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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 systems, geochemistry, and fuel chemistry. 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. Hydrous pyrolysis is a common method to simulate geochemical maturation of rocks containing organic material such as kerogen, and some data suggests that the water is acting as a reactant. 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 catalysts. 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 hydrosulfurization process that uses large quantities of H₂ and expensive catalysts. However, despite much recent work in this field, the chemical mechanisms of sulfur compound decomposition in SCW and the role of water is controversial.

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 recycling. 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 water. In the subcritical region, organic 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 in hydrolysis reactions. Many reactions that are acid-/base-catalyzed under ambient conditions have been shown to occur in this region without any added catalysts.

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 SCW. 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 bar. Klein et al. showed selectivity towards hydrolysis compared to pyrolysis increases with increasing water density under isothermal conditions for guiacol, dibenzylether, and phenethyl.
phenyl ether decomposition and suggested a $S_N2$ mechanism with 
$\text{H}_2\text{O}$ as the most likely nucleophile\(^\text{10}\). 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 
SCW\(^\text{23}\) 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\(^\text{24, 31}\). Thiophenic rings have been consistently found 
to be unreactive in SCW in the absence of catalysts/additives\(^\text{32}\). 
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 sulfide\(^\text{33}\). Abraham and Klein 
investigated reactions of benzylenesulfide (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 ethers\(^\text{34}\). 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, 
previously 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 chemistry\(^\text{35-37}\), and 
automated mechanism generation\(^\text{38-40}\) suggest it is time to 
address these longstanding questions.

In this Perspective, we take a combined experimental and 
thoretical approach to elucidate the reaction mechanism of the 
de 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 water\(^\text{41}\). 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 
alcohol 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$_6$H$_{13}$SC$_6$H$_{13}$) 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 experiments\(^\text{42}\). 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 (Technoe 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 250μm x 0.25μm) 
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$_2$S 
quantification (HP-1 column, 30.0μm x 2.5μm x 0.25μm), and a 
De Jaye 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 
CO$_2$ concentration measurement. In all cases, sulfur in 
the product is in the form of H$_2$S in the gas phase (about 23% 
of initial sulfur) and six carbon sulfur species (hexanethiol, 
ehtyltetrahydrothiophene 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$_2$S in the oil 
and aqueous product. The aqueous phase product turns to an
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 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

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 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 chains 44. 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 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 were allowed to re-optimize at each step holding the dihedral angle fixed. The effective moment of inertia I_{23} for each hindered rotor was calculated at the equilibrium geometry. NASA thermochemical parameters were calculated from the partition functions with bond additivity corrections using 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 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 using CCSD(T)-F12a/vtz-F12, which has been found to provide more accurate energies than CBS-QB336, 48. Barrier heights for reactions a, e, and f were taken from prior work44, 49.

4. Results and Discussion

4.1 Hexyl Sulfide Decomposition with and without SCW

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 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 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 C₅ alkyl chain to a C₄ species only occurs in the presence of water, the 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...
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.

Our results are in apparent contradiction to a previous literature report on octyl sulfide decomposition in SCW. 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. 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. 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 7.0mL of water or cyclohexane was reportedly loaded in a 12.5 mL reactor in their experiments while we loaded our 24mL reactor with 2.0 g of octyl sulfide and 3.5g 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 upgrading. 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 radical. Unsurprisingly, the major decomposition...
4.2 Putative Intermediate Studies

Subsequently undergoes water gas shift reaction to produce \( \text{CO}_2 \) (0.8±0.3). Our hypothesis is that \( \text{CO} \) is initially formed and subsequently undergoes water gas shift reaction to produce \( \text{CO}_2 \) and \( \text{H}_2 \). 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 \( \text{CO}/\text{CO}_2 \) measurements. We hypothesize that when hexyl sulfide is treated with SCW, water reacts with an intermediate of hexyl sulfide decomposition to generate pentane and \( \text{CO} \). In order to experimentally determine this intermediate, experiment 2 was performed.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Matrix</th>
<th>Conversion</th>
<th>Selectivity</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Octanol</td>
<td>1 min</td>
<td>10 min</td>
</tr>
<tr>
<td>Octanal</td>
<td>Hexyl Sulfide</td>
<td>-</td>
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<tr>
<td>Octanethiol</td>
<td>Hexyl Sulfide</td>
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<tr>
<td>Octanal</td>
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<td>Octanolic Acid</td>
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<tr>
<td>Thioacetic Acid</td>
<td>None</td>
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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.

Products of hexyl sulfide are the six-carbon compounds (hexane, hexene, and hexanethiol) that are expected from radical reactions. The formation of pentane and \( \text{CO}+\text{CO}_2 \) as major side products is counterintuitive from a mechanistic point of view. Since the reactant contains two six carbon chains, we hypothesize a functionalized six carbon intermediate of hexyl sulfide decomposition that reacts with water to break a terminal C–C bond to yield \( \text{CO} \) and pentane. The measured \( \text{CO}+\text{CO}_2/\text{pentane} \) molar ratio is 1:1 to within the limits of experimental uncertainty (0.8±0.3). Our hypothesis is that \( \text{CO} \) is initially formed and subsequently undergoes water gas shift reaction to produce \( \text{CO}_2 \) and \( \text{H}_2 \). 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 \( \text{CO}/\text{CO}_2 \) measurements. We hypothesize that when hexyl sulfide is treated with SCW, water reacts with an intermediate of hexyl sulfide decomposition to generate pentane and \( \text{CO} \). In order to experimentally determine this intermediate, experiment 2 was performed.

4.2 Putative Intermediate Studies

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 \( \text{CO}+\text{CO}_2 \). However, placing these compounds in SCW would not simulate the actual environment the intermediates are exposed to during 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 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 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 heptane and \( \text{CO}+\text{CO}_2 \) to get an insight into the route that di-\( C_m \) sulfide decomposition takes to make \( C_{m-1} \) alkanes and \( \text{CO}+\text{CO}_2 \). The compounds tested were aldehydes, thiols, alcohols, carboxylic acids, and thiocarboxylic acids. The experimental results are summarized in Table 1.

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 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 decomposition tests performed as part of experiment 1.

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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 experiment treating pure octanethiol (with no sulfides) in SCW resulted in the same mixture of octane/octenes and heptane in the liquid product, and \( \text{CO}+\text{CO}_2 \) 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 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 alcohols and the lack of observable alcohol product in experiment 1 show 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.
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 $C_n$ 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 $C_m$-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 $C_m$-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 work,[4] a free radical is expected to attack the $\alpha$ hydrogen on the hexyl sulfide. The following $\beta$ scission forms the key intermediate thioaldehyde. We propose the thioaldehyde reacts with water to form the geminal mercaptoalcohol $RC\text{H}(SH)\text{OH}$. This mercaptoalcohol loses $H_2S$ 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 $\alpha$-hydrogen. Abstraction of the $\alpha$-hydrogen has been shown to be favored due to the relative stability of the resulting radical species on the carbon adjacent to sulfur.[4] $\beta$-scission of I 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 polymerize.[5] 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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**Scheme 1.** Chain reaction that produces the major products pentane, CO, hexane, and $H_2S$ 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 $H_2S$.

**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 e) 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.

Octanoic acid in hexyl sulfide was stable in SCW and its decomposition was less than detection limits over a 30 minute reaction time. Thiocacetic acid was used as a model compound with a thioacarboxylic acid functional group since thioacarboxylic 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. Thiocacetic acid rapidly converted into acetic acid and $H_2S$ in SCW and the resulting carboxylic acid was shown to be stable under these conditions. Since no carboxylic acid is detected as
mole water), 3 reacts with water to form 4, a geminal mercaptoalcohol, via reaction c. 4 decomposes into H2S and hexanal either directly or via the water-catalyzed mechanism, reaction d. Reaction e [4 ⇄ thioaldehyde (3) + H2O] and reaction d [4 ⇄ aldehyde (5) + H2S] are sulfur homologs to the well known equilibrium between geminal diols and aldehyde + H2O. 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 al.41, 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 aH2O ≈ 0.5 [H2O], 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 decomposition.

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, presented in cm3/mol s for reactions 1 and 3, and 1/s for reaction 2.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH$_{\text{rxn}}$ (400 °C)</th>
<th>ΔS$_{\text{rxn}}$ (400 °C)</th>
<th>log(A)</th>
<th>n</th>
<th>E$_{\text{a}}$ (400 °C)</th>
<th>k (400 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c R&lt;sup&gt;S&lt;/sup&gt;H + H2O ⇌ OH R&lt;sup&gt;SH&lt;/sup&gt;</td>
<td>-9.16</td>
<td>-31.7</td>
<td>-2.57</td>
<td>3.95</td>
<td>100.7</td>
<td>6.07</td>
</tr>
<tr>
<td>d (uncatalyzed)</td>
<td>7.51</td>
<td>32.8</td>
<td>13.1</td>
<td>0.01</td>
<td>183.2</td>
<td>0.085</td>
</tr>
<tr>
<td>d (catalyzed)</td>
<td>7.51</td>
<td>32.8</td>
<td>0.39</td>
<td>3.08</td>
<td>88.7</td>
<td>162</td>
</tr>
</tbody>
</table>

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 CO+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 H2S are provided by the water, rather than from H2 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 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 intermediates and the inclusion of organosulfur species into automated modelling software such as RMG, 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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