FT-ICR MS for molecular comparison.

■ EXPERIMENTAL METHODS

Oil Samples. Gulf of Mexico crude oil (SRM 2779) (DWH) was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD). Surrogate oil was obtained from AECOM, Ft. Collins, CO (A0063S). Arabian heavy distillate (178−283 °C) was obtained from Nalco Company. All solvents were of HPLC grade from JT Baker chemicals (Phillipsburg, PA) and used as received: heptane, acetonitrile, acetone (ACE), toluene, dichloromethane (DCM), water, cyclohexane, and methanol (MeOH). Silver nitrate (>99% purity) was purchased from Acros Organics, and Bond Elut PRS and PPL SPE cartridges were obtained from Agilent Technologies (Santa Clara, CA).

Sulfur Separation. Crude oil samples were subjected to a previously described strong cation exchange (SCX) and SPE, with slight modifications, to isolate fractions enriched in sulfide, thiophenic, and thiol functionalities.[25] In short, a solution of silver nitrate was passed through a 1 g propyl sulfonic acid silica cartridge (Bond Elut PRS, part no. 12256010) to obtain a final stationary phase referred to as Ag + -SCX. Following silver-impregnation of the column and conditioning with DCM /heptane (2/3), 200 mg of oil was loaded, and saturates were eluted with DCM /heptane (2/3). Next, nonreactive sulfur (thiophenes) was eluted with DCM/ACE (9/1). Next, acetonitrile/DCM (1/1) is added to obtain a reactive sulfur (sulfides) fraction. Finally, thiols are eluted with HCl /MeOH (1/1) but were not analyzed because of inconsistent yields/irreversible binding. The separation was repeated seven times for each oil to obtain enough material in the sulfide and thiophene fractions to perform solar irradiation. Fractions were dried under nitrogen gas prior to solar irradiation. The gravimetric yields from the sulfur separation are shown for the three oil samples shown in Figure S1.

Solar Simulation Microcosm. A thin film of oil was created by pipetting 20 mg of oil (from the resultant sulfur fractions) dissolved in 50 μL of cyclohexane onto 25 mL of HPLC-grade water in a jacketed beaker attached to a water chiller. The beaker was then placed into a solar simulator (ATLAS Suntest CPS+) and irradiated for 24 h (equivalent to six days of natural sunlight[10]) at 25 °C. Following irradiation, the water-soluble portion was isolated by use of a pipet, and the oil layer was removed, dried under nitrogen gas, and stored in the dark at 4 °C to prevent further oxidation prior to mass analysis.

Isolation of Water-Soluble Organics. The water-soluble portion was then subjected to an SPE Priority Pollutant (PPL) extraction method as previously described.[34] In short, water samples were acidified to pH = 2 with concentrated hydrochloric acid and loaded onto a PPL cartridge (after stationary phase conditioning with methanol). The SPE was rinsed with acidified water (pH = 2) to remove salts and allowed to dry overnight prior to elution with methanol. The methanol extract, which contained water-soluble organic compounds, was infused into a mass spectrometer without further modification or dilution.

FT-ICR MS Analysis. A custom built 9.4 Tesla FT-ICR MS instrument was used for mass spectrometry analysis of virgin sulfur fractions as well as the resultant water- and oil-soluble photoproducts.[35] Oil-soluble fractions were dissolved in toluene to a final concentration of 150 μg/mL for (+) atomic pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry (APPI FT-ICR MS), as previously described.[36] For (+)/(−) ESI analysis of the oil-soluble photoproducts, fractions were reconstituted in toluene and then dissolved in methanol to a final concentration of 150 μg/mL in Tol/MeOH (1/1). Once dissolved in solvent, oil samples were acidified with formic acid to a final concentration of 2% acid (v/v) to access ketone/aldehyde species by (+) ESI, as previously

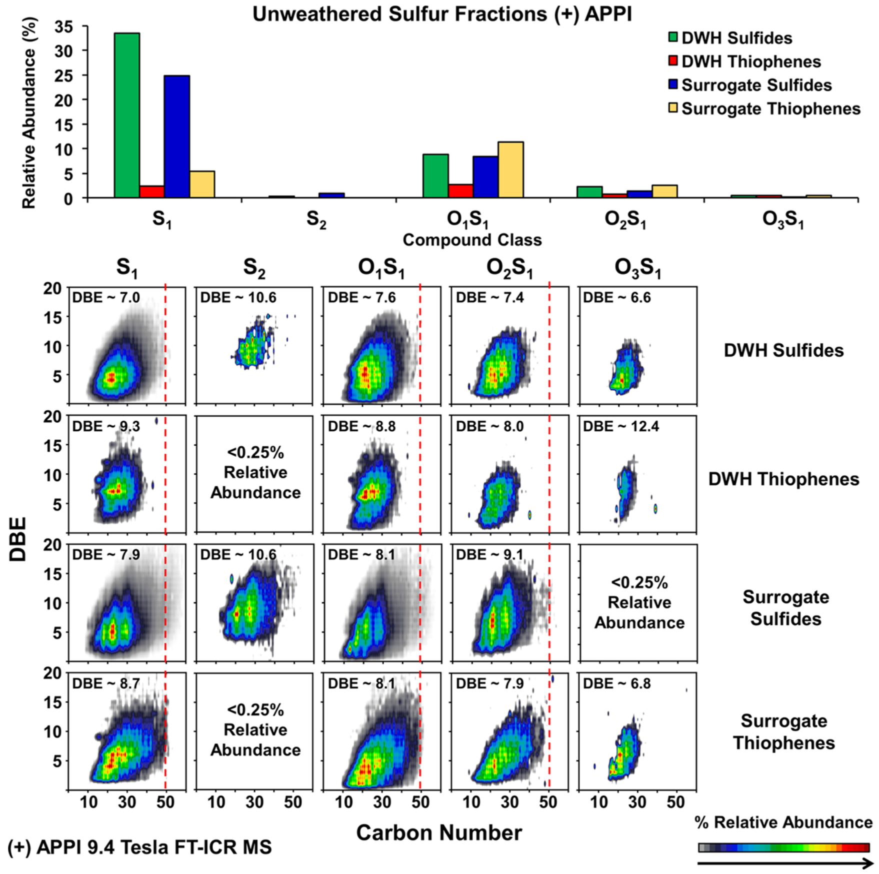

Figure 1. Heteroatom-compound class distribution (top panel) and isoabundance-contoured plots of double bond equivalents (DBE) versus carbon number (bottom panel) for sulfur-containing classes from (+) APPI FT-ICR MS analysis of DWH and surrogate sulfur fractions.

described.[7,33] Conversely, tetramethylammonium hydroxide (TMAH) base was added 0.25% (v/v) for (−) ESI analysis.[37] Water-soluble extracts were infused directly into the mass spectrometer at 0.5 μL/min for (−) ESI FT-ICR MS analysis as previously described.[38] Predator and PetroOrg software were used for molecular formula assignments.[39,40]

■ RESULTS AND DISCUSSION

Sulfur-Containing Species in Surrogate and DWH Parent Oils. Surrogate and DWH oils were separated into fractions enriched in thiophenic (aromatic sulfur) and sulfidic (nonaromatic sulfur) functionalities through a previously developed separation,[25] by Ag^+ exchange SPE, as shown in Figure S1. The surrogate oil has higher yield in the thiophenic fraction (∼1.7-fold) than the DWH crude oil, whereas both samples have similar yields in sulfidic fractions. Both oils have higher yields in the sulfidic fractions than the thiophene. A third fraction, thiols, was also collected but was not analyzed because of inconsistent yields, irreversible binding to the stationary phase, and production of ion pairs due to their elution with HCl. It is important to note that polyaromatic hydrocarbons (PAHs) may coelute in the thiophenic fraction because of their high electron density, and thus some compounds eluted in this fraction may not contain sulfur. The sulfur fractions from surrogate and DWH oils were analyzed by (+) APPI FT-ICR MS. The heteroatom-compound class distributions are shown in Figure 1 (top panel) and reveal a high sulfur (S_1) content in the sulfidic fractions from both oils (S_1 class, ∼25−35 RA%). Conversely, the thiophene fractions exhibit low relative abundances of S_1 compounds (<5%). Moreover, the sulfide fractions also contain detectable amounts of S_2 species, which are not present in the thiophene fractions. Furthermore, all fractions from both oils contain appreciable amounts of low-order O_xS_1 (e.g., O_1S_1−O_3S_1, usually accepted as sulfoxides), whose presence in petroleum is contentious, because it is believed that unaltered oils lack oxidized forms of sulfur.[22] It has been suggested that their presence is likely due to a minor degree of oxidation of S_1 species.[27,41]

Isoabundance-contoured plots of double bond equivalents (DBEs = number of rings + bonds to carbon) versus carbon number illustrate the molecular composition of the samples. The plots for surrogate and DWH, thiophenic and sulfide fractions, are displayed in the bottom panel of Figure 1 and reveal a remarkable similarity between the surrogate and DWH fractions. The sulfides and thiophenes from each oil occupy quite similar compositional ranges overall; however, the thiophenes generally have higher abundance-weighted average DBE (aromaticity) values (e.g., 9.3 versus 7.0 for S_1 DWH thiophenes and sulfides), which was expected. Furthermore, homologous series (i.e., species with the same DBE but varying carbon number) with increased relative abundance or "hot spots" (red) are present at DBE 6 for the S_1 class in both thiophene fractions and correspond to benzothiophene core structures with varying degrees of alkylation (across a wide carbon number range). In addition to this homologous series, surrogate thiophenes also display a hot spot at DBE 4, corresponding to cycloalkyl-substituted thiophenes and could indicate higher structural diversity than DWH. Other minor differences between oils include a trimodal distribution (as a

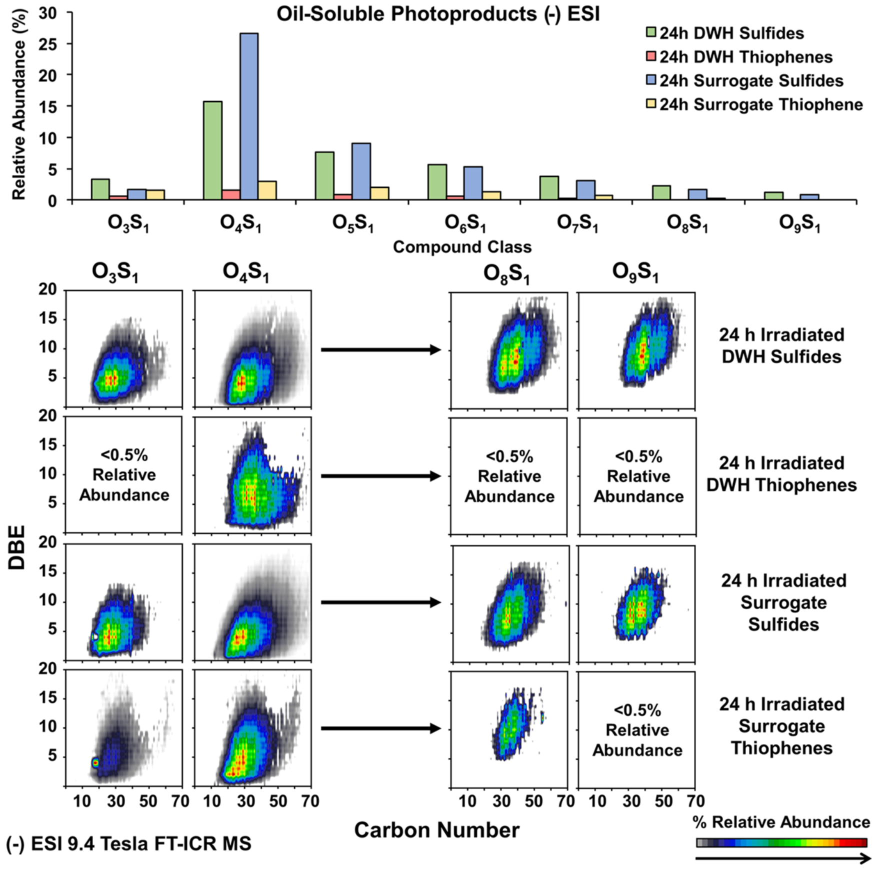

Figure 2. Heteroatom-compound class distribution (top panel) and DBE versus carbon number plots (bottom panel) for (−) ESI FT-ICR MS analysis of DWH and surrogate sulfur fractions after a 24 h irradiation period.

function of carbon number) for the surrogate sulfide species (e.g., hot spots at carbon numbers 18, 22−23, and 29 for the S_1 class). These hot spots are not present for the S_1 species in DWH sulfides, which appear as a pseudo-Gaussian distribution across the carbon number range. Multimodal distributions in surrogate oil are likely also due to higher structural diversity than DWH. Differences in degrees of alkylation (carbon number) between oils are observed; surrogate thiophenes are more alkyl-substituted than their DWH counterparts, as illustrated by the red line at carbon number = 50 for the S_1 and O_1S_1-O_2S_1 classes. Despite these small differences, major differences in the compositional range (DBE and carbon number values) are not observed between oils or fractions, thereby confirming the compositional similarities between the two parent oils in terms of their sulfur content/functionality. Moreover, the presence of low-DBE species in the thiophene fractions indicates potential coelution of sulfoxide (O_xS_1) and sulfide (S_1) species from the parent oils in both fractions.

Oil-Soluble Photoproducts from Surrogate and DWH Sulfur Fractions. Following 24 h solar irradiation in a laboratory photooxidation microcosm, oil-soluble photooxidized components were isolated and analyzed by (−) ESI FT-ICR MS for the characterization of acidic species (e.g., carboxylic acids and hydroxyls), which have been demonstrated to form after solar irradiation.[33] The heteroatom-compound class distribution is shown in Figure 2 (top panel) and illustrates a continuum of O_3S_1-O_9S_1 oil-soluble photoproducts from DWH and surrogate sulfur fractions. In agreement with the trend observed for the unirradiated fractions (Figure 1), the sulfides from both oils exhibit higher relative abundances of sulfur-containing species (O_xS_1) than the thiophenes (e.g., ∼27% relative abundance of O_4S_1 for surrogate sulfides).

The isoabundance-contoured plots of DBE versus carbon number for the sulfur-containing photoproducts (O_xS_1) from the DWH and surrogate sulfur fractions are displayed in Figure 2 (bottom panel) and demonstrate that the compositional range is similar throughout all fractions and resembles the S_1 and O_xS_1 species in the starting material (Figure 1). A notable difference in the oil-soluble photoproducts compared with the unirradiated fractions is that the irradiated surrogate sulfides are no longer present as a multimodal distribution across the carbon number, a trend which was observed for the parent fraction. An abbreviated version of the plots is shown (O_3S_1, O_4S_1, O_8S_1, and O_9S_1) to highlight differences between lower-order and higher-order oxygen-containing O_xS_1 species. A shift to higher aromaticity, as more oxygen atoms are incorporated (e.g., from O_3S_1 to O_9S_1), is observed for the DWH sulfides, as well as for the surrogate sulfides and thiophenes, and could indicate polymerization reactions in both fractions.

Figure S2 displays DBE versus carbon number plots for all O_xS_1 classes (O_3S_1 − O_9S_1) and shows remarkable similarity between classes and fractions. In particular, Figure S2 illustrates that the sulfides from both oils appear to be almost identical in terms of their carbon number and DBE ranges for each class. The thiophene fractions from both oils occupy similar compositional ranges for O_4S_1 and O_5S_1; however, the DWH thiophenes do not present with high enough abundance for comparison between other O_xS_1 classes (seen in Figure 2, top panel).

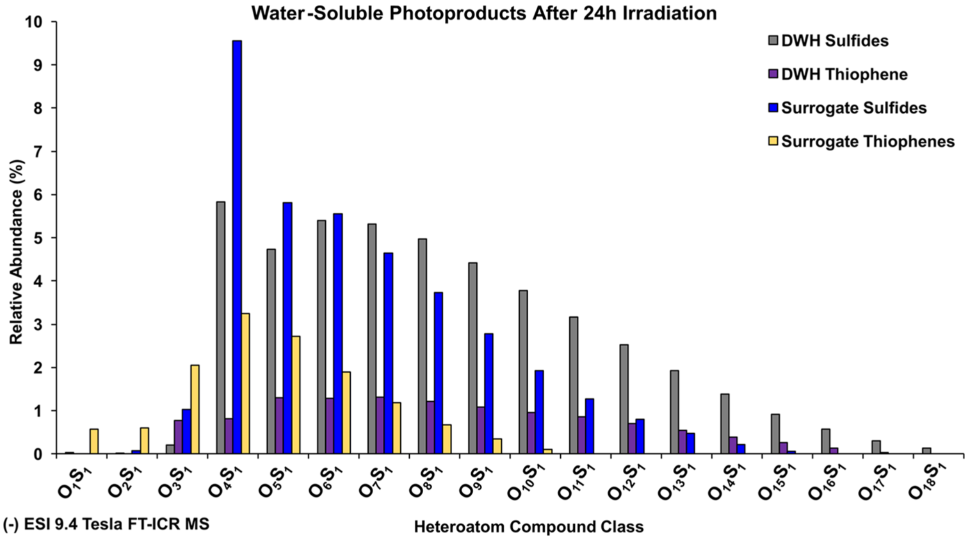

Figure 3. Heteroatom-compound class distribution for water-soluble photoproducts from DWH sulfides (gray), DWH thiophenes (purple), surrogate sulfides (blue), and surrogate thiophenes (yellow) after 24 h irradiation, showing abundant water-soluble SO_x compounds.

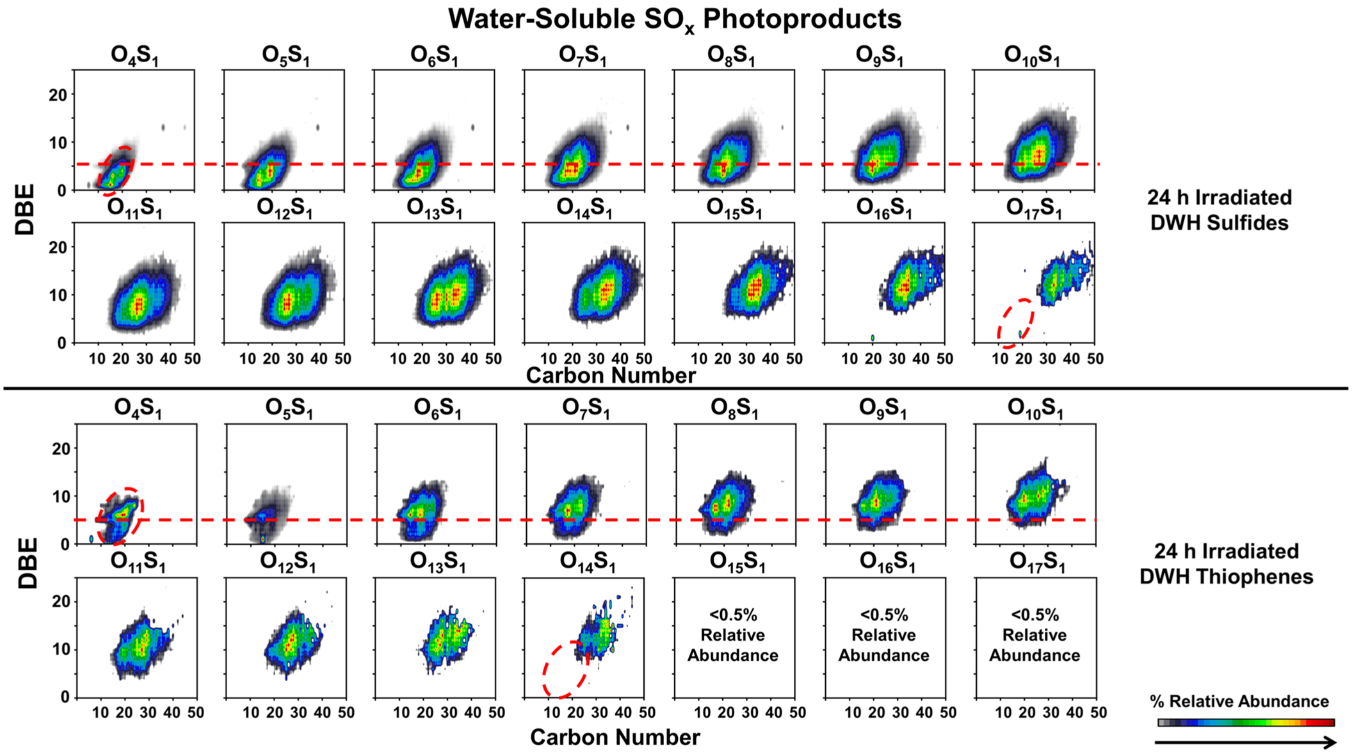

Figure 4. Isoabundance-contoured plots of DBE versus carbon number for water-soluble photoproducts from a 24 h irradiation period of DWH sulfides (top panel) and thiophenes (bottom panel) for the SO_x classes.

Water-Soluble Photoproducts from Surrogate and DWH Fractions. Water-soluble compounds have been demonstrated to form from DWH and surrogate crude oils;[42] however, the relative contributions from sulfur-containing species to the formation of water-solubles have not been studied. Following 24 h irradiation, the water-soluble species from DWH and surrogate sulfide/thiophene fractions were isolated and analyzed by (−) ESI FT-ICR MS. The heteroatom-compound class distribution for the water-soluble O_xS_1 species is shown in Figure 3; those compounds are considered to be phototransformation products from S_1 and lower-order O_xS_1 (x = 1−3) classes, which are present in high abundance for the fractions prior to irradiation (Figure 1). Figure 3 demonstrates that the water-soluble photoproducts from DWH and surrogate sulfides (gray and blue) are enriched in higher-order O_xS_1 species, with up to 18 oxygen atoms, which have formed through photooxidation. In agreement with the oil-soluble photoproducts, thiophene fractions from DWH and surrogate oils (purple and yellow) produce water-soluble O_xS_1 species in lower abundances than the sulfide fractions. Generally, the O_xS_1 distribution presents as a pseudo-Gaussian envelope for all fractions; an exception to this trend is the O_4S_1 species from DWH and surrogate sulfides, which exhibit the highest abundance relative to other O_xS_1 species.

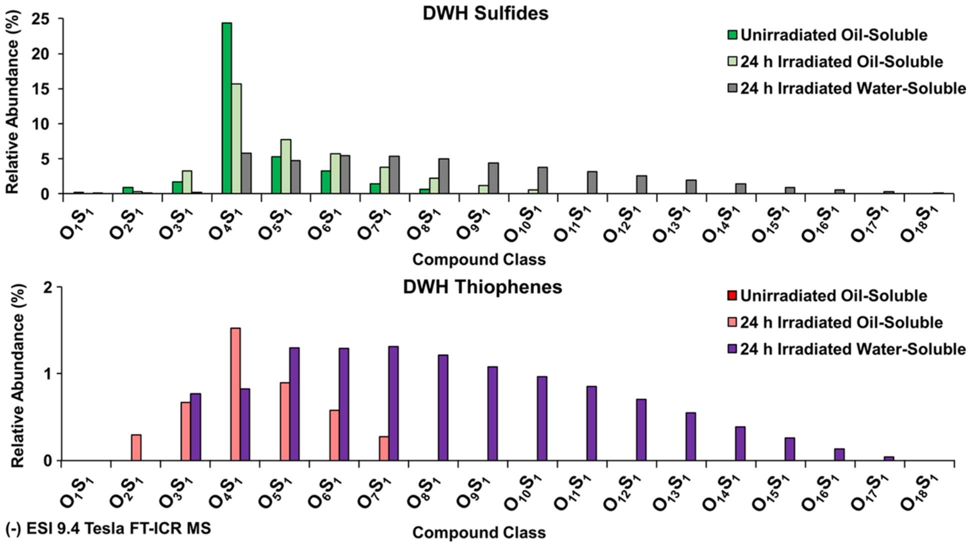

Figure 5. Heteroatom-compound class distributions for DWH sulfides (top panel) and thiophenes (bottom panel), showing the relative abundances of SO_x compounds detected by (−) ESI FT-ICR MS for the unirradiated fraction (green/red), 24 h irradiated oil-soluble fraction (light green/pink), and water-soluble fraction from 24 h irradiation (gray/purple), illustrating an oxygen continuum.

The sulfides from both oils and the thiophenes from both oils exhibit similar trends; however, it is important to note that the DWH sulfides and thiophenes extend to notably higher-ordered oxygenated O_xS_1 species ($O_{18}S_1$ and $O_{17}S_1$), whereas the surrogate sulfides and thiophenes are enriched in lower-order oxygenated species (e.g., O_3S_1) and contain only up to $O_{15}S_1$ and $O_{10}S_1$. This observation suggests that DWH sulfur fractions may be capable of incorporating additional oxygen atoms relative to surrogate fractions.

The isoabundance-contoured plots of DBE versus carbon number for the water-soluble photoproducts from 24 h irradiated DWH sulfide and thiophene fractions are displayed in Figure 4 and share similarity in terms of their compositional range. As previously noted for petroleum-derived water-soluble photoproducts, the higher-oxygenated compounds (e.g., $O_{17}S_1$) have higher aromaticity and carbon number than the less-oxygenated photoproducts (e.g., O_4S_1). This phenomenon is illustrated by the compositional range for O_4S_1 (traced in red), which is superimposed on higher-order photoproducts for the sulfide and thiophene fractions ($O_{17}S_1$ and $O_{14}S_1$). Polymerization reactions have been indicated as a possible explanation for the formation of high-DBE photoproducts from petroleum-derived materials.[13,14] Lower-order O_xS_1 species (e.g., O_4S_1-O_8S_1) occupy a compositional range with DBE < 5 for the sulfides and DBE > 5 for the thiophenes; this trend is illustrated by a horizontal red line at DBE = 5. However, in the higher-order O_xS_1 compounds (> $O_{10}S_1$), the difference is lost, for reasons that are still being investigated. The water-soluble photoproducts from the thiophene fraction also contain compounds with a major homologous series at DBE = 6 for the O_4S_1−O_6S_1 classes, corresponding to alkyl-substituted benzothiophene and were present in the starting material (Figure 1). The present results suggest that alkyl-substituted benzothiophene cores can survive early stages of photooxidation (low oxygen content).

The surrogate sulfide and thiophene water-soluble photoproducts from 24 h irradiation follow trends similar to those for DWH and are displayed in Figure S3. As previously noted, the surrogate photoproducts do not contain higher-order oxygenated compounds to the extent of the DWH photoproducts. Note that the thiophene fraction water-soluble products do not show the same benzothiophene hot spots at DBE = 6, which were observed in the surrogate oil starting material and in the DWH water-soluble photoproducts. However, generally, the water-soluble photoproducts from both DWH and surrogate oils have similar compositional ranges (carbon number and DBE).

photooxidation Trends for Light Crude Oil. Previous reports have noted trends in the prevalence of lower-order versus higher-order oxygenated compounds among virgin oil, oil-soluble photoproducts, and water-soluble photoproducts.[12−14] In particular, the virgin oil has been shown to contain only lower-order oxygenated species (e.g., O_1−O_3), whereas the oil-soluble photoproducts are composed of a combination of lower-order oxygenated species and some higher-order oxygenated compounds (from O_1−O_{10}). The water-soluble photoproducts contain a mixture of lower-order oxygenated species and very high-order oxygenated species (up to O_{18}).[13,14] These trends are observed for the (−) ESI FT-ICR MS extract for DWH thiophene and sulfide fractions (unirradiated oil, 24 h irradiated oil, and 24 h irradiated water), shown in Figure 5. The DWH sulfides (top panel) contain lower-order oxygenated O_xS_1 species (O_1S_1−O_8S_1), whereas the oil- and water-soluble photoproducts extend to higher-order oxygenated species (O_2S_1−$O_{10}S_1$ and O_1S_1−$O_{18}S_1$). The DWH thiophenes contain no appreciable O_xS_1 compounds before irradiation. Figure 1 might explain that result, because it shows low amounts of S_1 species in that fraction (~3% relative abundance), which can oxidize to form O_xS_1 compounds. Therefore, low-relative abundance (<2%) O_xS_1 photoproducts from DWH thiophenes are detected in the oil- and water-soluble fractions, which are illustrated in the bottom panel of Figure 5. The O_xS_1 photoproducts from DWH thiophenes present as a pseudo-Gaussian envelope, similar to the sulfides, and the oil-soluble photoproducts are enriched in lower-order oxygenated species (O_2S_1-O_7S_1), whereas the water-soluble photoproducts contain O_3S_1-$O_{17}S_1$ species.

In addition to differences in oxygen content between oil- and water-soluble photoproducts, previous work has also noted differences in their carbon number and DBE ranges. In particular, water-soluble species have been demonstrated to be smaller (lower carbon number) and less aromatic than their oil-soluble counterparts[12−14,43] and are observed from comparison of the DBE versus carbon number plots for oil-soluble photoproducts (Figure 2) and water-soluble photoproducts (Figure 4) from the sulfur fractions. Figure 6 presents the water- and oil-soluble O_6S_1 photoproducts from 24 irradiated DWH sulfides and demonstrates a difference in the compositional range; the most abundant O_6S_1 species in the water-soluble fraction (left panel, outlined in red) occupy a range at a lower carbon number and DBE than the oil-soluble species (right). Furthermore, the abundance-weighted average DBE and carbon number values displayed in each plot illustrate the differences in composition between water- and oil-soluble photoproducts. These results confirm that solubility/insolubility in water is dictated not only by oxygen content, but also by carbon content: a higher carbon content confers a higher hydrophobicity in a molecule and therefore requires a higher number of oxygen-containing functionalities to become water-soluble, in agreement with previous reports.[12,44]

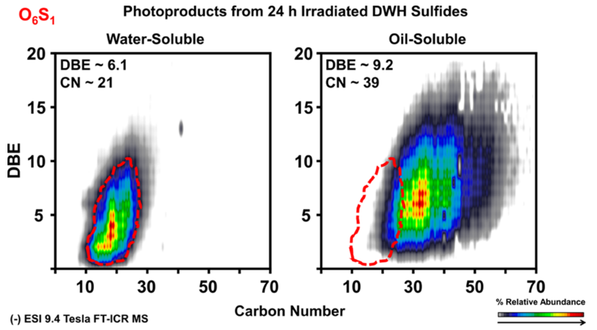

Figure 6. Isoabundance-contoured plots of DBE versus carbon number for O_6S_1 compounds from water- (left) and oil-soluble (right) photoproducts from 24 h irradiated DWH sulfides.

(+) ESI Analysis of Sulfur-Containing Photoproducts from Light Oil. Sulfur-Containing Photoproducts from Light Oil. Acidic species have been demonstrated to form through photooxidation and are readily detected by (−) ESI; however, ketones/aldehydes also form through photooxidation and can be analyzed by (+) ESI.[7] The sulfur fractions from DWH were therefore subjected to (+) ESI FT-ICR MS analysis to access ketone/aldehyde functionalities. The virgin sulfide and thiophene fractions from DWH contain appreciable amounts of O_1S_1 compounds (6 and 2% obtained by (+) APPI), and abundant O_xS_1 species are detected photoproducts by (+) ESI, which can be seen from the heteroatom-compound class plot in Figure 7. The sulfide fraction produces abundant oil-soluble O_xS_1 photoproducts (from O_1S_1 to O_5S_1), whereas the thiophenes do not, in agreement with the trend observed for the acidic O_xS_1 species accessed by (−) ESI (Figure 2). However, unlike the acidic photoproducts from the DWH sulfur fractions that contained higher-order oxygenated O_xS_1 species (up to O_9S_1), the (+) ESI photoproducts from DWH sulfides and thiophenes do not extend to higher-order oxygenated O_xS_1 species (only up to O_5S_1 and O_2S_1). The DBE versus carbon number plots for O_1S_1-O_5S_1 compounds from 24 h irradiated DWH sulfides are displayed in Figure 7 (insets) and reveal a shift to a higher DBE and carbon number with increased oxygen content (e.g., for O_5S_1). Sulfoxides (SO_x) may also ionize by (+) ESI upon addition of an acidic modifier, similar to ketones/aldehydes, suggesting the formation of sulfoxide species as photoproducts from sulfidic sulfur in DWH.[22] Conversely, DWH thiophenes do not produce abundant O_xS_1 photoproducts detected by (+) ESI.

Heavy Oil Distillate Cut Sulfur Separation. The light oils analyzed (DWH and surrogate) produced similar water- and oil-soluble photoproducts, and the sulfides were shown to produce more higher-order oxygenated species than the thiophenes. However, clear separation between the virgin sulfur fractions for thiophene and sulfides was not observed (Figure 1), and highly overlapped compositional ranges were revealed in both fractions. Furthermore, the sulfide and thiophene fractions from the light oils amounted to only <5 wt % of the total mass loaded onto the SPE cartridge and therefore comprised a small amount of the whole crude. To compare light oil sulfur photochemistry to that for heavy oil, a distillation cut from Arabian heavy crude oil was subjected to the sulfur separation, and the resulting fractions were irradiated for the analysis of the water- and oil-soluble sulfur-containing photoproducts. Figure S1, which was previously described for the light oils, also presents the gravimetric yields for the distillate, which yields much higher wt % for the sulfur fractions (~68 and ~18 wt % for the thiophene and sulfide classes), in accordance with their higher aromaticity. The thiophene fraction likely contains PAHs in addition to

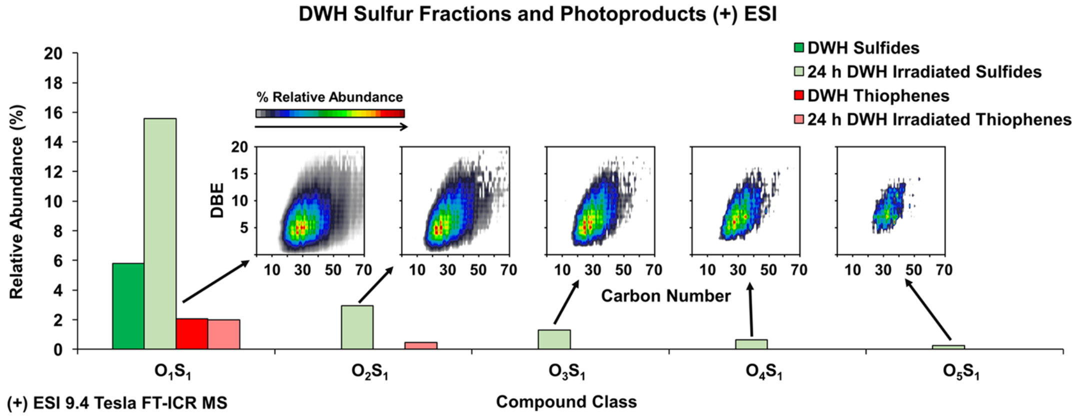

Figure 7. Heteroatom-compound class distribution and DBE versus carbon number plots (insets) for oil-soluble analysis of SO_x species in DWH sulfides and thiophenes (before and after 24 h irradiation), derived from (+) ESI FT-ICR MS.

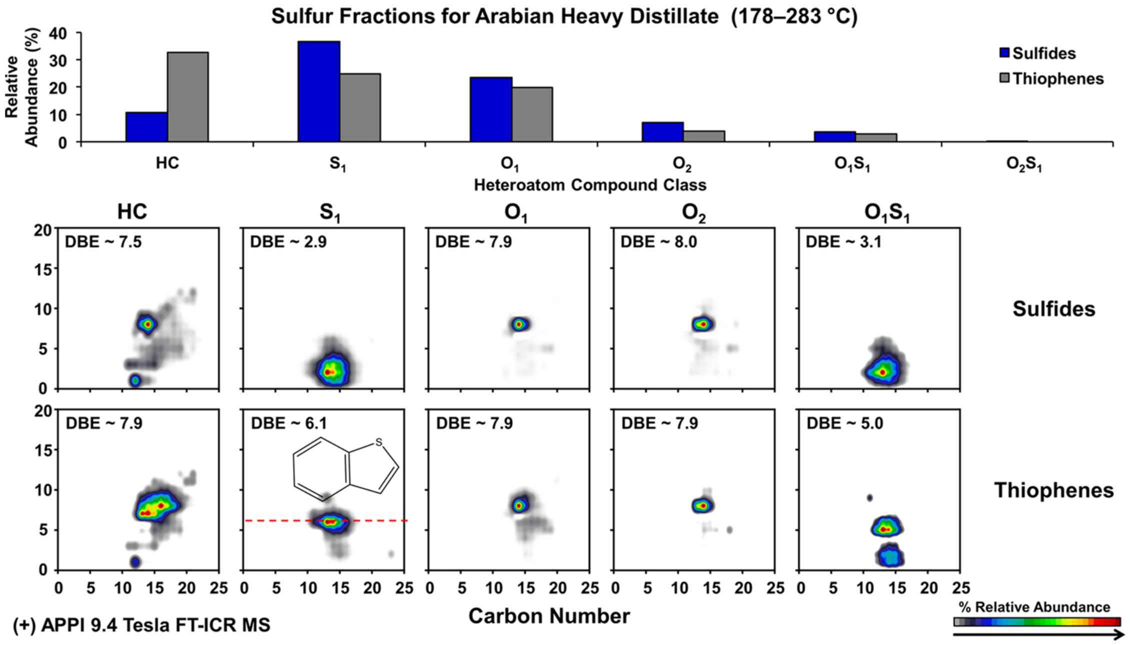

Figure 8. Isoabundance-contoured plots of DBE versus carbon number from (+) APPI FT-ICR MS analysis of Arabian heavy distillate sulfide and thiophene fractions, revealing differences in aromaticity between the two fractions.

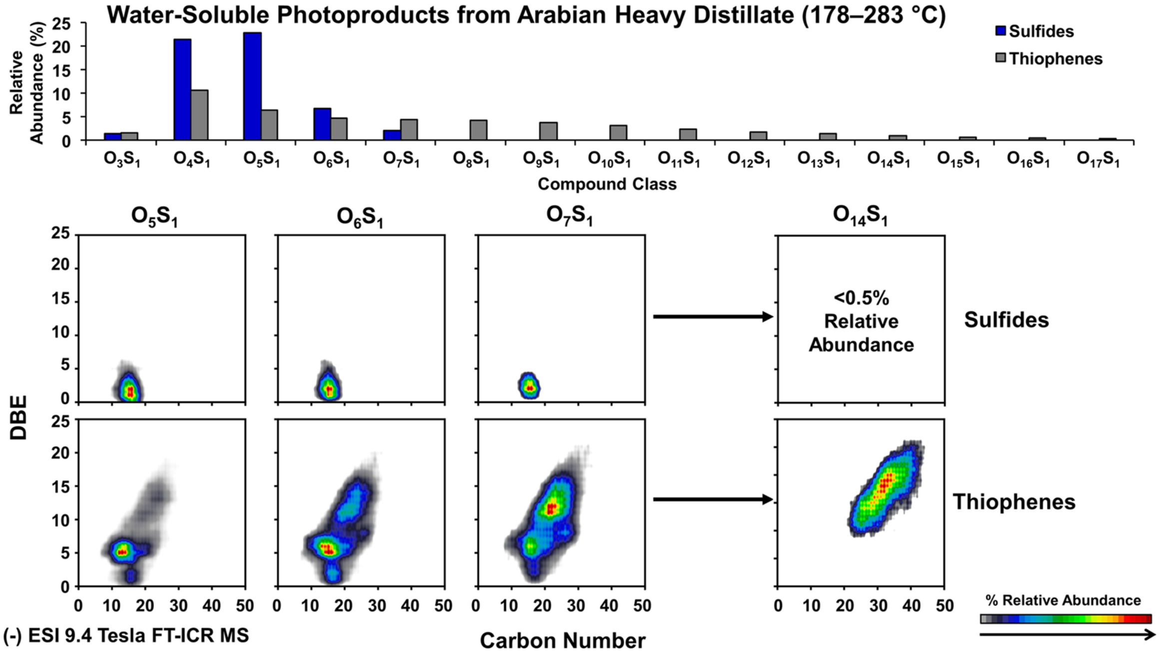

Figure 9. Heteroatom-compound class distribution (top panel) and DBE versus carbon number plots (bottom panel) for water-soluble SO_x photoproducts from 24 h irradiation of Arabian heavy distillate sulfur fractions.

aromatic sulfur because both motifs interact strongly with the Ag + stationary phase; therefore, the gravimetric yield for the thiophene fraction should be considered as the sum of aromatic sulfur and PAHs in the parent oil.

Figure 8 shows the heteroatom-compound class distribution (top panel) and corresponding DBE versus carbon number plots (bottom panel) for (+) APPI FT-ICR MS analysis of the sulfide and thiophene fractions from the Arabian heavy distillate cut (178−283 °C). The heteroatom-compound class distribution (top) reveals appreciable amounts of S_1, HC, O_1-O_2, and O_1S_1-O_2S_1 for both sulfur fractions from the Arabian heavy distillate. Generally, the sulfides are more abundant in S_1, O_x, and O_xS_1, whereas the thiophenes contained high amounts of hydrocarbon compounds without heteroatoms.

The DBE versus carbon number plots (Figure 8, bottom) illustrate a clear difference in the compositional range for sulfur-containing classes (S_1 and O_1S_1); the sulfides contain low-DBE species, whereas the thiophenes have higher DBE-compounds, as shown by their abundance-weighted average DBE values (top left corner). This observation is especially noticeable for the S_1 class, which illustrates good separation between sulfides and thiophene species; the sulfides exist at lower DBE values (DBE < 5), whereas the thiophene fraction

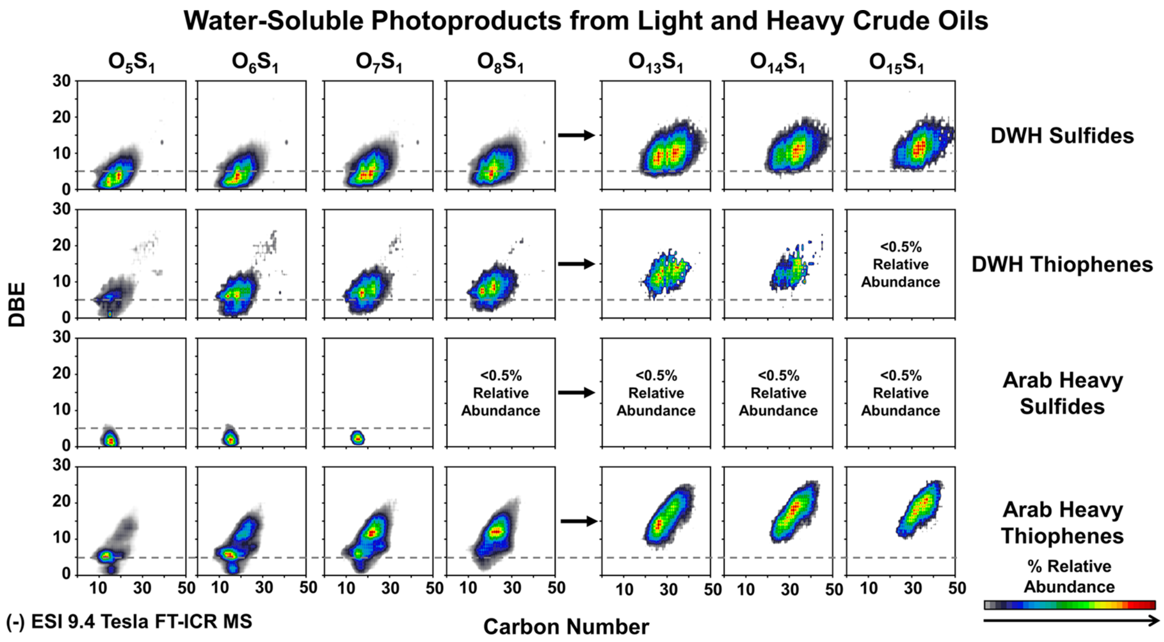

Figure 10. Isoabundance-contoured plots of DBE versus carbon number, illustrating differences in the compositional range for sulfur-containing water-soluble photoproducts from thiophene and sulfide fractions from DWH and Arabian heavy distillate derived from (−) ESI FT-ICR MS.

contains compounds with abundant S_1 species at DBE 6, which correspond to benzothiophene structures with various degrees of alkylation. The O_1S_1 class for thiophenes also contains a lower-DBE hot spot (separate distribution) with a compositional range similar to the sulfides, which may indicate some sulfidic compounds eluting in the thiophene fraction. However, a much clearer separation of the two functionalities (sulfides and thiophenes) is observed than for the light oils (DWH and surrogate). The HC and O_x classes contain higher-aromaticity species than the S1 and O_1S_1 classes; however, all species reside in a relatively small compositional range (10−23 carbons, 1−13 DBE), which is typical of distillation cuts of petroleum.

Water-Soluble Photoproducts from a Heavy Oil Distillate Cut. Following 24 h laboratory irradiation of the Arabian heavy distillate, the water-soluble fraction was analyzed by (−) ESI FT-ICR MS for the characterization of acidic photoproducts from a heavy oil distillate cut. Figure 9 displays the heteroatom-compound class distribution (top) and DBE versus carbon number plots (bottom) for the water-soluble photoproducts from sulfide and thiophene fractions and shows a much higher degree of photooxidation in the thiophene fraction than for the sulfide fraction. The water-soluble photoproducts from the sulfides (blue) produce only low oxygenated photoproducts (O_3S_1-O_7S_1), whereas those from the thiophene fraction (gray) are highly oxygenated and span from O_3S_1 to $O_{17}S_1$. The DBE versus carbon number plots suggest that sulfide photooxidation does not result in a significant change in the compositional range. The lack of a decrease in the carbon number and DBE suggests that sulfidic compounds do not undergo photofragmentation. Because the distillate cut has a constrained compositional range, with carbon numbers between 10 and 20 and DBE < 10, any increase in both carbon content and aromaticity would suggest that solar irradiation induces addition reactions, also known in oil spill chemistry as polymerization.[4,14] The thiophene fraction is highly susceptible to photooxidation reactions and produces abundant water-solubles that exhibit a ∼2.4-fold increase in DBE upon addition of more oxygen atoms (e.g., the abundance-weighted DBE values for O_5S_1 and $O_{15}S_1$ are 7.8 and 19.0). The abundance-weighted carbon numbers for those classes (O_5S_1 = 16.9 and $O_{15}S_1$ = 34.9) also indicate a ∼2.1-fold increase in the carbon number upon the addition of more oxygen atoms. These results indicate that thiophene-containing compounds are prone to photoinduced polymerization.

However, we suspect that the differences in the number of oxygen atoms incorporated depend upon the carbon number range of the fractions and not because of differences in photoreactivity between thiophenes and sulfides. For example, the sulfides occupy a narrow carbon number range (10−20 carbons) and thus are unable to take on more than seven oxygen atoms due to limited carbons. Conversely, the thiophenes undergo photoinduced polymerization and thus contain up to 45 carbons (e.g., $O_{14}S_1$) and can therefore incorporate more oxygen atoms (up to 17). It is important to note that previous studies have indicated that sulfides readily oxidize to sulfoxides (but not sulfones) upon thermal and chemical oxidation, whereas thiophenes do not oxidize.[26,27,45] However, we do not observe this trend for the heavy distillate cut and hypothesize that photooxidation versus other forms of oxidation involve different reaction pathways and thus produce different oxidized products. Moreover, the presence of aromatics in the thiophene fractions promotes photooxidation from sunlight because they are known to act as chromophores.

Comparison of Heavy Distillate Cut and Light Oil Photoproducts. The DBE versus carbon number plots for water-soluble photoproducts from DWH and Arabian heavy distillate sulfur fractions in Figure 10 reveal that the heavy oil distillate cut species appear to produce very different photoproducts upon irradiation of the two sulfur fractions, whereas the DWH sulfide and thiophene fractions produce almost identical photoproducts. However, the water-solubles from Arabian heavy distillate thiophenes exhibit trends similar to those observed for light oil (DWH sulfides and thiophenes). The distillate sulfides, which are largely aliphatic, do not appear to undergo polymerization reactions which are observed for the distillate cut thiophenes and in the light oil fractions. However, we suspect that the photoreactivity of the sulfides from light oils is enhanced in the presence of aromatic species that coelute in the sulfide fraction and act as chromophores to absorb light and promote photooxidation. The distillate cut showed better separation of sulfides and thiophenes than the light oils, and we suspect that the lack of aromatic species in the sulfides from the distillate cut made them poor chromophores and thus less photoreactive than the thiophenes.

Finally, highly oxygenated photoproducts (e.g., $O_{15}S_1$) from irradiation of Arabian heavy distillate thiophenes strongly suggest the formation of high-DBE compounds through photopolymerization reactions, because they exist at DBE values much higher than for the starting material and lower-oxygenated compounds (e.g., O_5S_1), indicated by the gray line. Another explanation for an increase in DBE values with increasing oxygen content is the formation of ketone/aldehyde functionalities through photooxidation, as previously demonstrated for DWH oil.[7]

CONCLUSIONS

In conclusion, sulfide- and thiophene-enriched fractions from light oils and a heavy distillation cut readily undergo photooxidation in the laboratory to produce abundant oil- and water-soluble O_xS_1 compounds, of unknown toxicity. Only slight differences were observed between the light oils; sulfur-containing photoproducts from DWH (e.g., O_xS_1) contained more oxygen atoms than those from the surrogate oil. Moreover, the low-DBE O_xS_1 species from the irradiated light oils match what was observed for field samples and preliminary studies. Although the separation of sulfides and thiophenes from light oils was complicated by the presence of sulfoxides in the starting material, the sulfide fractions produced higher-oxygenated O_xS_1 water-soluble species than the thiophenes. Both oils produced photoproducts similar to each other with only slight differences, and thus we conclude that the sulfur chemistry between surrogate and DWH oils is quite similar, with only subtle differences. Finally, we determined that the source of low-DBE photoproducts that were reported in a previous study was likely produced from photooxidized sulfide species[15] and that PAHs may act as chromophores to promote photooxidation of these species.

The distillate cut was fractionated more effectively than the light oils because of the low abundance of O_xS_1 species in the starting material, and the photoproducts varied accordingly. The sulfide fraction produced high abundances of water-soluble O_xS_1 species with up to only seven oxygen atoms, whereas the water-solubles from the thiophene fraction contained up to 17 oxygen atoms. Moreover, photoinduced polymerization occurred in the thiophenic fraction, which was enriched in chromophores, whereas the sulfide fraction does not appear to polymerize, in accordance with its low aromaticity. We hypothesize that the aliphatic sulfides in the distillate do not allow for polymerization because of the low abundance of aromatic species, which act as chromophores. Conversely, the sulfide fractions in the light oils contain aromatic species, which facilitate polymerization of the sulfides.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c02869.

Separation scheme for sulfur-containing species into three fractions (thiophenes, sulfides, and thiols) along with associated mass yields; DBE versus carbon number plots for surrogate and DWH sulfides and thiophene SO_x 24 h photoproducts (extension of Figure 2); and DBE versus carbon number plots for water-soluble SO_x species from (−) ESI FT-ICR MS analysis of the water-soluble extract from 24 h irradiated surrogate fractions (PDF)

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Notes

The authors declare no competing financial interest.

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