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Sulfur isotope exchange between thiophenes and inorganic sulfur compounds under hydrous pyrolysis conditions

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ABSTRACT

Sulfur isotope fractionation during thermal degradation of aromatic organic sulfur compounds was studied utilizing quartz tube-hydrous pyrolysis at 360 °C. BT (benzothiophene), DBT (dibenzothiophene), 3-PT (3-phenylthiophene) and 2-OT (2-octylthiophene) were used to represent organic sulfur compounds with a range of thermal stabilities. These compounds were heated for 40 h with and without the addition of reduced inorganic sulfur species: elemental S, sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) and sodium sulfite (Na_2SO_3). The extent of degradation of each compound showed good correlations with its aromatic stabilization and strongly depended on the added inorganic sulfur species, with DBT being the most stable and 2-OT the least stable. Sulfur isotope enrichments up to 2.2‰ resulted from the thermal degradation of thiophenes. A significant decrease in stability of thiophenes was observed in the presence of reduced sulfur species. In contrast, BT and DBT did not show any exchange of S isotopes with external reduced S pool, while 3-PT did experience S isotope exchange. The results of the present study suggest that the main controls on the $\delta^{34}\text{S}$ values of BT and DBT during TSR are the relative rates of their degradation and their formation from the reaction between TSR- H_2S and petroleum hydrocarbons. This finding improves our confidence in using the $\delta^{34}\text{S}$ of individual thiophenes as reliable proxies for the occurrence and extent of thermal maturation and thermochemical sulfate reduction.

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1. Introduction

Thermochemical sulfate reduction (TSR) is one of the most important secondary reactions that affect oil compositions in petroleum reservoirs (Orr, 1974; Machel, 2001). Sulfate in the reservoir is reduced by complex reactions to H_2S and other reduced species and is coupled to the oxidation of organic compounds (Goldstein and Aizenshtat, 1994; Machel, 2001). Laboratory experiments and theoretical calculations have shown that the sulfur isotopic fractionation between source sulfate and H_2S can reach about 20‰ (Harrison and Thode, 1957; Kiyosu, 1980; Kiyosu and Krouse, 1993; Goldstein and Aizenshtat, 1994; Watanabe et al., 2009; Oduro et al., 2011; Meshoulam et al., 2016). However, in most cases, field observations show that the sulfur isotope composition of the evolved H_2S is usually similar to its sulfate source, probably due to the solubility limitation of the gypsum in petroleum reservoirs (Krouse, 1977; Worden and Smalley, 1996). The H_2S produced reacts further with organic compounds, producing labile and aromatic organic sulfur compounds (OSCs) (Orr, 1974; Powell and Macqueen, 1984; Zhang et al., 2008, 2012; Walters

et al., 2011; Amrani et al., 2012). OSCs originally present in the petroleum are gradually replaced by new OSCs produced from the back reaction of H_2S with organic compounds. These neoformed OSCs carry the $\delta^{34}\text{S}$ value of their H_2S source which itself is similar to the sulfate source in most systems (Manzano et al., 1997). $\delta^{34}\text{S}$ values of specific OSCs were suggested to shift towards the coexisting H_2S in the reservoir according to their thermal stability and rate of formation (Amrani et al., 2012; Amrani, 2014). Based on this principle, the S-isotopic compositions of benzothiophene species (BTs) and dibenzothiophenes (DBTs) were suggested as a proxy for the occurrence and extent of reaction for TSR (Amrani et al., 2012). Because BTs are less thermally stable than DBTs (Katritzky and Balasubramanian, 1992), the measured S-isotopic signature of BTs is observed to shift to the original sulfate value faster than for DBTs. The difference between the $\delta^{34}\text{S}$ values of the two compounds (and their alkylated forms) has been used as a proxy for the occurrence and extent of TSR that an oil has experienced (Amrani et al., 2012; Gvirtzman et al., 2015; Li et al., 2015; Cai et al., 2016; Ellis et al., 2016).

A recent compound specific sulfur isotope analysis (CSSIA) study of TSR reaction mechanisms was conducted using *n*- C_{16} and several S species (elemental S, Na_2SO_3 , CaSO_4 , Na_2SO_4) in sealed gold tubes at 360 °C (Meshoulam et al., 2016). The ^{34}S values

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of early generated BT and DBT in these experiments were depleted up to 22.2‰ relative to the source sulfate, and rapidly converged to the $\delta^{34}\text{S}$ values of sulfate at the later stages of the reaction. Meshoulam et al. (2016) interpreted this fractionation pattern to be the result of two large kinetic isotope effects (KIE), the first one between sulfate and sulfite and the second between sulfite and OSCs. The convergence of the $\delta^{34}\text{S}$ values of the H_2S and the BT and DBT toward that of the sulfate was explained by the complete consumption of the reactive aqueous sulfate followed by sulfate dissolution becoming the rate limiting step. The H_2S evolved at this stage was suggested to be the main sulfurization agent of hydrocarbons. The balance between formation and degradation of OSCs and their associated fractionations was suggested to control the different rates in which BT and DBT converged to the $\delta^{34}\text{S}$ values of sulfate (Meshoulam et al., 2016). While the results of these experiments have shown that fractionation of $\delta^{34}\text{S}$ during the formation of BT and DBT from reaction of elemental S or H_2S and *n*-C16 is around 2–4‰, there are no such data for the thermal degradation of these compounds (Meshoulam et al., 2016).

Isotope exchange between reduced S species and OSCs may also contribute to the S isotope homogenization reported in Meshoulam et al. (2016). Amrani et al. (2006) showed that the degree of isotopic mixing/exchange is strongly dependent on the sulfur bonding in the compound. While compounds containing S–S bonds experienced rapid isotope mixing, thiols (C–SH) and DBT (aromatic C–S–C) did not react (Amrani et al., 2006). Other experiments, using radiolabeled (^{35}S) compounds under variable conditions suggested isotope exchange with thiols and sulfides at very different rates (Edwards et al., 1948; Douglas et al., 1949; Guryanova et al., 1952; Obloentsev and Nikitin, 1964; Fedoseev, 1990; Zielinski and Kanska, 1993; Yamada et al., 2003). However, because the temperatures in these prior studies were significantly lower (25–200 °C) than in the recent work by Meshoulam et al. (2016), it is difficult to directly deduce the possible isotopic exchange at 360 °C. At this relatively high temperature other S-bonding (e.g. thiophenes) may be active as well.

The aim of the present work was to study the sulfur-isotopic fractionation associated with the degradation of different thiophenic compounds with and without the presence of an external inorganic sulfur source. We employed similar experimental conditions (temperature of 360 °C) as Meshoulam et al. (2016) in order to gain insights comparable to those results and to explain and expand some of their conclusions. Furthermore, we endeavored to enhance our understanding of sulfur isotope fractionations of aromatic OSCs during TSR and possible sulfur isotope exchange reactions. Finally, we also aimed to improve our ability to use individual thiophenes as reliable proxies for the occurrence and extent of TSR.

2. Experimental

2.1. Reagents and standards

Sulfur hexafluoride (SF_6 , 500 ppm in He) was purchased from Praxair (PA, USA). The sulfur isotope reference materials NBS-127 (BaSO_4 ; $\delta^{34}\text{S} = 21.1\text{‰}$), IAEA-S-1 (Ag_2S ; -0.3‰), and IAEA-SO-6 (BaSO_4 ; -34.1‰) were purchased from the National Institute of

Standards and Technology (NIST) and used for calibration of in-house standards. Dichloromethane was purchased from BioLab, was analytical grade and distilled before use. All other chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and were > 95% pure.

2.2. Pyrolysis experiments

Pyrolysis experiments were conducted in quartz tubes with 6 mm internal diameter and 1 mm wall thickness. After flame sealing, each tube was 7 cm long with approximately 2 mL reactor volume. Prior to loading the tubes, they were cleaned using distilled mill-Q water and heated to 450 °C overnight. Each tube was loaded with 30 mg talc, 30 mg silica and 460 mg water containing 5.6 wt% MgCl_2 and 10 wt% NaCl as mineral buffer (Zhang et al., 2008), and thiophenes (BT, DBT, 3-PT, 2-OT) as detailed in Table 1. For the isotope exchange experiments, reduced sulfur species were added to the quartz tubes (Table 1).

The quartz tubes were flushed with Ar for 1.5 min and introduced into liquid nitrogen while being flame sealed. Six tubes were placed in a 100 mL Hastalloy C-276 reactor (Parr 4970). To ensure equal water pressure on both sides of the tube, 15 mL distilled mill-Q water was added to the reactor. The reactor was sealed and heated to 360 °C and reached an internal pressure of 187 ± 2 bar. The reaction times were measured once the reactor reached 360 °C (approximately 1.5 h). After 40 h, the reactors were turned off, cooled to room temperature over ~2 h. The exterior of the quartz tubes were cleaned, first with acetone and then by dichloromethane using an ultrasonic cleaner for 10 min each. Each tube was then cooled in liquid nitrogen, cut into three parts. Each part was then submerged in 10 mL dichloromethane in a sealed glass vial. The vials were then shaken on a vortex apparatus and agitated in an ultrasonic bath for 20 min assure quantitative extraction of the content. The solvent extracts were filtered using glass paper filters (Whatman-size 55 mm \times 435 μm , pore size 1.5 μm), recovered and combined.

2.3. GC-MS analysis and quantification

A gas chromatograph (GC) coupled to a quadrupole mass spectrometer (GC/MS Agilent 7890/5750, Agilent DB5-MS capillary column, 30 m, 0.25 mm, 0.25 μm) was used to identify individual OSC following previously published methods (Gvirtzman et al., 2015).

Peaks of specific compounds (e.g., BT, DBT, 3-PT, 2-OT, and thiophenol) were identified using retention times and mass spectra of authentic standards. Quantification of the reaction products relied upon using internal standards by adding squalane and naphthalene to each sample prior to the filtration of the samples. Relative response factors (RRF) of each compound against the standards were calculated using calibration curves in the range of 0–260 pmol/ μL . Blank experiments for each compound were conducted using the same procedure. All investigated samples were normalized to the recovery of the blank samples. The precision of the quantification was estimated by performing at least one duplicate experiment. The analytical errors, described in terms of relative standard deviation (1σ), were in the range of 5–10% except for the experiments of 3-PT with Na_2SO_3 where the standard

Table 1
Quantities of reagents used for the quartz-tube pyrolysis experiments.

S-source	Pyrolysis time (h)	BT (mmol)	DBT (mmol)	3-PT (mmol)	2-OT (mmol)	Talc (mg)	Silica (mg)	Solution (mg)	External S (mmol)
Non	40	0.027	0.027	0.025	0.027	30	30	460	0
$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	40	0.027	0.027	0.025	0.027	30	30	460	0.095
Na_2SO_3	40	0.027	0.027	0.025	0.027	30	30	460	0.095
Elemental S	40	0.027	0.027	0.025	0.027	30	30	460	0.095

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