Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

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

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1. Experimental Methods

1.1 Reactor

A high pressure/temperature batch reactor was constructed from SS316 Sitek parts. A 20mm length 11/16" nipple (730.1003) is used as the reactor body with a plug (725.2117) on the bottom and a cross (725.1324) at top. The cross has a safety head (720.5013) with an Inconel 625 rupture disk (rated for 1400 bar at 20°C) on the top opening , one arm leading to a pressure transducer (Omega) and the other to a gas inlet/outlet valve (figure 1).

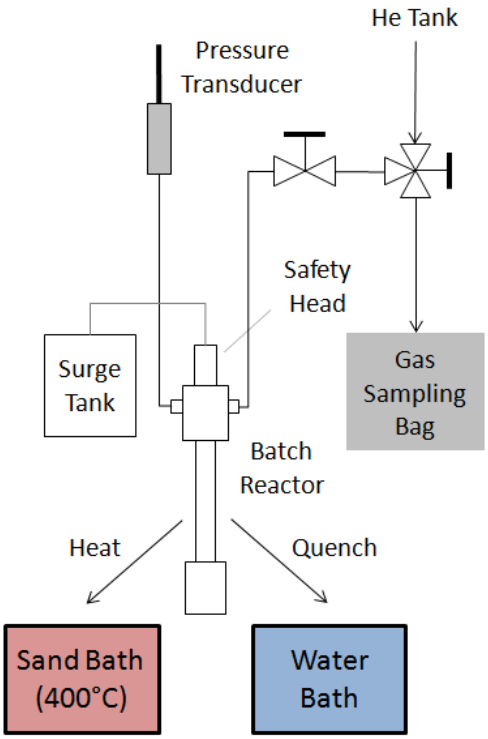


Figure 1. Batch Reactor Setup

1.2 Material

Di-n-hexyl Sulfide (95%), Di-n- octyl sulfide (96%), Di-n-dodecyl sulfide (93%), naphthalene (99%), octanal (99%), octanethiol (≥99%), octanoic acid (98%), and thioacetic acid (96%) were all purchased from Sigma

Aldrich. Di-n-pentyl sulfide (97%) was purchased from Alfa Aesar. Water used in SCW experiments were filtered with Elga Purelab Ultra.

2. Details of Experiment 1 Results

Figure 2 shows the oil phase product of the SCW experiment and non-SCW experiment after 30 minutes of treatment. The SCW experiment product is clear and slightly yellow while the non-SCW experiment product is dark brown, indicating formation of heavy molecules (coke or its precursor).

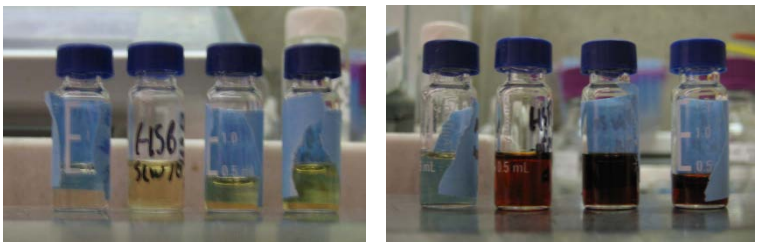


Figure 2 Organic Phase Product of Hexyl Sulfide SCW Experiment 5, 10, 20, 30 min (Left) and non-SCW 5, 10, 20, 30 min experiment (Right)

Products from the SCW experiments (Table 1) and non-SCW experiments (Table 2) are in the tables below. Although we are confident about hexene 1 being 1-hexene, the position of the double bond in hexene 2 and hexene 3 were not determined. Similarly for ethylthiophene, the positions of the ethyl group (2- vs 3-) were not identified for these experiments.

Table 1 Products obtained from SCW Treatment of Hexyl Sulfide

Compound	0 min	5 min	10 min	20 min	30 min
Pentane	-	-	0.17	0.46	0.41
Hexene 1	-	-	0.12	0.10	0.08
Hexane	-	-	0.34	0.74	0.82
Hexene 2	-	-	0.06	0.17	0.19
Hexene 3	-	-	0.05	0.09	0.11
Hexanal	-	-	0.03	-	-
Ethylthiophene 1	-	-	-	-	-
Ethylthiophene 2	-	-	-	-	-
Dimethylthiophene	-	-	-	-	-
Hexanethiol	-	-	0.13	0.19	0.14
Ethyltetrahydrothiophene	-	-	0.01	0.02	0.02
Hexyl Sulfide	1.00	1.00	0.55	0.04	-

Table 2 Products obtained from Thermal Treatment (Non-SCW) of Hexyl Sulfide

Compound	0 min	5 min	10 min	20 min	30 min
Pentane	-	-	-	-	-
Hexene 1	-	-	0.18	0.09	0.09
Hexane	-	-	0.41	0.60	0.67
Hexene 2	-	-	0.21	0.25	0.27
Hexene 3	-	-	0.11	0.13	0.13
Ethylthiophene 1	-	-	0.04	0.04	0.03
Ethylthiophene 2	-	-	0.01	0.02	0.03
Dimethylthiophene	-	-	-	0.02	0.03
Hexanethiol	-	-	0.30	0.12	0.06
Ethyltetrahydrothiophene	-	-	0.01	0.02	0.02
Hexyl Sulfide	1.00	1.01	0.23	0.00	0.00

The GC-FID chromatogram of the 30 minute oil phase product is shown below (Figure 3). Figures 4-6 shows the close-ups of the various retention time (RT) segments that contain important peaks. In both SCW and non-SCW products, most of the hexyl sulfide is gone (Figure 6). The most significant difference of the SCW and non-SCW treated product is the presence of pentane in the SCW product and the lack of this peak in the non-SCW product (Figure 4). There are a few sulfur compounds containing 6 carbons seen in Figure 5.

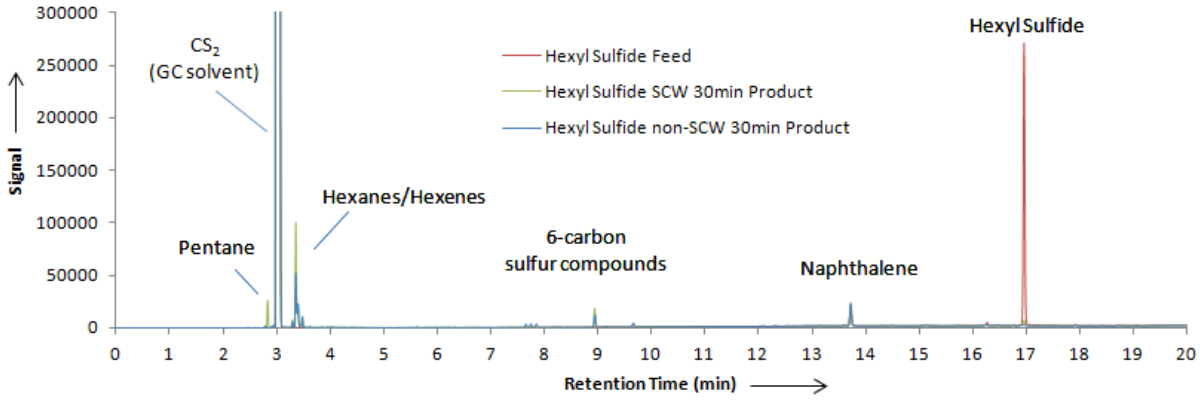


Figure 3. GC-FID Chromatogram of Hexyl Sulfide Experiment 1 Oil Products

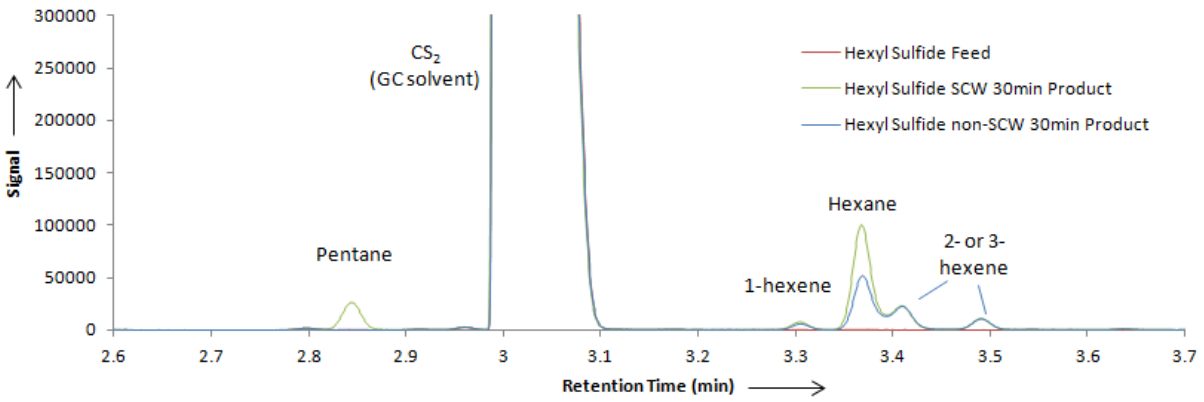


Figure 4. GC-FID Chromatogram of Hexyl Sulfide Experiment 1 Oil Products (Close Up RT 2.6-3.7min)

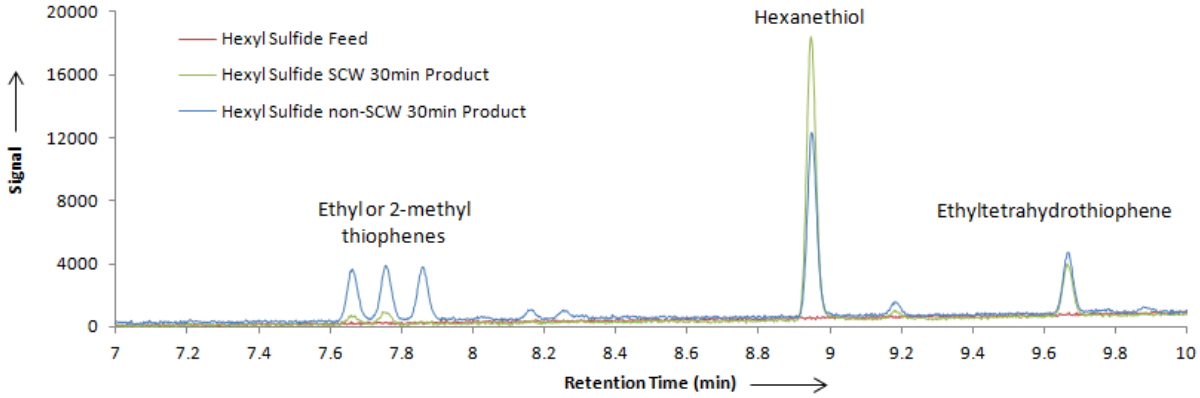


Figure 5. GC-FID Chromatogram of Hexyl Sulfide Experiment 1 Oil Products (Close Up RT 7-10min)

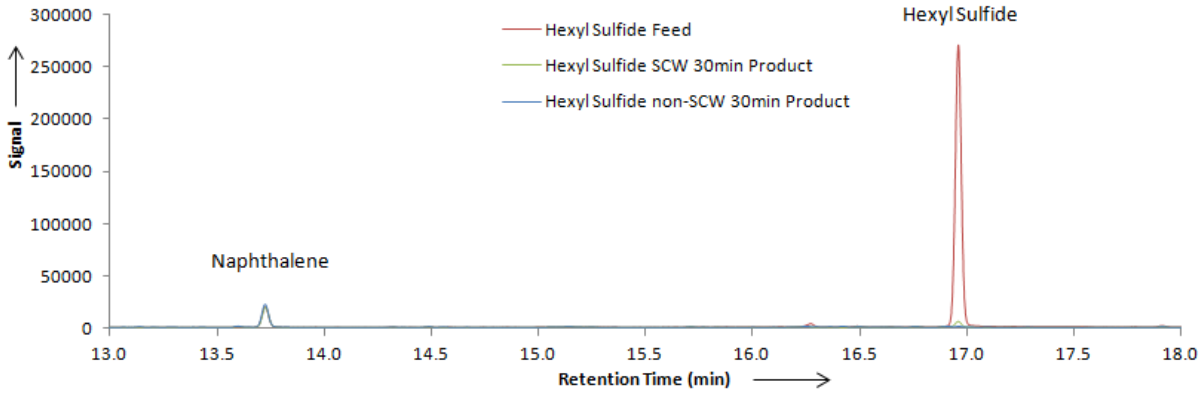


Figure 6. GC-FID Chromatogram of Hexyl Sulfide Experiment 1 Oil Products (Close Up RT 13-18min)

The gas phase product was analyzed by GC-FID for light hydrocarbons. Similar to the oil phase products, the SCW-treated product contains a lot of pentane and hexane/hexene while the non-SCW product has significantly more hexane/hexene than pentane. Note that there small amounts of C1-C5 species in the gas phase which are normal pyrolysis products of alkanes. The total gas phase hydrocarbon products only amounts to less than 4% of the carbon balance.

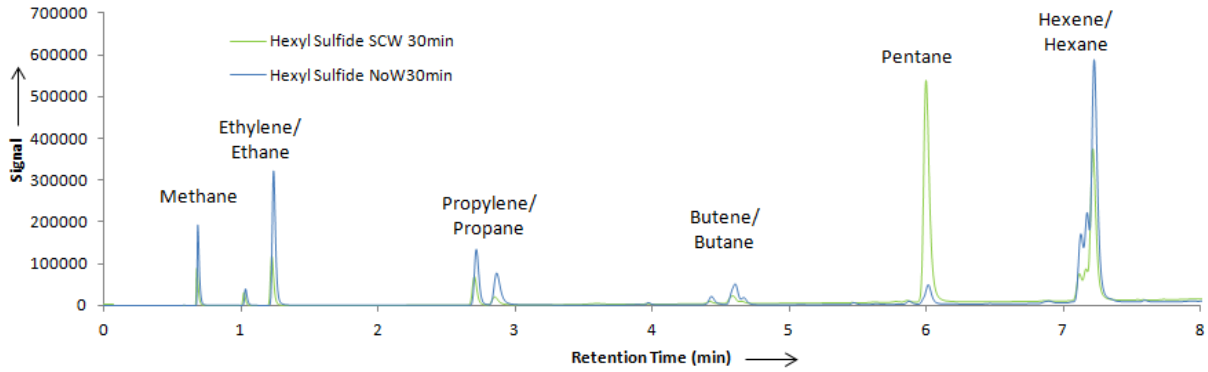


Figure 7. GC-FID of gas phase product

GC-TCD is capable of detecting % level concentrations of gas phase products. The SCW treated gas product contains about 2 vol% CO_2 in the gas phase while the non-SCW treated gas product contains almost none. Both SCW and non-SCW treated product gas contain 4-5 vol% H_2S. Unfortunately, N_2 and CO could not be separated with the column used so a separate NDIR measurement is taken to determine the CO/CO_2 ratio. This ratio ranged from about 1.5-2.5 for both SCW and non-SCW 30 minute gas products. The high variability of the ratio is thought to be due to the dependence of the water gas shift reaction on the brief ionic phase during the quenching phase which is not as consistent as other experimental parameters. The important point is that the CO/CO_2 ratio is of the same order meaning the amount of CO in the non-SCW product is also negligible.

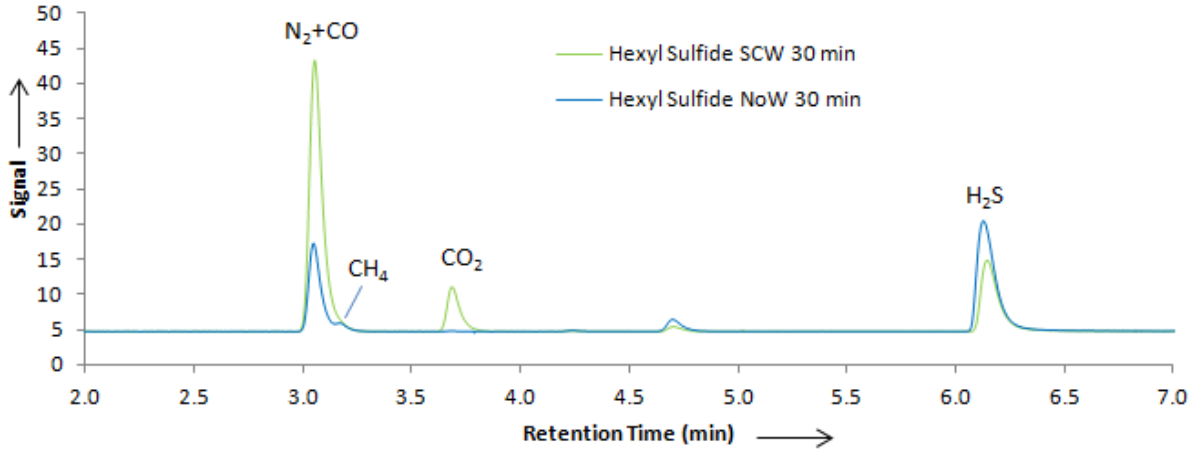


Figure 8. GC-TCD Chromatogram of Experiment 1 Gas Phase Product

3. Octanethiol Decomposition in presence of HS decomposition in SCW

A mixture of hexyl sulfide and octanethiol (10-1 mol ratio) is treated with SCW and without SCW for 30 minutes by the same procedure as experiment 1. With SCW treatment, octanethiol decomposes mostly into octane and octenes, but also produces some heptane. Without SCW, octanethiol decomposes mostly into the C8 species and there is negligible amount of heptane product.

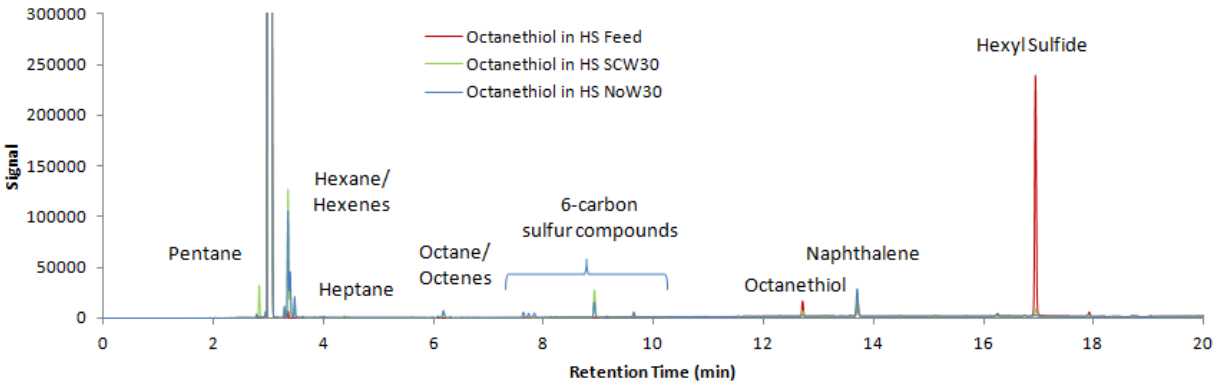


Figure 9. GC-FID of Hexyl Sulfide spiked with Octanethiol treated with SCW30 and NoW30

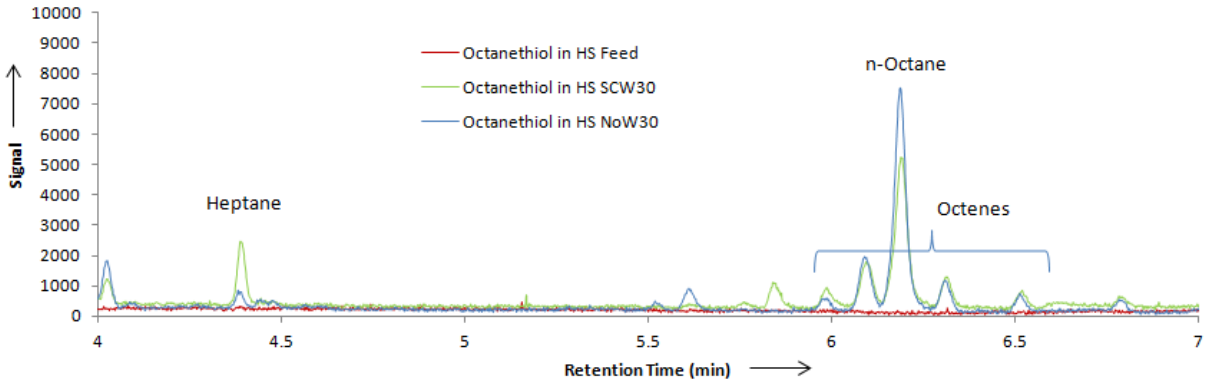


Figure 10. Close up of Figure 8, C7-C8 products

A mol balance of the C8/C7 species product show that in 30 minutes of SCW treatment, about 70% of the octanethiol has converted. The yield of heptane is only about 10%.

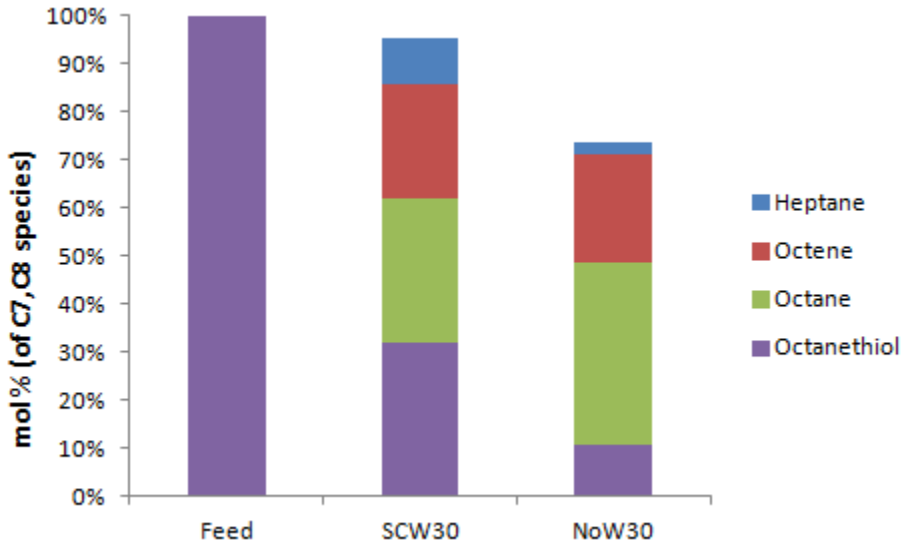
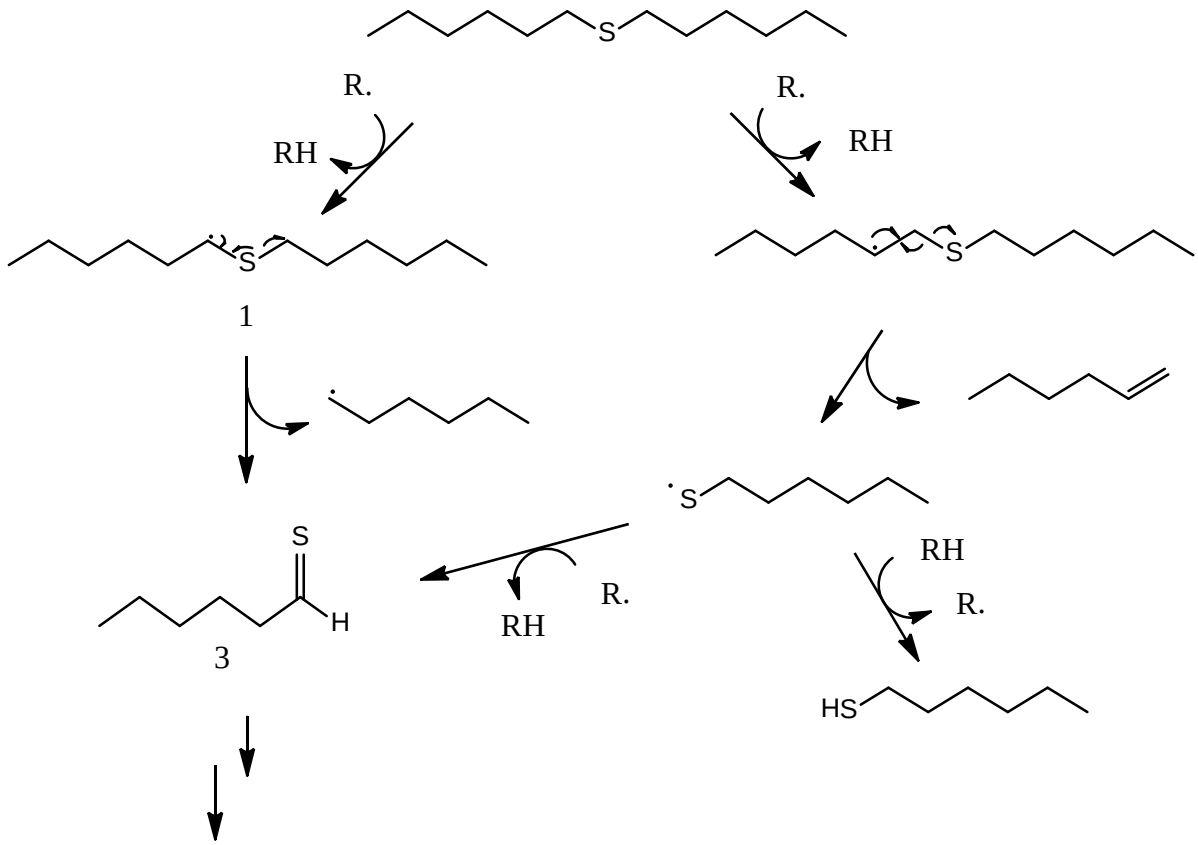


Figure 11. Octanethiol Decomposition Product

We propose that the thiol is formed from the abstraction of the β-hydrogen of hexyl sulfide followed by a beta scission to produce the hexanethiyl radical (the reactive radical form of the thiol). The left route in scheme 1 is the major pathway to form the thioaldehyde intermediate that reacts with water to form pentane and $CO+CO_2$, as discussed in the main body. An alternative minor route is the pathway to the right where instead of the α-hydrogen, the β-hydrogen is abstracted from the hexyl sulfide resulting in a less stable radical (hence is the minor pathway). A beta scission of this radical yields a hexene and the hexanethiyl radical. When the thiyl radical abstracts a hydrogen, it turns into a hexanethiol which is relatively stable as seen by its presence in the hexyl sulfide decomposition products and its slow decomposition in the intermediate study experiment. We propose that the thiyl radical further loses the α-hydrogen to make a thioaldehyde which is the same reactive intermediate proposed in the main pathway. The reaction following the thioaldehyde formation to produce the C_{m-1} species and $CO+CO_2$ is the same as discussed in the main body.



Scheme 1 Proposed mechanism of hexanethiyl formation
followed by hexanethioaldehyde formation

4. Z-Matrices for the Optimized Geometries of Reactants and Transition States

Reactant 1

0 1
S
C 1 B1
H 2 B2 1 A1

H	2	B3	1	A2	3	D1
C	1	B4	2	A3	3	D2
H	5	B5	1	A4	2	D3
H	5	B6	1	A5	2	D4
C	5	B7	1	A6	2	D5
H	8	B8	5	A7	1	D6
H	8	B9	5	A8	1	D7
C	8	B10	5	A9	1	D8
H	11	B11	8	A10	5	D9
H	11	B12	8	A11	5	D10
H	11	B13	8	A12	5	D11
C	2	B14	1	A13	5	D12
H	15	B15	2	A14	1	D13
H	15	B16	2	A15	1	D14
C	15	B17	2	A16	1	D15
H	18	B18	15	A17	2	D16
H	18	B19	15	A18	2	D17
H	18	B20	15	A19	2	D18

B1	1.83286691
B2	1.09418602
B3	1.09418638
B4	1.83286691
B5	1.09418622
B6	1.09418559
B7	1.52993128
B8	1.09486122
B9	1.09486131
B10	1.53225698
B11	1.09420493
B12	1.09302157
B13	1.09420526
B14	1.52993128
B15	1.09486145
B16	1.09486172
B17	1.53225761
B18	1.09420423
B19	1.09302294
B20	1.09420419
A1	108.69576260
A2	108.69581474
A3	99.94540037
A4	108.69578402
A5	108.69576808
A6	110.64905792
A7	109.22399701
A8	109.22396885
A9	112.28642586
A10	111.31681867
A11	110.97706950
A12	111.31684528
A13	110.64905792
A14	109.22402722
A15	109.22400244
A16	112.28639655
A17	111.31677438
A18	110.97702180
A19	111.31680610
D1	-117.55659051
D2	58.77800234
D3	58.77847214
D4	-58.77815457
D5	-180.00000000
D6	-58.05240841
D7	58.05249344
D8	-180.00000000
D9	60.09145413
D10	-180.00000000
D11	-60.09131565
D12	180.00000000

D13	58.05234626
D14	-58.05253762
D15	180.00000000
D16	60.09139029
D17	180.00000000
D18	-60.09148363

Reactant 2

0 2
S

C	1	B1					
H	2	B2	1	A1			
H	2	B3	1	A2	3	D1	
C	2	B4	1	A3	3	D2	
H	5	B5	2	A4	1	D3	
H	5	B6	2	A5	1	D4	
C	1	B7	2	A6	5	D5	
H	8	B8	1	A7	2	D6	
C	8	B9	1	A8	2	D7	
H	10	B10	8	A9	1	D8	
H	10	B11	8	A10	1	D9	
C	10	B12	8	A11	1	D10	
H	13	B13	10	A12	8	D11	
H	13	B14	10	A13	8	D12	
H	13	B15	10	A14	8	D13	
C	5	B16	2	A15	1	D14	
H	17	B17	5	A16	2	D15	
H	17	B18	5	A17	2	D16	
H	17	B19	5	A18	2	D17	

B1	1.83483793
B2	1.09252119
B3	1.09337046
B4	1.52910069
B5	1.09487192
B6	1.09478425
B7	1.73065170
B8	1.08565014
B9	1.49645422
B10	1.10220572
B11	1.09580676
B12	1.53717760
B13	1.09279331
B14	1.09361127
B15	1.09414892
B16	1.53248215
B17	1.09413012
B18	1.09289958
B19	1.09400358
A1	107.84180570
A2	108.07846735
A3	110.75594905
A4	109.29656633
A5	109.37004206
A6	101.58319518
A7	117.48549469
A8	119.84473816
A9	110.66794526
A10	109.61997566
A11	112.51856426
A12	110.92639148
A13	110.94969024
A14	110.98561340
A15	112.08692890
A16	111.33396860
A17	110.91625434
A18	111.26453367
D1	117.14141526
D2	-121.51259225

D3	57.77148082
D4	-58.51156757
D5	-179.98476395
D6	-23.08125673
D7	175.76138760
D8	89.96235587
D9	-26.23875218
D10	-148.32196115
D11	61.08354307
D12	-178.45563229
D13	-58.72299208
D14	179.54650784
D15	60.24273207
D16	-179.85683804
D17	-59.97312913

Reactant 3

0 1

C							
C	1	B1					
H	2	B2	1	A1			
S	2	B3	1	A2	3	D1	
H	1	B4	2	A3	4	D2	
H	1	B5	2	A4	4	D3	
C	1	B6	2	A5	4	D4	
H	7	B7	1	A6	2	D5	
H	7	B8	1	A7	2	D6	
H	7	B9	1	A8	2	D7	

B1	1.54000000
B2	1.07000000
B3	1.56640000
B4	1.07000000
B5	1.07000000
B6	1.54000000
B7	1.07000000
B8	1.07000000
B9	1.07000000
A1	120.00000000
A2	120.00000000
A3	109.47122063
A4	109.47122063
A5	109.47122063
A6	109.47122063
A7	109.47122063
A8	109.47122063
D1	180.00000000
D2	-90.00000000
D3	150.00000000
D4	30.00000000
D5	-180.00000000
D6	-60.00000000
D7	60.00000000

Reactant 4

0 1

C							
H	1	B1					
S	1	B2	2	A1			
H	1	B3	3	A2	2	D1	
O	1	B4	3	A3	2	D2	
H	3	B5	1	A4	5	D3	
C	1	B6	5	A5	3	D4	
H	7	B7	1	A6	5	D5	
H	7	B8	1	A7	5	D6	
C	7	B9	1	A8	5	D7	
H	10	B10	7	A9	1	D8	
H	10	B11	7	A10	1	D9	

H	10	B12	7	A11	1	D10

B1	1.09048552
B2	1.86078422
B3	1.93273142
B4	1.40770086
B5	1.34378990
B6	1.53113914
B7	1.09694377
B8	1.09434082
B9	1.53133853
B10	1.09139945
B11	1.09258576
B12	1.09395990
A1	107.60419848
A2	94.96540335
A3	111.97160606
A4	95.39442757
A5	113.24310404
A6	108.55913773
A7	108.92222458
A8	112.26110141
A9	110.80571403
A10	110.75959819
A11	111.12375186
D1	138.92696503
D2	115.38946402
D3	56.37650528
D4	-122.54880092
D5	63.22114369
D6	178.96904156
D7	-58.65623844
D8	56.43656289
D9	176.81078747
D10	-63.38460230

H_2S

0 1

S						
H	1	B1				
H	1	B2	2	A1		

B1	1.34327993
B2	1.34327993
A1	92.58329996

***Transition State* c**

0 1

C						
H	1	B1				
S	1	B2	2	A1		
H	1	B3	3	A2	2	D1
O	1	B4	3	A3	2	D2
H	5	B5	1	A4	3	D3
C	1	B6	5	A5	3	D4
H	7	B7	1	A6	5	D5
H	7	B8	1	A7	5	D6
C	7	B9	1	A8	5	D7
H	10	B10	7	A9	1	D8
H	10	B11	7	A10	1	D9
H	10	B12	7	A11	1	D10

B1	1.09241006
B2	1.79658311
B3	2.12327006
B4	1.59671168
B5	1.15532024
B6	1.51209272

B7	1.09654537
B8	1.09297196
B9	1.53242997
B10	1.09220528
B11	1.09168655
B12	1.09424066
A1	114.59448553
A2	102.07345850
A3	96.55246307
A4	82.19312673
A5	106.23520644
A6	108.90981510
A7	108.35071455
A8	111.33938850
A9	110.26078754
A10	110.54686150
A11	111.54751453
D1	84.00842439
D2	109.35927488
D3	2.33201560
D4	-123.24658056
D5	-59.01941864
D6	58.01521388
D7	179.26799570
D8	179.45862584
D9	-60.67338652
D10	59.72805879

***Transition State* d (uncatalyzed)**

0 1

C							
H	1	B1					
S	2	B2	1	A1			
H	1	B3	3	A2	2	D1	
O	1	B4	3	A3	2	D2	
H	3	B5	2	A4	1	D3	
C	1	B6	5	A5	3	D4	
H	7	B7	1	A6	5	D5	
H	7	B8	1	A7	5	D6	
C	7	B9	1	A8	5	D7	
H	10	B10	7	A9	1	D8	
H	10	B11	7	A10	1	D9	
H	10	B12	7	A11	1	D10	

B1	1.08263566
B2	2.58419939
B3	1.81750188
B4	1.28309019
B5	1.34560587
B6	1.48152946
B7	1.10267814
B8	1.09595158
B9	1.52767534
B10	1.09072160
B11	1.09136697
B12	1.09172499
A1	87.63527427
A2	46.23955852
A3	78.32047736
A4	112.93879552
A5	120.16257597
A6	105.86882580
A7	106.87857733
A8	115.68609744
A9	111.25641026
A10	110.11418597
A11	110.80784736
D1	-113.31573096
D2	-128.09409136

D3	21.36069627
D4	134.07509410
D5	104.74702722
D6	-144.37231026
D7	-18.84596679
D8	58.83587233
D9	179.08327593
D10	-61.16090483

***Transition State* d (catalyzed)**

0 1

C								
H	1	B1						
C	1	B2	2	A1				
H	3	B3	1	A2	2	D1		
H	3	B4	1	A3	2	D2		
S	1	B5	3	A4	4	D3		
H	6	B6	1	A5	3	D4		
O	1	B7	3	A6	6	D5		
H	8	B8	1	A7	3	D6		
H	6	B9	1	A8	8	D7		
O	8	B10	1	A9	3	D8		
H	11	B11	8	A10	1	D9		
C	3	B12	1	A11	8	D10		
H	13	B13	3	A12	1	D11		
H	13	B14	3	A13	1	D12		
H	13	B15	3	A14	1	D13		

B1	1.09626867
B2	1.51291302
B3	1.09102204
B4	1.09414566
B5	2.54225836
B6	1.34489062
B7	1.26069094
B8	1.33995871
B9	1.76257045
B10	2.39617585
B11	0.96544447
B12	1.54084657
B13	1.09254285
B14	1.09189429
B15	1.09362992
A1	115.81582775
A2	109.74917168
A3	109.56806733
A4	96.06716356
A5	93.18644706
A6	121.38295120
A7	111.96099705
A8	74.56752237
A9	105.48899890
A10	118.68540537
A11	109.49576675
A12	110.26748182
A13	110.95457462
A14	111.26869836
D1	41.01862950
D2	159.37407730
D3	-53.96623474
D4	172.34103954
D5	-111.03192676
D6	66.49149858
D7	28.89589267
D8	74.55881872
D9	-78.46540361
D10	73.51705098
D11	179.82091471
D12	-59.95844211

D13	60.32270333