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Perspective

Combining Experiment and Theory to Elucidate the Role of Supercritical Water in Sulfide Decomposition

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The cleavage of C-S linkages plays a key role in fuel processing and organic geochemistry. Water is known to affect these processes, and several hypotheses have been proposed, but the mechanism has been elusive. Here we use both experiment and theory to demonstrate that supercritical water reacts with intermediates formed during alkyl sulfide decomposition. During hexyl sulfide decomposition in supercritical water, pentane and CO+CO₂ were detected in addition to the expected six carbon products. A multi-step reaction sequence for hexyl sulfide reacting with supercritical water is proposed which explains the surprising products, and quantum chemical calculations provide quantitative rates that support the proposed mechanism. The key sequence is cleavage of one C-S bond to form a thioaldehyde via radical reactions, followed by a pericyclic addition of water to the C=S bond to form a geminal mercaptoalcohol. The mercaptoalcohol decomposes into an aldehyde and H₂S either directly or via a water-catalyzed 6-membered ring transition state. The aldehyde quickly decomposes into CO plus pentane by radical reactions. The time is ripe for quantitative modelling of organosulfur reaction kinetics based on modern quantum chemistry.

1. Introduction

Sulfur linkages are ubiquitous and important in biological systems¹, geochemistry^{2, 3}, and fuel chemistry⁴. Of particular interest is the chemistry of organosulfur compounds in the presence of water at high temperatures and pressures. Petroleum formation is thought to be accelerated by the presence of sulfur compounds with weak C-S bonds because they initiate free radical reactions^{5, 6}. Hydrous pyrolysis is a common method to simulate geochemical maturation of rocks containing organic material such as kerogen⁷, and some data suggests that the water is acting as a reactant⁸⁻¹⁰. However, the specific chemical reactions that occur in these conditions remain unclear.

Petroleum that formed over millions of years by this process retains its sulfur content. These sulfur atoms now have to be removed to form fuel and petroleum products. Sulfur in fuel damages the environment and human health directly (e.g. forming particulates and acid rain), and also indirectly by poisoning emission control catalysts¹¹⁻¹⁴. A new method for removing sulfur is supercritical water (SCW) desulfurization. SCW treatment of various oils has been shown to reduce its sulfur content, making it a potential alternative desulfurization method to the conventional hydrodesulfurization process that uses large quantities of H₂ and expensive catalysts¹⁵⁻¹⁸. However, despite much recent work in this field, the chemical mechanisms of sulfur compound decomposition in SCW and the role of water is controversial¹⁹⁻²¹.

Organic reactions in high temperature aqueous media have

been studied by many researchers, not just for sulfur compounds but for a wide range of compounds for applications such as biomass gasification and polymer recycling²². The interest stems from the interesting properties of water near its critical point at 374°C and 221 bar. Several recent reviews have been published on the topic of organic reactivity in near and supercritical water²³⁻²⁷. In the subcritical region, ionic reactions usually dominate, in part because the ion product K_w is three orders of magnitude higher than that of ambient liquid water. Water interacts strongly with ionic intermediates and transition states, and is often involved as a reagent e.g. in hydrolysis reactions. Many reactions that are acid-/base-catalyzed under ambient conditions have been shown to occur in this region without any added catalysts²³.

Water undergoes a drastic change in its properties as it passes through the critical point. The density and dielectric constant drop significantly and the ion product decreases by over 10 orders of magnitude. Generally, free-radical reactions are favored in SCW²⁸. When free radical reactions dominate, water is rather inert compared to most organics since the O-H bond strength in water is about 20 kcal/mole stronger than typical C-H bonds. However, there are a number of studies that show that organic compounds containing heteroatoms undergo both hydrolysis and radical reactions in both subcritical and supercritical water. For example, Taylor *et al.* showed that methyl tert-butyl ether undergoes acid-catalyzed hydrolysis up to 550°C at 250 bar²⁹. Klein *et al.* showed selectivity towards hydrolysis compared to pyrolysis increases with increasing water density under isothermal conditions for guaiacol, dibenzylether, and phenethyl

phenyl ether decomposition and suggested a S_N2 mechanism with H_2O as the most likely nucleophile³⁰. While several studies of organics in SCW have reported a range of products that suggest a mix of free radical and hydrolysis chemistry, often additional unexpected products have been observed as well, indicating gaps in current understanding of the chemistry.

The energy crisis of the 1970's and 1980's motivated research to convert coal and other heavy hydrocarbons into useful fuels using SCW²⁵ and recently interest in the process is rising again for upgrading heavy oil fractions and bitumen. These heavy hydrocarbons contain high amounts of sulfur and the ability to remove this impurity is a key feature of SCW upgrading processes. There has been much work done to evaluate the reactivities of various organosulfur compounds contained in these hydrocarbons^{24, 31}. Thiophenic rings have been consistently found to be unreactive in SCW in the absence of catalysts/additives³². On the other hand, aliphatic sulfur compounds such as thiols and sulfides have been found to react in SCW to varying degrees. However, the mechanism of the decomposition of these sulfur compounds is unclear. Katrizky *et al.* postulated radical mechanisms (not involving water) to explain their observation of alkene formation from octyl sulfide³³. Abraham and Klein investigated reactions of benzylphenylsulfide (BPS) in subcritical water and observed benzaldehyde as a major product, indicating that water was involved as a reactant, similar to Klein group's experiments on ethers³⁴. Abraham and Klein's measurements indicate free radical pyrolysis and hydrolysis are occurring on similar timescales. For the hydrolysis reaction, they proposed initial formation of benzyl alcohol through a substitution reaction, presumably followed by free-radical conversion of the alcohol to the aldehyde.

At the time those experimental studies were performed, accurate quantum chemical calculations on such complex systems were impractical, and most of the experiments were not designed to measure rate coefficients, so most of the proposed mechanistic hypotheses in the literature have not been comprehensively tested. Until recently it has been prohibitively expensive to make quantitatively-accurate theoretical predictions about how SCW will affect the chemistry of even simple organics, and even less is known about its effects on organosulfur chemistry. However, recent advances in computers, quantum chemistry³⁵⁻³⁷, and automated mechanism generation³⁸⁻⁴⁰ suggest it is time to address these longstanding questions.

In this Perspective, we take a combined experimental and theoretical approach to elucidate the reaction mechanism of the decomposition of alkyl sulfides (thioethers). In our prior work we demonstrated that the initial decomposition of alkyl sulfide in SCW is consistent with a simple free radical mechanism that does not include any reactions of water⁴¹. However, here we show that the detailed chemistry is more complicated than that simple picture suggests, and that water is intimately involved. A multi-step mechanism that involves a pericyclic hydrolysis step as well as several free radical reaction propagation steps explains all the data, including the unexpected observation of pentane and CO formation from hexyl sulfide decomposition in SCW. The proposed elementary steps are validated by a combination of experiments and quantum chemistry calculations.

2. Experimental Methods

The experimental component of this present work consists of two parts. In experiment 1, hexyl sulfide is treated with SCW with a detailed analysis of both oil and gas products in order to achieve carbon and oxygen balance. We also performed control experiments where we heated neat hexyl sulfide in the absence of water (a normal pyrolysis reaction) to elucidate the role of water in hexyl sulfide decomposition chemistry. Control experiments were also performed using other alkyl sulfides, to test the effect of alkyl chain length. In experiment 2, we performed studies on putative intermediate compounds with various sulfur and oxygen containing functional groups. In these experiments, a small amount of the putative intermediate was added to the alkyl sulfide / water mixture (1:10 mole ratio) under the same conditions as experiment 1, and its decomposition rate and products were measured.

For experiment 1, 0.92g of hexyl sulfide ($C_6H_{13}SC_6H_{13}$) spiked with naphthalene as an internal standard (10:1 mole ratio) was loaded with 3.5g water in a 24 mL 316-stainless steel batch reactor (SITEC). Naphthalene is a suitable inert standard due to its stability in SCW within the reaction time and temperature range of our experiments⁴². Air in the head space and dissolved in the liquids is flushed out with helium. 20 bar helium is left in the headspace of the reactor upon sealing to prevent water condensation in the cold spots (the small i.d. tubes leading to the pressure transducer and to the valve) and for ease of gas phase product collection. The sealed reactor was lowered into a 400°C fluidized sand bath (Techne FB-05) where, after 5 minutes, the pressure reached 275 bar. After the desired reaction time, the reactor is quenched in a water bath. The gas phase product is released into a gas sampling bag (Supel-inert multi-layer foil). Air downstream of valve 1 was pumped out with a vacuum pump prior to opening the valve to prevent air mixing in with the product gas. The reactor was then opened to recover the liquid products, which contained both oil and water phases. The liquid product is centrifuged at 1000 rpm for a minimum of 5 minutes for phase separation of the oil and aqueous phase product. This experiment was repeated without water (400°C, 55 – 66 bar) for the control experiments, and both experiments were also performed with pentyl sulfide, octyl sulfide, and dodecyl sulfide instead of hexyl sulfide.

The oil phase product was analyzed with a 7890A Agilent GC-FID equipped with a HP-5MS column (30m x 250 μ m x 0.25 μ m) and the gas phase product was analyzed with a Shimadzu GC-FID for light hydrocarbon products (GC-2014 with RT-Q bond column), 6890N Agilent GC-TCD for CO_2 and H_2S quantification (HP-1 column, 30.0m x 250 μ m x 0.25 μ m), and DeLuxe 5 Gas analyzer (NDIR) to measure the CO/CO_2 ratio. Since CO could not be detected directly in GC-TCD due to its retention time overlap with trace N_2 and O_2 , the amount of CO was calculated from the NDIR CO/CO_2 ratio measurement and the GC-TCD CO_2 concentration measurement. In all cases, sulfur in the product is in the form of H_2S in the gas phase (about 23% of initial sulfur) and six carbon sulfur species (hexanethiol, ethyltetrahydrothiophene and dimethyl- or ethyl-thiophene) in the oil phase (about 17%). Unfortunately, quantitative sulfur balance could not be obtained due to the high solubility of H_2S in the oil and aqueous product. The aqueous phase product turns to an

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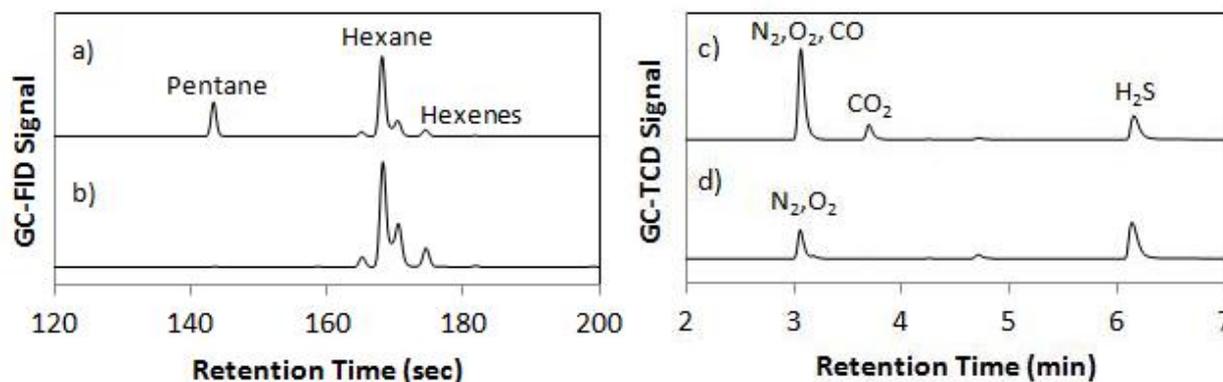


Fig 1. GC-FID Chromatogram of major oil phase products a) with SCW and b) without SCW, and GC-TCD chromatogram of major gas phase products c) with SCW and b) without SCW. A separate measurement of CO:CO₂ by an NDIR showed there is significant CO that overlaps with air (N₂+O₂) that leaked into the gas sampling bag in c) while there is no CO in d).

5 opaque white color after a few days suggesting the presence of H₂S dissolved in this liquid (which would slowly oxidize to form colloidal sulfur).

A control experiment where the stainless steel surface area was increased by adding a piece of SS 316L wool gave the same
10 conversion and product yields as when performed in the empty reactor, indicating that the rate-controlling steps for both sulfide conversion and the major product branching do not involve heterogeneous catalysis.

3. Computational Methods

15 Thermochemical and kinetic data were calculated at the CBS-QB3 level of theory using the Gaussian 03 quantum chemistry package⁴³. For the computational study, propyl sulfide was chosen as the reactant instead of hexyl sulfide. This reduces the computational time necessary with a negligible penalty in
20 accuracy compared with running calculations on the full hexyl sulfide molecule, as the substitution of groups more than one position away from a reactive center is known to have a minor effect on the rate parameters and enthalpies of reaction, particularly in alkyl chains⁴⁴. Thermochemistry parameters for ethane, ethyl radical, propane, propyl radical, H₂O, and CO had previously been calculated using CBS-QB3, and these values were used in this study⁴⁵. All stable compounds were calculated in their singlet state, and radical compounds were calculated in their doublet states. Partition functions were calculated using the
30 CanTherm software package⁴⁶, using a scaling factor of 0.99 for the frequency analysis. One-dimensional hindered rotations were also included in the analysis, using scans at the B3LYP/6-311G(2d,p) level for each rotatable bond. Hindered rotor scans were stepped in 20-degree increments, and all other coordinates
35 were allowed to re-optimize at each step holding the dihedral angle fixed. The effective moment of inertia I^(2,3) for each hindered rotor was calculated at the equilibrium geometry. NASA thermochemical parameters were calculated from the

partition functions with bond additivity corrections using
40 CanTherm, and these were used to calculate the enthalpy of the reactants and radicals at 673 K⁴⁷.

The reaction rates were computed using conventional transition state theory at the saddle point geometries. No saddle point could be found for reaction **b** (Scheme 1), and a scan of the
45 likely reaction coordinate showed the maximum energy at the product geometry. Thus, it was assumed the reverse of this reaction is barrierless. Transition states were optimized for reactions **c** and **d**, and the single-point energies for the reactants, products, and transition states of these reactions were recalculated
50 using CCSD(T)-F12a/vtz-F12, which has been found to provide more accurate energies than CBS-QB3^{36, 48}. Barrier heights for reactions **a**, **e**, and **f** were taken from prior work^{44, 49}.

4. Results and Discussion

4.1 Hexyl Sulfide Decomposition with and without SCW

55 In experiment 1, the decomposition products of hexyl sulfide with and without SCW were dramatically different. The product distribution of the SCW-treated hexyl sulfide and the non-SCW treated hexyl sulfide both contained hexane, isomers of hexene, and hexanethiol as major products. However, the SCW-treated
60 product also contained a large amount of pentane and CO+CO₂ while the non-SCW treated product contained none of these species to our detection limits (Fig. 1). NDIR measurement of the gas phase showed that the CO:CO₂ ratio in the SCW treatment product gas to be 1.9 ± 0.5 while the non-SCW treated product
65 had no CO or CO₂. Since water is the only oxygen containing species in the system, the observation of CO+CO₂ shows conclusively that water is reacting rather than merely acting as a solvent. Also, since the unexpected transformation of a C_m alkyl chain to a C_{m-1} species only occurs in the presence of water, the
70 data imply that the reaction that involves water results in breaking a C-C bond of the alkyl chain.

The results using other linear di-n-alkyl sulfides rather than

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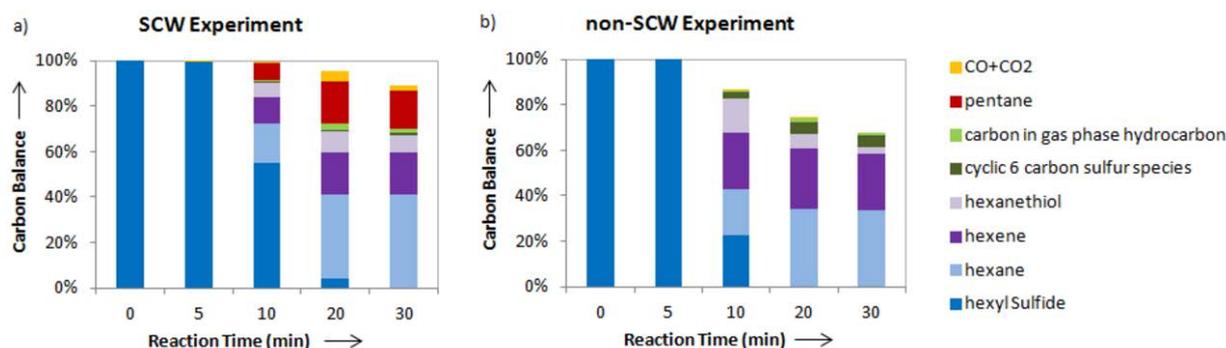


Fig. 2. Carbon Distribution of hexyl sulfide decomposition products after a) supercritical water (SCW) and b) non-SCW treatment. When hexyl sulfide is treated with SCW, pentane and CO/CO₂ are formed. These species are not produced without water. Carbon balance is maintained in the SCW experiment while in the non-SCW experiment, only 70% carbon balance is achieved in 30 minutes of thermal treatment, indicating formation of species which cannot pass through a GC.



Fig. 3. Oil phase product of hexyl sulphide with SCW (left) and without SCW (right). The color difference indicate that there are heavy compounds (coke or its precursor) not detected in GC-FID in normal pyrolysis of hexyl sulphide, showing that SCW treatment has the advantage of coke suppression in sulphide pyrolysis.

hexyl sulfide are completely analogous to the hexyl sulfide results. When reacted with SCW, octyl sulfide forms heptane+CO+CO₂ in addition to the normal pyrolysis products *n*-octane, octenes, and octanethiol. Similar results were obtained with di-*n*-pentyl sulfides and di-*n*-dodecyl sulfides: di-*n*-C_{*m*} sulfides reacted with water to form *n*-C_{*m*-1} alkane + CO+CO₂ in addition to the normal pyrolysis products (*n*-C_{*m*} alkane, C_{*m*} alkenes, and C_{*m*} thiols).

Our results are in apparent contradiction to a previous literature report on octyl sulfide decomposition in SCW.³³ Specifically, Katritzky *et al.* showed that octyl sulfide decomposed into 1-heptene (rather than the heptane we observed), 1-octene, and some octanethiol in water at 460°C.³³ They reported the same products were observed after replacing the water with cyclohexane. This is a major contradiction to our results. We attempted to replicate Katritzky's octyl sulfide experiments in SCW and cyclohexane in our reactor, but found only 1-heptane (not 1-heptene reported) and a mixture of octane,

octenes, and octanethiol in the presence of water. We did not observe any C₇ products when the water was replaced by cyclohexane. We suspect an error in the earlier report, but note that our apparatus does not achieve exactly the same conditions as the experiments of Katritzky *et al.*³³ so we cannot be definitive. In their experiments, the pressure in the reactor was not measured but from the amount of water they reported using, their pressure was higher than in our conditions. 1.0 g of octyl sulfide and 7.0 mL of water or cyclohexane was reportedly loaded in a 12.5 mL reactor in their experiments⁵⁰ while we loaded our 24 mL reactor with 2.0 g of octyl sulfide and 3.5 g of water or 3.0 g of cyclohexane. We were constrained to lower pressure (275 bar) in our reactor due to safety considerations.

In the present hexyl sulfide experiments including SCW, >90% of the carbon is accounted for by species detectable in both oil and gas phase by our analytical methods (Fig. 2). For the non-SCW experiments, on the other hand, only 60% carbon balance is achieved with our analytical method for the 30 minute oil product. We suggest that this is due to formation of heavy compounds that cannot be analyzed via GC due to their low volatilities. These heavy compounds are presumably responsible for a visible difference between the SCW-treated and non-SCW treated products: the SCW treated oil is a lightly yellow clear liquid whereas the non-SCW treated oil has a dark brownish black color (Fig. 3). These heavy compounds are likely to be coke or coke-precursors. The lack of color of the SCW treated product suggests coke suppression by SCW which is known to be one of major advantages of SCW upgrading¹⁷. Note that all the major species in Fig. 2 are colorless.

Having shown experimentally that water reacts in the SCW hexyl sulfide reaction, we sought to understand its role from a mechanistic point of view. Note that while water is clearly reacting, the alkyl sulfide is consumed at least as fast in the absence of water; consistent with this, our prior work on kinetics strongly suggested that the hexyl sulfide is consumed by reaction with a free radical⁴¹. Unsurprisingly, the major decomposition

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Compound	Matrix	Conversion				Selectivity		
		1 min	10 min	20 min	30 min	Heptane	Octene	Octane
Octanal	Hexyl Sulfide	-	87%	100%	100%	100%	0%	0%
Octanethiol	Hexyl Sulfide	-	-	-	68%	16%	37%	48%
Octanol	Hexyl Sulfide	-	-	-	33%	30%	-	-
Octanoic Acid	Hexyl Sulfide	-	-	-	0%	-	-	-
Thioacetic Acid	None	100%	100%	100%	100%	100% Acetic Acid		

Table 1. Compounds with various functional groups spiked into hexyl sulfide were treated in SCW to determine its conversion rate and selectivity towards C_{m-1} vs C_m products. The fast decomposition rate of octanal and its selectivity towards heptane as the product make aldehydes the most likely intermediates leading to the C_{m-1} alkane product.

5 products of hexyl sulfide are the six-carbon compounds (hexane, hexene, and hexanethiol) that are expected from radical reactions. The formation of pentane and $CO+CO_2$ as major side products is counterintuitive from a mechanistic point of view. Since the reactant contains two six carbon chains, we hypothesize a
 10 functionalized six carbon intermediate of hexyl sulfide decomposition that reacts with water to break a terminal C-C bond to yield CO and pentane. The measured $(CO+CO_2)/$ pentane molar ratio is 1:1 to within the limits of experimental uncertainty (0.8 ± 0.3). Our hypothesis is that CO is initially formed and
 15 subsequently undergoes water gas shift reaction to produce CO_2 and H_2 . The water gas shift reaction in SCW has been studied by a number of groups^{20, 51, 52} and while there is some uncertainty regarding the rate constant, the reported reaction time scales are consistent with our CO/CO_2 measurements. We hypothesize that
 20 when hexyl sulfide is treated with SCW, water reacts with an intermediate of hexyl sulfide decomposition to generate pentane and CO. In order to experimentally determine this intermediate, experiment 2 was performed.

4.2 Putative Intermediate Studies

25 In experiment 2, studies were performed to determine which proposed intermediate compounds decompose to lose one carbon from its carbon chain in SCW. One way to test this is to simply expose relevant model compounds to SCW and see if we detect products with one less carbon (e.g. pentane) and $CO+CO_2$.
 30 However, placing these compounds in SCW would not simulate the actual environment the intermediates are exposed to during the sulfide decomposition: our prior work indicates that the sulfides form free radicals which drive the chemistry.⁴¹ To replicate the reaction environment experienced during hexyl sulfide decomposition, we doped a small amount of the test
 35 compounds into the hexyl sulfide/SCW mixture. Our aim was to replicate the reaction mixture and conditions experienced by the intermediates during decomposition of neat hexyl sulfide in SCW, since the composition of the radical pool might influence
 40 decomposition rates and mechanisms.

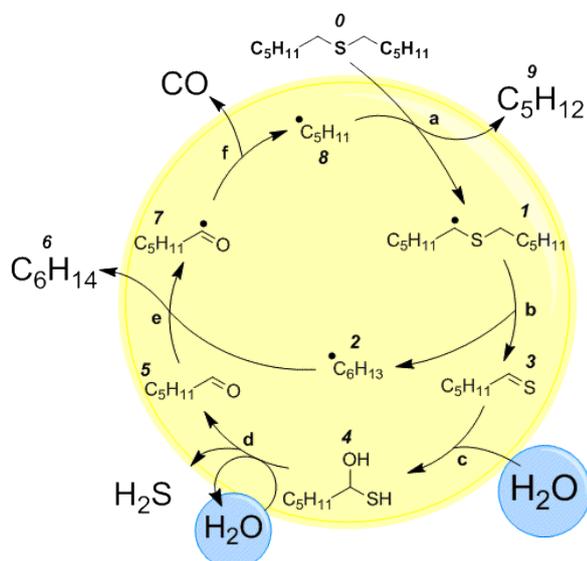
To distinguish the hexyl sulfide decomposition products from the products resulting from decomposition of the trial intermediates, we use the eight carbon equivalents of the potential

intermediates with the same functional groups (e.g. octanal rather than hexanal) so that these will decompose into 8 and 7 carbon species which can be distinguished from the hexyl sulfide decomposition species with 6 and 5 carbons. The goal is to test whether any eight carbon species likely to be formed from octyl sulfide decomposition would decompose rapidly to produce
 50 heptane and $CO+CO_2$ to get an insight into the route that di- C_m sulfide decomposition takes to make C_{m-1} alkanes and $CO+CO_2$. The compounds tested were aldehydes, thiols, alcohols, carboxylic acids, and thiocarboxylic acids. The experimental results are summarized in Table 1.

55 First, a mixture of octanal and hexyl sulfide was treated with SCW using the same procedure as in experiment 1. The octanal in hexyl sulfide experiment resulted in rapid decomposition of octanal into heptane (87% of octanal decomposed in 10 minutes, which includes a 5 min heat-up time; all of the aldehyde was
 60 consumed at >20 min). The fast decomposition rate combined with its high selectivity towards C_{m-1} alkane makes aldehyde a potential fast reacting intermediate to produce the correct products. This is also supported by our detection of trace amount of hexanal in 5 and 10 minute oil products during hexyl sulfide
 65 decomposition tests performed as part of experiment 1.

Octanethiol spiked into hexyl sulfide treated with SCW decomposed (68% conversion in 30 minutes) primarily into octane/octenes plus some (16% selectivity) heptane, while without SCW it formed only octane and octene. A separate
 70 experiment treating pure octanethiol (with no sulfides) in SCW resulted in the same mixture of octane/octenes and heptane in the liquid product, and $CO+CO_2$ was measured in the gas phase product. Based on these observations, we infer that the radicals from sulfide decomposition are apparently not needed to drive the
 75 chemistry in this case.

Only 33% of the octanol spiked into hexyl sulfide was decomposed in 30 minutes at 400°C. 30% of the octanol converted to heptanes. The slow decomposition rate of alcohol and the lack of observable alcohol product in experiment 1 show
 80 that alcohols can be ruled out as an intermediate for the C_{m-1} alkane formation from alkyl sulfide. Therefore, at 400°C alkyl sulfide reacts in water by a pathway that is different from that suggested by Abraham and Klein for benzyl phenyl sulfide



Scheme 1. Chain reaction that produces the major products pentane, CO, hexane, and H₂S from hexyl sulfide and water. Water plays two key roles in these steps: 1) in step c, water adds to a thioaldehyde to make a geminal mercaptoalcohol, and 2) in step d, water catalyzes the fragmentation of this geminal mercaptoalcohol into an aldehyde plus H₂S.

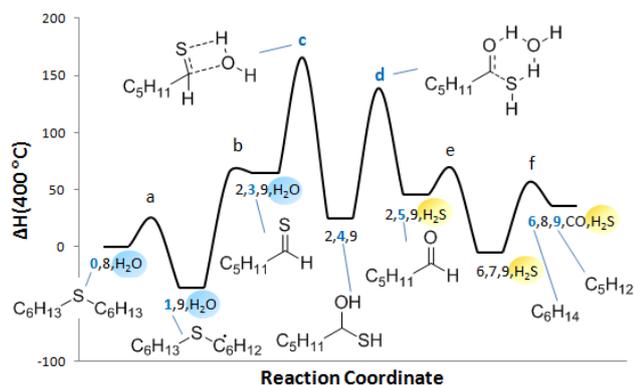


Fig. 4 Energy Diagram of Proposed Mechanism of Pentane Formation (energy in kJ/mol). Key steps in this otherwise radical-driven mechanism include the pericyclic addition of water to the C=S bond of the thioaldehyde (TS **c**) to form a geminal mercaptoalcohol (species 4) and the water catalyzed decomposition of species 4 to an aldehyde via TS **d**. Since there is a high concentration of water, the reaction proceeds to the right. The numbers separated by commas correspond to the species shown here and in Scheme 1.

(BPS)³⁴. Although both BPS and alkyl sulfides have the same sulfide linkage as the reaction center, one C-S bond in BPS is extraordinarily weak due to the adjacent aromatic rings, and the aromatic rings apparently also accelerate the hydrolysis chemistry.

Octanoic acid in hexyl sulfide was stable in SCW and its decomposition was less than detection limits over a 30 minute reaction time. Thioacetic acid was used as a model compound with a thiocarboxylic acid functional group since thiocarboxylic acids with longer carbon chains are not commercially available. Also, the compound was tested without any sulfide since it would interfere with the sulfide pyrolysis product in our GC analysis. Thioacetic acid rapidly converted into acetic acid and H₂S in SCW and the resulting carboxylic acid was shown to be stable under these conditions. Since no carboxylic acid is detected as

products from alkyl sulfide decomposition in SCW (experiment 1) these intermediates are ruled out. Experiment 2 indicates carboxylic acids and thiocarboxylic acids would not form pentane even if they were formed in experiment 1.

Experiment 1 shows that both hexanal and hexanethiol are formed during hexyl sulfide decomposition, and experiment 2 indicates that C_m aldehydes and C_m thiols both form C_{m-1} alkanes under our conditions, so both compounds contribute to the pentane observed in experiment 1. However, the C_{m-1} alkane is only a minor (16%) product from thiol decomposition, as ~84% of the thiol decomposes to C_m species instead. Moreover, thiol decomposition rates are relatively slow compared to the sulfide and aldehyde. So pathways via thiol, while undoubtedly contributing, are not nearly sufficient to explain the high (~40%) observed yield of C_{m-1} alkane during alkyl sulfide decomposition.

From all these studies, we conclude that the only viable major decomposition pathway leading to pentane + CO from hexyl sulfide is via a hexanal intermediate, which rapidly breaks down to pentane and CO. A secondary pathway involves sulfide conversion to hexanethiol, some of which slowly converts to pentane and CO.

While the experiments clearly implicate the importance of a hexanal intermediate, the experimental evidence does not clarify the mechanism of initial hexanal formation. To answer this question, we performed a series of quantum chemical simulations. Below we propose a mechanism via a thioaldehyde intermediate, which is an expected primary product from free radical decomposition of alkyl sulfides.

4.3 Mechanism of Hexyl Sulfide Decomposition in SCW

In accord with the available experimental data and subsequent calculations, we propose a radical mechanism for hexyl sulfide decomposition followed by a series of pericyclic reactions. As discussed in our previous work⁴¹, a free radical is expected to attack the α hydrogen on the hexyl sulfide. The following β scission forms the key intermediate thioaldehyde. We propose the thioaldehyde reacts with water to form the geminal mercaptoalcohol RCH(SH)OH. This mercaptoalcohol loses H₂S to form the corresponding aldehyde either directly or via a water-catalyzed reaction with a six-membered-ring transition-state. The aldehyde then decomposes into carbon monoxide and an alkane via well-known radical-catalyzed reactions. The net reaction explains the unexpected formation of CO and pentane from hexyl sulfides (Scheme 1). This mechanism is supported by transition state calculations, Fig. 4.

The first step (**a**) is hydrogen abstraction from the carbon adjacent to the sulfur atom, i.e., the α-hydrogen. Abstraction of the α-hydrogen has been shown to be favored due to the relative stability of the resulting radical species on the carbon adjacent to sulfur⁴⁴. β-scission of **1** makes a hexyl radical (**2**) which abstracts an H to form hexane (e.g. by reaction **e**), and hexanethioaldehyde (**3**). C=S bonds are known to be unstable and react rapidly, and on their own C=S bearing species will react rapidly with each other and polymerize⁵³. Indeed, this type of polymerization reaction could be responsible for the formation of high molecular weight material in the pyrolysis experiments performed in the absence of water. However, when the C=S bearing species remain dilute and are in the presence of excess water as in the SCW-treated experiments (the system of Experiment 1 is 97% by

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	Reaction	ΔH_{rxn} (400 °C) kJ/mol	ΔS_{rxn} (400 °C) J/mol*K	log(A) see note	n unitless	E_a kJ/mol	k_f (400 °C) see note
c	$\text{R}-\text{CH}_2-\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{R}-\text{C}(\text{OH})_2-\text{SH}$	-9.16	-31.7	-2.57	3.95	100.7	6.07
d (uncatalyzed)	$\text{R}-\text{C}(\text{OH})_2-\text{SH} \rightleftharpoons \text{R}-\text{CHO} + \text{H}_2\text{S}$	7.51	32.8	13.1	0.01	183.2	0.085
d (catalyzed)	$\text{R}-\text{C}(\text{OH})_2-\text{SH} + \text{H}_2\text{O} \rightleftharpoons \text{R}-\text{CHO} + \text{H}_2\text{S} + \text{H}_2\text{O}$	7.51	32.8	0.39	3.08	88.7	162

Table 2. Enthalpies and entropies of reaction, modified Arrhenius parameters, and forward rate constants at 400 °C for three reactions important to the formation of carbon monoxide from hexyl sulfide. A and k_f presented in $\text{cm}^3/\text{mol}\cdot\text{s}$ for reactions 1 and 3, and 1/s for reaction 2.

mole water), **3** reacts with water to form **4**, a geminal mercaptoalcohol, via reaction **c**. **4** decomposes into H_2S and hexanal either directly or via the water-catalyzed mechanism, reaction **d**. Reaction **c** [$\text{4} \rightleftharpoons$ thioaldehyde (**3**) + H_2O] and reaction **d** [$\text{4} \rightleftharpoons$ aldehyde (**5**) + H_2S] are sulfur homologs to the well known equilibrium between geminal diols and aldehyde + H_2O . Interestingly, only reaction **d** is significantly water catalyzed (according to our quantum chemistry calculations, water catalysis has negligible effect on reaction **c**). The decomposition of hexanal to pentane and carbon monoxide is predicted to be very fast under these radical-rich conditions, as seen in the low barriers **e** and **f** in Fig. 4. Because of the entropy gain due to forming several product molecules from a single large molecule reactant, and the large concentration of water, this partially equilibrated endothermic reaction sequence proceeds to the right (Fig. 4). The computed rates of the reactions shown in Table 2 are fast enough to explain the pentane yield observed in the experiments on the overall timescale of hexyl sulfide destruction measured here and previously by Patwardhan et al⁴¹, i.e. at the water concentrations used here, the thioaldehyde is predicted to be converted to pentane faster than it is formed by the free radical reactions, so it does not accumulate, which is in agreement with our failure to observe thioaldehyde in any of the product mixtures.

The computed thermochemistry and rates for the reactions involving water are given in Table 2. The standard state is ideal gas, $P=1$ atm. At our conditions the compressibility is approximately 2, so the activity $a_{\text{H}_2\text{O}} \sim 0.5 [\text{H}_2\text{O}]$, reducing the rates of reactions **c** and the water-catalyzed version of reaction **d** by about a factor of 2 from what one would compute using concentration mass action kinetics. All the other species in these reactions are dilute and so are assumed to have activities equal to their concentrations. At our experimental conditions, reaction **c** is computed to be the rate-controlling step for the secondary chemistry forming pentane. Free radical attack on hexyl sulfide, e.g. reaction **a**, is rate controlling for the overall decomposition⁴¹.

5. Conclusion

C_m alkyl sulfides have been shown to react with water (via a multistep radical-mediated mechanism) to form C_{m-1} alkanes and $\text{CO}+\text{CO}_2$. Experiments with several potential intermediates suggest that the reaction proceeds via the C_m aldehyde that breaks down into the C_{m-1} alkane plus CO . Quantum calculations support this reaction path, indicating that the C_m thioaldehyde is a key intermediate and that this species hydrolyzes via a pericyclic reaction similar to the well-known aldehyde to geminal-diol conversion. Interestingly, the conversion of the geminal mercaptoalcohol into aldehyde is catalyzed by water, and the hydrogen atoms needed to convert the sulfur to H_2S are provided by the water, rather than from H_2 gas. Water plays at least three important roles in the SCW decomposition of alkyl sulfides: as a reactant in a hydrolysis reaction of thioaldehyde, as the source of many of the H atoms needed for desulfurization, and as an H-transfer catalyst. Water also inhibits the formation of high-molecular weight products which are a major product in alkyl sulfide pyrolysis. This important effect is not fully understood, but it appears to be in part due to water removing thioaldehydes prone to polymerization, and in part by supplying H atoms and so reducing the formation of unsaturates. These multiple roles of water may also be important in understanding reactions of other organics in SCW.

The complexity of the chemistry of this relatively simple system may seem daunting. Unlike the situation with hydrocarbons, organosulfur chemistry is data-sparse, and the thermochemistry as well as the reaction rates of many of the key intermediates such as thioaldehydes and sulfur-containing radicals is highly uncertain. Many of the technologically important processes (e.g. SCW desulfurization; geochemistry) occur at pressures which make *in situ* experimental probing very difficult. However, the increasing availability of accurate quantum chemical calculations for organosulfur reactions and reactive intermediates⁵⁴ and the inclusion of organosulfur species into automated modelling software such as RMG³⁸, coupled with recent improvements in analytical chemistry technology, now make it practical to understand complicated systems involving sulfur at a level of detail which was impossible in the past. These

new tools should allow us to resolve many long-standing mechanistic questions, and to quantitatively predict the chemistry of important high pressure, high temperature organosulfur systems.

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