

Sulfur isotope fractionation during sulfur nucleophiles incorporation into organic compounds

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Supplementary data

1. Chemicals

All chemicals were analytical grade and purchase from Aldrich or Merck and used without further purification.

2. Reaction between H₂S/CH₃SNa and organic model compounds

Method A (H₂S). Solution prepared by addition of 2g of NaHCO₃ into 30ml distilled water in a two necks round flask equipped with valves. Argon bubbled through the solution for 1 hour to remove O₂ and then H₂S bubbled through the solution for 2 hours. Sample of the solution were taken by syringe trough septum to determine the initial value of the δ³⁴S of the solution and the concentration of S (20-40mmol) by precipitation with 5 wt% Ag₂NO₃ .solution. The organic substrate (0.5mmol) was introduced through septum and the reaction begins. The pH of the solutions was in the range of 8 to 9. Reactions stopped after 3 days, extracted 3 times with CH₂Cl₂, dried with Na₂SO₄, filtered and carefully evaporated under gentle N₂ stream.

Method B (Na₂S). Stock solution of 0.3M SH⁻ were prepared as followed: Into 300ml of distilled water 8.2g NaHCO₃ was added. The solution bubbled 2 hours with argon, sealed, and introduced into anaerobic glovebox. Solid crystals of Na₂S 9H₂O (32g) were added and to the solution and the pH adjusted to 8.5-9 by addition of concentrated HCl solution. The solution then added into the reaction vials (each 15 ml) and sealed with cups equipped with Teflon septum. The organic model

compounds were injected into the vials through the Teflon septum and the reaction begins. The vials were shaken using automatic shaker for three weeks, extracted 3 times with CH_2Cl_2 , dried with Na_2SO_4 , filtered and carefully evaporated under gentle N_2 stream.

Method C (CH_3SNa). Into a 15 ml vial equipped with magnetic stirrer, 100mg (1.4mmol) of CH_3SNa powder were introduced and dissolved in 5ml of distilled water. The pH adjusted to ~ 9 by slow addition of concentrated HCl solution and distilled water was added to reach 10ml of total volume. Organic substrate (0.2 mmol) then introduced and the vial sealed under N_2 atmosphere. Reactions stopped after 10-14 days, extracted 3 times with CH_2Cl_2 , dried with Na_2SO_4 , filtered and carefully evaporated under gentle N_2 stream.

3. Polysulfides (S_x^{2-}) reactions with organic substrates

Preparation of polysulfide solutions: General procedure: 0.94g (29mmol) of elemental sulfur was dissolved in 10 ml of ammonium sulfide solution ($(\text{NH}_4)_2\text{S}$, 20% w/w in water, Merck) to give a stoichiometric ratio of sulfide to elemental sulfur of 1:1. The pH buffered by the ammonium solution to 8.5-9.0. Na_2S_x was prepared by dissolving 6.96g $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (29mmol, Merck) in 10ml distilled water and adding of 0.94g elemental sulfur (29mmol). The pH was reduced to 8.5 by addition of diluted HCl.

General procedure (aqueous conditions) : Into a round bottom flask, 10-20 ml polysulfides solution were introduced (concentration of polysulfides 0.3-3 Molar ; pH= 8.5-9) with 1.6mmol organic substrate. The solution was magnetically stirred overnight under nitrogen atmosphere at 25°C . The aquatic solution was extracted

three times with dichloromethane (CH_2Cl_2). The organic solution was dried over anhydrous MgSO_4 and filtered. Elemental sulfur was removed from the organic extracts by reaction with activated copper curls and subsequent filtration. The extracts were evaporated at ambient temperature, and weighed.

General procedure under Phase Transfer catalysis (PTC) conditions: Into a round bottom flask, ~200 mg organic substrate and 20mg dimethyldidecylammonium-bromide (DDAB) were introduced and dissolved in 10ml toluene. One g of elemental sulfur was dissolved in 10 ml of ammonium sulfide (Merck). The mixture of the two liquids was magnetically stirred at ambient temperature under N_2 . The aqueous layer was removed and the organic layer was repeatedly washed with saturated NaCl solution until the washing was colorless, dried over MgSO_4 and filtered. Elemental sulfur was removed from the extracts by reaction with activated Cu turnings and subsequent filtration. The extracts were evaporated under vacuum at ambient temperature. The residue was analyzed by GC (FID and FPD), GC-MS, and subjected to elemental analysis.

Gas chromatography and mass spectroscopy

GC-MS analyses were carried out on an HP 5890 II gas chromatograph directly coupled to the source of a HP-G-1800B quadrupole mass-spectrometer. The mass-spectrometer was run in the electron impact (EI) mode with electron energy at 70 eV, source temperature at 200 °C, mass range 45-450 Da, a resolution of 800 and scan time of 1s. A fused capillary column (silica 30m X 0.32mm, ID 0.25 μ , and CP-SIL 24CB coating) was used with He as the carrier gas. The GC was programmed at 4

°C/min between 50 and 300 °C. The initial and final temperatures were maintained for 5 and 20 min, respectively.

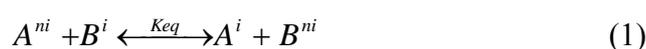
4. Isotopic ratio measurements

The $\delta^{34}\text{S}$ of the precipitated Ag_2S and the organic samples was measured by a continuous-flow elemental analyzer connected to a Finnigan Delta Plus stable-isotope ratio monitoring mass spectrometer (EA-irmMS). Sulfur isotope compositions are expressed as per mil (‰) deviations from V-CDT (Vienna Canyon Diablo Troilite) standard using the conventional delta notation with a standard deviation better than 0.3‰ ($n \geq 2$). The measurements were directly calibrated against sulfur isotopic standards IAEA-S-1 (Ag_2S , -0.3‰) and NBS-127 (BaSO_4 , +20.3‰) with a standard deviation better than 0.2‰ ($n \geq 3$).

5. Molecular modeling

5.1 The delta-G method to determine isotope exchanges

The thermal equilibrium of the isotopic exchange is governed by:



where A^i , A^{ni} , B^i , and B^{ni} are the concentrations of the isotopic and non-isotopic species of molecular compounds A and B, and K_{eq} is the thermal equilibrium constant.

Therefore we have:

$$K_{eq} = \frac{A^i * B^{ni}}{A^{ni} * B^i} = \frac{A^i}{A^{ni}} / \frac{B^i}{B^{ni}} \quad (2)$$

According to the definition of the standard isotope fractionation, we have:

$$\begin{aligned} \delta^{34}S_A &= [R_A / R_0 - 1] * 1000 \\ \delta^{34}S_B &= [R_B / R_0 - 1] * 1000 \end{aligned} \quad (3)$$

where $R_A = A^i/A^{ni}$, $R_B = B^i/B^{ni}$, and R_0 is the ratio of isotopic and non-isotopic concentrations of the standard sample. So:

$$R_A = \left[\frac{\delta^{34}S_A}{1000} + 1 \right] * R_0; R_B = \left[\frac{\delta^{34}S_B}{1000} + 1 \right] * R_0 \quad (4)$$

Substituting equations (4) into equation (2), we have:

$$K_{eq} = \frac{\delta^{34}S_A + 1000}{\delta^{34}S_B + 1000} \quad (5)$$

Therefore, the isotope fractionation difference between compounds A and B is:

$$\begin{aligned} & \Delta\{\delta^{34}S_A - \delta^{34}S_B\} \\ &= ((\delta^{34}S_B + 1000)K_{eq} - 1000) - \delta^{34}S_B \\ &= (K_{eq} - 1)(\delta^{34}S_B + 1000) \\ &\approx (K_{eq} - 1) * 1000 \end{aligned} \quad (6)$$

The approximation made in the last step is because $\delta^{34}S \ll 1000$.

Since the thermal equilibrium constant K_{eq} is related to the Gibbs' free energy difference of compounds A and B, $\Delta\Delta G = \Delta G(B) - \Delta G(A)$, we have:

$$\Delta\{\delta^{34}S_A - \delta^{34}S_B\} = 1000 * (e^{-\Delta\Delta G/RT} - 1) \quad (7)$$

5.2 First-principle Quantum Mechanics calculations to determine $\Delta\Delta G$

Within the Density Functional Theory (DFT) framework, the Gibbs' free energy ΔG is evaluated from several individual terms as:

$$\Delta G = E_0 + ZPE + \delta G(T) \quad (8)$$

where E_0 is the total electronic energy at temperature $T = 0$ K, ZPE is the Zero-Point Energy due to the quantum mechanics vibrational motion, and $\delta G(T) = \delta H(T) - T\delta S(T)$ is the Gibbs free energy change from temperature $T = 0$ to T K, and the $\delta H(T)$ and $\delta S(T)$ are the enthalpy and entropy changes from temperature $T = 0$ to T K.

In general, the total Gibbs free energy is contributed from several different molecular motions, namely electronic, translational, vibrational and rotational. The

biggest contribution from the electronic motion E_0 remains unchanged for both the isotopic and non-isotopic complexes such that the majority of the Gibbs' free energies for both cases cancelled each other. The individual energy terms from different motions can be evaluated as follows:

Contribution from the translation motion

The partition function for the translational motion at temperature T is defined as:

$$Q_{t,T} = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \frac{k_B T}{P} \quad (9)$$

where $P = 1$ atm is the pressure under the standard condition.

Using the Stirling's approximation, the enthalpy and entropy changes due to the translational motion are:

$$H_{t,T} = \frac{3}{2} RT, \quad S_{t,T} = R \left(\ln Q_{t,T} + \frac{5}{2} \right) \quad (10)$$

Therefore, for different isotopomers with different molecular mass m , the entropic contribution $S_{t,T}$ will be different.

Contributions from the vibrational motion

Vibrational motions have contributions to both ZPE and ΔG energy terms. The ZPE is calculated from:

$$ZPE = \sum_i \frac{1}{2} h\nu_i \quad (11)$$

where ν_i are the calculated vibrational frequencies of normal vibrational modes.

The partition function of vibrational motion at temperature T is defined as:

$$Q_{v,T} = \prod_i \frac{e^{-\Theta_{v,i}/2T}}{1 - e^{-\Theta_{v,i}/T}} \quad (12)$$

where $\Theta_{v,i} = h\nu_i/k_B$ is the i^{th} vibrational temperature (in unit of K), h and k_B are the Planck's and Boltzmann constants.

The vibrational enthalpy and entropy contributions are calculated from:

$$H_{v,T} = R \sum_i \frac{\Theta_{v,i}}{e^{\Theta_{v,i}/T} - 1}, S_{v,T} = R \sum_i \left\{ \frac{\Theta_{v,i}/T}{e^{\Theta_{v,i}/T} - 1} - \ln(1 - e^{-\Theta_{v,i}/T}) \right\} \quad (13)$$

Contributions from the rotational motion

The partition function of the rotational motion at temperature T is defined as:

$$Q_{r,T} = \frac{\pi^{1/2}}{\sigma_r} \left\{ \frac{T^{3/2}}{(\Theta_{r,x} \Theta_{r,y} \Theta_{r,z})^{1/2}} \right\} \quad (14)$$

where $\Theta_{r,x} = h^2/(8\pi k_B I_x)$, $\Theta_{r,y} = h^2/(8\pi k_B I_y)$, $\Theta_{r,z} = h^2/(8\pi k_B I_z)$ are the x-, y- and z-components of rotational temperature, I_x , I_y , and I_z are the x-, y- and z- components of the principal moment of inertia, and σ_r is the rotational symmetry number. And the rotational enthalpy and entropy contributions are calculated from:

$$H_{r,T} = 2RT \quad (15)$$

$$S_{r,T} = R \left(\ln Q_{r,T} + \frac{3}{2} \right) = R \left\{ \frac{3}{2} \ln T + \ln \frac{\pi^{1/2}}{\sigma_r (\Theta_{r,x} \Theta_{r,y} \Theta_{r,z})^{1/2}} + \frac{3}{2} \right\} \quad (16)$$

5.3 Quantum Mechanics Density Functional Theory (DFT) calculations

Molecular geometry in gas-phase is fully optimized at the DFT/B3LYP/6-31G** level to determine the electronic energy E0. Thermodynamic calculations are then performed to determine the individual contributions of enthalpy and entropy terms. All calculations are carried out using the commercially computational software package Jaguar 5.5 version 11 (Jaguar 5.5; Schrodinger, Inc., Portland, OR, 2005)

To ensure the higher computational accuracy needed for the small isotopic changes, we recalculated the energy terms by a MATLAB program according to above equations instead of directly taking the computational outputs.

6. Complete isotopic data

Table 1S: Experimental measurements of ^{34}S enrichment (‰) in sulfurized products of reactions between S nucleophiles and organic substrates under aqueous conditions.

Precursor compound	Reactant/method	Initial $\delta^{34}\text{S}$ value of reactant	$\delta^{34}\text{S}$ value of sulfurized products	$\Delta^{34}\text{S}$
Citral (+ammonium)	CH_3SNa	-4.9	-1.2	3.7
Citral	CH_3SNa	-4.9	-1.8	3.1
<i>Trans</i> 2-octenal	CH_3SNa	-4.9	-1.4	3.5
Octanal (+ammonium)	CH_3SNa	-4.9	-0.5	4.4
Octanal	CH_3SNa	-4.9	0.5	5.4
<i>Trans</i> 2-octenal	H_2S	12.9	17.7	4.8
Butanal	H_2S	12.6	19.9	7.3
<i>Trans</i> 2-octenal	Na_2S	-1.8	2.7	4.5
Trans 2,4-heptadienal	Na_2S	-1.8	3.0	4.8
Octanal	Na_2S	-1.8	5.3	7.1
Butanal	Na_2S	-1.8	6.3	8.1
1-bromobutan	Na_2S	-1.8	-4.3	-2.5

Table 3S. Experimental measurements of ^{34}S enrichment (‰) in the sulfurized products of the reactions between polysulfide anions (S_x^{2-}) and organic substrates under PTC conditions.

Precursor	Reactant	Method	Initial $\delta^{34}\text{S}$ value of Total S in solution	$\delta^{34}\text{S}$ value of sulfurized products	$\Delta^{34}\text{S}$
Citral	$(\text{NH}_4)_2\text{S}_x$	Water	2.8	7.2	4.4
Citral	$(\text{NH}_4)_2\text{S}_x$	PTC	2.8	8.9	6.1
Geranyl bromide	$(\text{NH}_4)_2\text{S}_x$	Water	2.8	3.9	1.1
Geranyl bromide	$(\text{NH}_4)_2\text{S}_x$	PTC	2.8	6.6	3.8
1,2-dibromohexane	$(\text{NH}_4)_2\text{S}_x$	Water	2.8	2.9	0.1
1,2-dibromohexane	$(\text{NH}_4)_2\text{S}_x$	PTC	2.8	5.1	2.3
1-chlorooctane	$(\text{NH}_4)_2\text{S}_x$	Water/methanol	2.8	3.8	1
1-chlorooctane	$(\text{NH}_4)_2\text{S}_x$	PTC	2.8	7.2	3.4

Table 2S. Molecular modeling prediction of the ^{34}S enrichment (%) of S containing molecules in equilibrium with S nucleophiles at 20°C.

Molecule	E_0	E_0	ZPE	E_{sol}	$\delta G_{T=20\text{C}}$	$\Delta G_{T=20\text{C}}$	$\Delta\Delta G$	$\delta(\Delta\Delta G)$	$^{34}\text{K}_{\text{eq}}/^{32}\text{K}_{\text{eq}}$	$\Delta^{34}\text{S}$
	(Hartree)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(cal/mol)		(‰)
Reactants										
H ₂ S			9.1000	-2.8494	-12.0684	-250621.88				
H ₂ ³⁴ S	-399.382097	-250616.06	9.0917		-12.1198	-250621.94	-0.060			
CH ₃ SH			29.0792	-1.5319	-14.9966	-275264.22				
CH ₃ ³⁴ SH	-438.681441	-275276.77	29.0641		-15.0431	-275264.28	-0.062			
Products										
CH ₂ =CHSCH ₃	-516.057999	-323831.30	53.3580	-1.6660	-17.9493	-323797.55	-0.065	-2.9	1.0050	5
CH ₂ =CH ³⁴ SCH ₃			53.3321		-17.9879	-323797.62				
CH ₃ CH ₂ SCH ₃			66.7746	-1.1254	-18.1465	-324555.21	-0.064	-2.0	1.0034	3.4
CH ₃ CH ₂ ³⁴ SCH ₃	-517.287323	-324602.71	66.7494		-18.1849	-324555.27				
CH ₃ CH(SCH ₃)(SCH ₃)	-954.765593	-599124.48	85.5489	-2.7840	-21.1134	-599062.83	-0.063	-1.6	1.0028	2.8
CH ₃ CH(³⁴ SCH ₃)(SCH ₃)			85.5208		-21.1485	-599062.89				
CH ₃ CH(SCH ₃)CH ₂ CH=O	-669.883729	-420358.40	90.9038	-6.3512	-20.9909	-420294.84	-0.062	-0.9	1.0015	1.5
CH ₃ CH(³⁴ SCH ₃)CH ₂ CH=O			90.8768		-21.0264	-420294.90				
CH ₂ (SCH ₃)(OH)	-553.180617	-347126.09	51.5188	-8.4935	-17.8946	-347100.96	-0.064	-2.0	1.0034	3.4
CH ₂ (³⁴ SCH ₃)(OH)			51.4936		-17.9330	-347101.03				
CH ₃ CH ₂ (SCH ₃)CH ₂ -CHOH	-669.867978	-420348.52	92.2269	-9.7620	-21.0663	-420287.12	-0.063	-1.7	1.0029	2.9
CH ₃ CH ₂ (³⁴ SCH ₃)CH ₂ -CHOH			92.1989		-21.1016	-420287.18				
CH ₂ =CHSH	-476.757231	-299169.69	33.9384	-1.2924	-16.0790	-299153.12	-0.063	-3.5	1.0060	6.0
CH ₂ =CH ³⁴ SH			33.9191		-16.1229	-299153.19				
CH ₃ CH ₂ SH			47.3734	-1.6891	-16.4041	-299912.00	-0.061	-1.8	1.0031	3.1
CH ₃ CH ₂ ³⁴ SH	-477.986832	-299941.28	47.3559		-16.4481	-299912.06				
CH ₃ CH(SH)(SH)	-876.165787	-549802.36	46.7453	-4.1834	-18.3455	-549778.14	-0.062	-2.2	1.0038	3.8
CH ₃ CH(³⁴ SH)(SH)			46.7244		-18.3865	-549778.20				
CH ₃ CH(SH)CH ₂ CH=O	-630.581658	-395695.98	71.5898	-4.1834	-19.9076	-395648.48	-0.063	-2.8	1.0048	4.8
CH ₃ CH(³⁴ SH)CH ₂ CH=O			71.5678		-19.9481	-395648.54				
CH ₂ (SH)(OH)	-513.878789	-322463.82	32.2836	-9.5393	-16.1500	-322457.23	-0.062	-1.9	1.0033	3.3
CH ₂ (³⁴ SH)(OH)			32.2660		-16.1940	-322457.29				
CH ₃ CH ₂ (SH)CH ₂ CHOH	-630.570082	-395688.72	72.9170	-9.2890	-19.6359	-395644.72	-0.061	-1.5	1.0026	2.6
CH ₃ CH ₂ (³⁴ SH)CH ₂ CHOH			72.8967		-19.6768	-395644.79				
CH ₂ =S	-437.452683	-274505.71	16.3534	-0.5393	-13.7579	-274503.66	-0.065	-5.5	1.0095	9.5
CH ₂ = ³⁴ S			16.3355		-13.8052	-274503.72				
CH ₃ SSSCH ₃	-1274.361253	-799673.79	50.3685	-0.8509	-21.6532	-799645.93	-0.060	-0.5	1.0009	0.9
CH ₃ S ³⁴ SSCH ₃			50.3431		-21.6880	-799645.99				

The optimized coordinates of all compounds studied:

H₂S

atom	x	y	z
H1	.0000000000	1.0125270727	.8791276258
S1	.0000000000	.0000000000	-.0554238001
H2	.0000000000	-1.0125270727	.8791276258

CH₃SH

atom	x	y	z
H1	.3740093890	1.6936178770	-.9051015852
C1	-.0950155038	1.2823372879	.0000000000
H2	.3740093890	1.6936178770	.9051015852
S1	.0053428302	-.6135267425	.0000000000
H4	-1.1678723009	1.5216895111	.0000000000
H3	1.3816918074	-.7140771607	.0000000000

CH₂=CHSCH₃

atom	x	y	z
H1	-.8859396321	2.5339982540	.0000000000
C1	.1646530493	2.2262950882	.0000000000
H7	1.2313318742	-1.8668339662	.9063575511
C2	.5418554469	.9420365120	.0000000000
H4	.9161481551	3.0215630265	.0000000000
S1	-.6226223441	-.4659769431	.0000000000
H5	1.5968336950	.6511793790	.0000000000
H8	1.2313318742	-1.8668339662	-.9063575511
C3	.6085211357	-1.8979702215	.0000000000
H3	.0044273256	-2.8164743776	.0000000000

CH₃CH₂SCH₃

atom	x	y	z
H1	-.6086169609	1.4406032231	-1.5773793454
C1	-.5913022379	1.4224460586	-.4742056422
H2	.4454855615	1.6126303410	-.1454735747
C2	-1.1249867981	.0960676036	.0614827695
H4	-1.2142460962	2.2594822343	-.1053065444
S1	-.1748192360	-1.4338912649	-.5550787406
H5	-2.1578965557	-.0849431230	-.2779766601
H6	-1.1217846640	.0660504428	1.1644659005
C3	1.4325218120	-1.2462980602	.4192725019
H3	2.0451205458	-2.1259987252	.1716259273
H7	1.2240975528	-1.2380656205	1.5007978805
H8	1.9710610174	-.3340551958	.1223108590

CH₃CH(SCH₃)(SCH₃)

atom	x	y	z
H1	-.9155232907	-.9517558424	-2.0497057551
C1	-.7366009147	.0046121672	-1.5254709008

H2	.3491074784	.1985244866	-1.5175791402
C2	-1.3307670555	-.0342712183	-.1219773552
H4	-1.2168309143	.8121762002	-2.1038572486
S1	-.7663267317	-1.5249548833	.9257084765
H5	-2.4205753045	-.1782907498	-.1751099654
S2	-1.2042776189	1.6365230501	.7883829571
C3	.9714350418	-1.9029012683	.2826056639
C4	.6118962858	1.6809519519	1.2866982099
H3	1.3113140294	-2.7575842862	.8870929317
H7	1.6539230347	-1.0552596916	.4377432960
H8	.9484963855	-2.1946697408	-.7768090327
H6	1.2712708947	1.6836065897	.4057161851
H9	.8325023011	.8302333244	1.9484161046
H10	.7440101376	2.6221143540	1.8411470439

CH₃CH(SCH₃)CH₂CH=O

atom	x	y	z
S1	-.7506622260	.7393829173	-1.0719571172
C1	-.0447212956	.1165805777	.6084810649
H2	1.0500342934	.1977515111	.5114205738
C2	-.4378779633	-1.3485177273	.8281666354
C4	-.5518134359	1.0253731537	1.7331013435
C3	.2579297113	-2.3597593851	-.0476343748
H5	-1.5313775143	-1.4835090894	.7168281942
H3	-.1575348375	-3.3918981398	-.0088344615
H6	-.2115228192	-1.6451133345	1.8779088028
O1	1.2493844281	-2.1244450446	-.7542229470
H4	-.2507006711	2.0709409476	1.5587322049
H7	-.1383661011	.7021496065	2.7078339629
H8	-1.6544784047	.9989492013	1.8035959522
C5	.8321359450	.8948981326	-2.0979512743
H1	1.3505918670	-.0733046084	-2.1275631388
H9	1.4812750946	1.6782975776	-1.6784981306
H10	.5077654210	1.1875260712	-3.1078154088

CH₂(SCH₃)(OH)

atom	x	y	z
O1	-1.3584430456	-.7684526807	-.9885927605
C1	-1.1669223580	-.3980863978	.3912391551
S1	.6298404180	-.5088138287	.9743837152
H3	-1.7293038533	-1.0438820671	1.0855119393
H4	-1.5148799645	.6398655328	.4641073521
C2	1.3889757885	.8324282658	-.1222370229
H1	2.4768238052	.7806816598	.0295171143
H2	1.0174912460	1.8240569575	.1781997473
H5	1.1459544707	.6286262079	-1.1747510761
H6	-1.0968351005	-1.7102196581	-1.1416486845

CH₃CH(SCH₃)CH₂-CHOH

atom	x	y	z
H1	-.8548228720	1.4580743924	-2.0185633765
C1	-.5266419988	1.6600377818	-.9813053896
H2	.5500108758	1.9063154624	-1.0147868804

C2	-.7932724509	.4340166692	-.1007108606
H4	-1.0697696334	2.5415454602	-.6038588318
C3	-.0833009771	-.7944459629	-.5724733585
H5	-1.8787241232	.2484800132	-.0328982027
S1	-.3961270900	.8399729124	1.7649858934
H10	-1.6923271961	-2.1914341834	-.3462048347
H7	.9610212625	-.6946435290	-.8865689155
C4	-.6541001739	-2.0026099548	-.6386428302
O1	.0723090139	-3.1141968647	-1.0921608491
H8	-.4625463650	-3.9393189313	-1.0843166796
C5	1.4925582329	.8087869835	1.7644451528
H3	1.9013627367	1.5508365270	1.0621616229
H6	1.8617574208	-.1991912947	1.5251472387
H9	1.7944575488	1.0762946281	2.7881635700

CH₂=CHSH

atom	x	y	z
H6	1.6180706808	0.6685687303	0.0000000000
C1	-0.1950685725	1.7856696860	0.0000000000
H2	-1.2901957624	1.7938684140	0.0000000000
C2	0.5249283950	0.6585051116	0.0000000000
H4	0.3064499268	2.7581160597	0.0000000000
S1	-0.0982469792	-1.0579668359	0.0000000000
H3	-1.4451387079	-0.7601630062	0.0000000000

CH₃CH₂SH

atom	x	y	z
H13	-1.6065832498	-0.3684773299	-0.0795228575
H14	-0.6048182493	-0.3140993811	1.3942471169
H12	1.4698330273	-1.7002989100	0.2903335952
H11	0.1338635377	0.9928420821	-1.3285741035
C6	-0.5735774356	-0.2851188839	0.2938390849
C5	0.1115588752	0.9748996734	-0.2256638067
S1	0.2421858630	-1.9060300455	-0.3077677648
H1	-0.4317926962	1.8733185231	0.1241351373
H8	1.1519816464	1.0509503321	0.1386886405

CH₃CH(SH)(SH)

atom	x	y	z
S2	-0.7476214663	-0.3377041587	1.8949149645
H12	1.4053448526	-1.7201314921	-0.3066611613
H14	0.6066885868	-0.2228227209	2.1440450074
C6	-0.6107035007	-0.3227879132	-0.0039196739
S1	0.1091312416	-1.9248053881	-0.7390761668
C1	0.0914505625	0.9260304308	-0.5274856961
H13	-1.6614682711	-0.3528446894	-0.3285072120
H1	1.1483361598	0.9616234661	-0.2051646880
H2	-0.4115272635	1.8330565210	-0.1502993709
H3	0.0710147206	0.9411084962	-1.6308064495

CH₃CH(SH)CH₂CH=O

atom	x	y	z
S1	-.3491866193	.7093986503	-1.8769943614
C1	.2233976944	.4243148671	-.0553940331
H2	1.3100919658	.2560882928	-.1078074265
C2	-.4560043662	-.8627518806	.4247385591
C4	-.1056730908	1.6368477591	.8160865543
C3	.1897138529	-2.1467545678	-.0470380661
H5	-1.5316542867	-.8781663495	.1635436044
H3	-.4351662634	-3.0628813451	.0470354677
H6	-.4258886412	-.8963066878	1.5365641072
O1	1.3496095896	-2.2328254586	-.4720792779
H4	.3661707804	2.5521319893	.4210858212
H7	.2700691556	1.4790701438	1.8459497487
H8	-1.1949737184	1.8117148193	.8636927855
H1	.7120452165	1.5004869131	-2.2627084648

CH₂(SH)(OH)

atom	x	y	z
O1	-.5628520945	.0254615793	-1.2129255205
C1	-.4884211807	-.0689065435	.2169056232
S1	1.2913236742	-.0655261064	.9007716537
H3	-.9253064077	-1.0010348411	.6102346682
H4	-1.0301221978	.8029305674	.5989345385
H2	1.6189741307	1.2027805577	.4689486801
H1	-.1191559886	-.7438891014	-1.6486819065

CH₃CH(SH)CH₂CHOH

atom	x	y	z
H1	-.3281061493	1.5525604776	-1.6567216558
C1	-.0339298382	1.7670152628	-.6123892785
H2	1.0602115675	1.9251307249	-.5952654642
C2	-.4395064105	.5995439301	.2936640397
H4	-.5205565900	2.7030379866	-.2944299169
C3	.2018785309	-.6989366430	-.0774928626
H5	-1.5369109739	.4931237842	.3075125222
S1	-.0848379180	1.0576515271	2.1589800526
H10	-1.5672128129	-1.9191273191	-.1678806373
H7	1.2941395077	-.6929929712	-.1950165948
C4	-.4841540035	-1.8364401206	-.2669686401
O1	.0491164834	-3.0790011751	-.6114277765
H3	1.0345743118	-3.0616582300	-.6832563559
H6	1.2717293325	1.2642331532	1.9990469479

CH₂=S

atom	x	y	z
H4	.0000000000	.9309562253	1.7096815052
C1	.0000000000	.0000000000	1.1267377652
S1	.0000000000	.0000000000	-.5306810742
H3	.0000000000	-.9309562253	1.7096815052

CH₃SSSCH₃

atom	x	y	z
S3	-.8839817714	-.7311694000	.0000000000
H6	.5886230672	2.0801367642	1.3933516407
S2	.3966475796	-.3730080835	1.8327069689
C2	.0989176380	1.4684627331	2.1635949982
S4	.3966475796	-.3730080835	-1.8327069689
C1	.0989176380	1.4684627331	-2.1635949982
H1	.5587711743	1.6659225867	-3.1456508770
H3	.5886230672	2.0801367642	-1.3933516407
H4	-.9796651301	1.6740788259	-2.2072376283
H2	.5587711743	1.6659225867	3.1456508770
H5	-.9796651301	1.6740788259	2.2072376283

7. Identification of the products:

The identification of the products done by using a GC-MS. Since these reactions were studied and their chemistry is relatively established we choose to present some representative reactions (short time reactions, low conversions) with H₂S or CH₃SH, in order to be able to see some of the intermediate species that are important for the isotope exchange.

Fig. 1S shows the reaction the GC/MS for products of the reaction between Butanal and H₂S at pH 8-9 at aqueous conditions according to method 1. The reaction products consist of: **1**, **2**, **3**, and **4** which give a clue for the mechanism involved as shown in Scheme 1. Detailed discussions on the mechanism and products were published elsewhere¹⁻⁷.

Fig . 1S

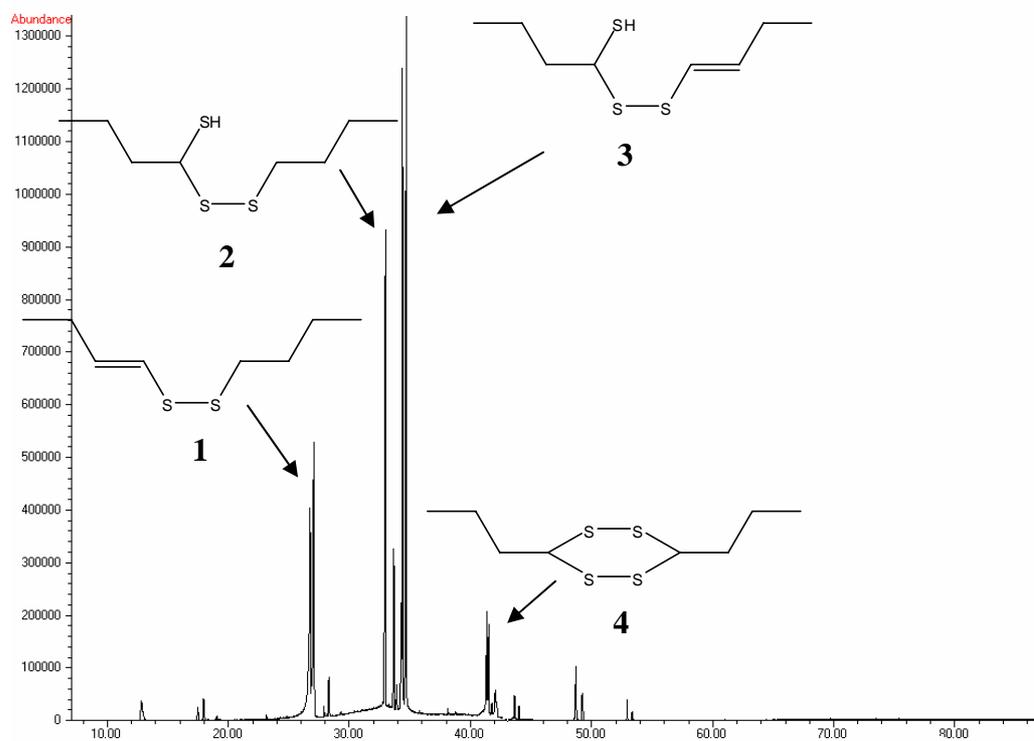


Fig 2S. GC-MS trace for the reaction products of octanal and CH_3SNa under aqueous conditions (Method 3) demonstrating the formation of the gem-disulfide **6**. Other trace quantities products include some intermediates such as **5**.

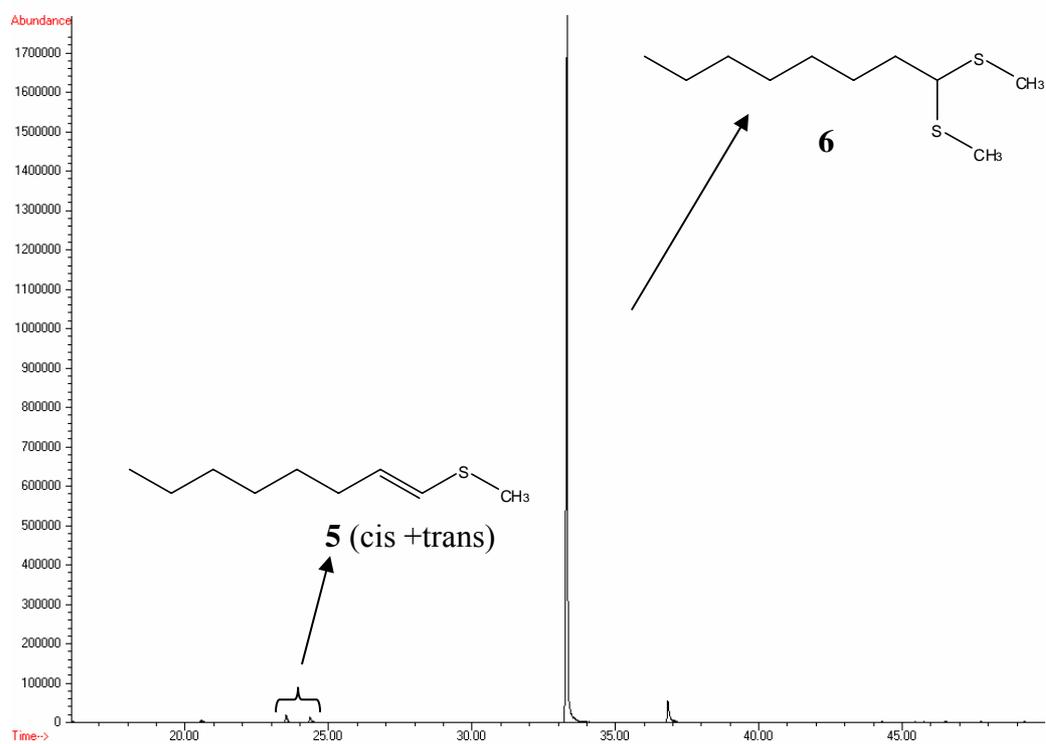


Fig. 3S . GC-MS trace for the reaction products of 2-octenal and CH_3SNa under aqueous conditions (Method 3) demonstrating the predominance of the Michael addition adduct **7**.

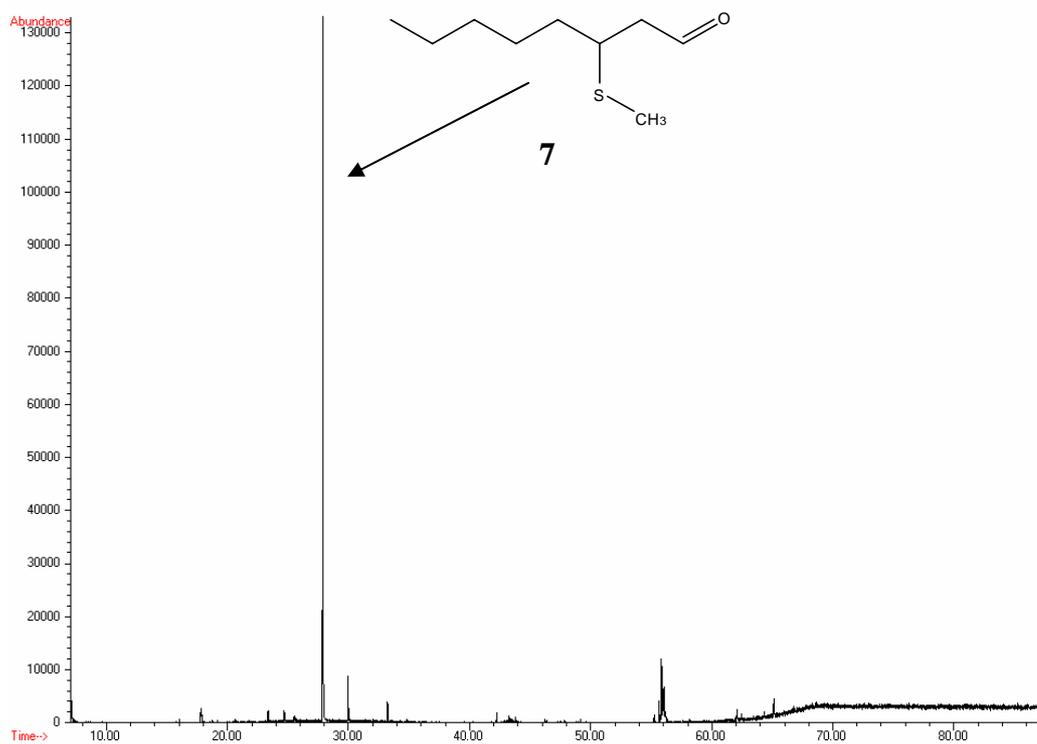
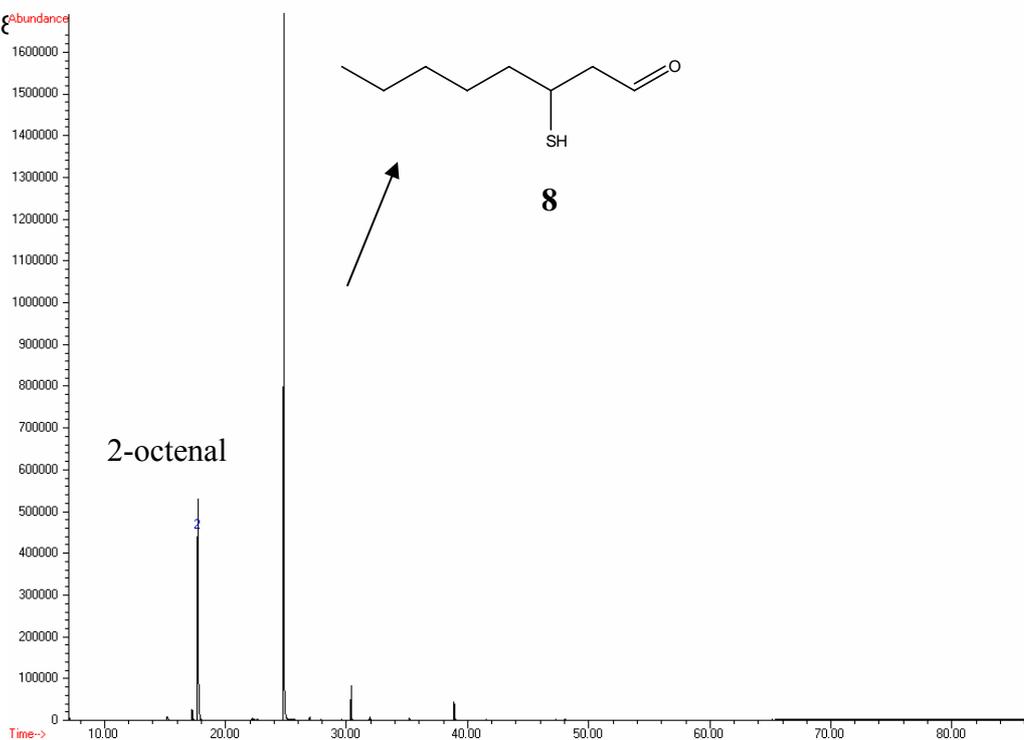


Fig. 4S . GC-MS trace for the reaction products of 2-octenal and HS^- under aqueous conditions (Method 3) demonstrating the predominance of the Michael addition adduct **8**.

Molecule	E_0 (Hartree)	E_0 (kcal/mol)	ZPE (kcal/mol)	E_{sol} (kcal/mol)	$\delta G_{T=20C}$ (kcal/mol)	$\Delta G_{T=20C}$ (kcal/mol)	$\Delta\Delta G$ (kcal/mol)	$\delta(\Delta\Delta G)$ (cal/mol)	k_i/k_0	$R_i \cdot R_0$ (per mil)						
CH ₃ S- CH ₃ ³⁴ S-	-438	125028	274028	18	22	2572	72	8204	14	57660	274002	22	0.058	3.9	0.9933	-6.7
HS- H ³⁴ S-	-39													4.1	0.9930	-7.0



Additional data for the protonation effect of MeSH and H₂S

Final coordinates:

HS⁻

atom	x	y	z
H1	0.0000000000	0.0000000000	1.3491275168
S1	0.0000000000	0.0000000000	-0.0425272575

CH₃S⁻

atom	x	y	z
H1	-0.3754893042	1.7065428089	0.8963401365
C1	0.1070125404	1.2699469338	0.0000000000
H2	-0.3754893042	1.7065428089	-0.8963401365
S1	-0.0534214534	-0.6339080466	0.0000000000
H4	1.1715317658	1.5758653526	0.0000000000

References:

1. A. Amrani, J. W. Turner, Q. Ma, Y. Tang and P.G. Hatcher, *Geochimica et Cosmochimica Acta*, 2007, In press, available online.
2. P. Schneckenburger, P. Adam and P. Albrecht, *Tetrahedron Letters*, 1998, **39**, 447-450.
3. A. Amrani and Z. Aizenshtat, *Organic Geochemistry*, 2004, **35**, 1319.
4. A. Amrani and Z. Aizenshtat, *Organic Geochemistry*, 2004, **35**, 909.
5. E. B. Krein and Z. Aizenshtat, in *ACS Symposium Series, vol.612*, eds. M. A. Vairavamurthy, M. A. A. Schoonen, T. I. Eglinton, G. W. Luther, III and B. Manowitz, American Chemical Society, Washington, Edition edn., 1995, pp. 110-137.
6. E. B. Krein and Z. Aizenshtat, *Journal Of Organic Chemistry*, 1993, **58**, 6103-6108.
7. A. R. Loch, K. A. Lippa, D. L. Carlson, Y. P. Chin, S. J. Traina and A. L. Roberts, *Environmental Science & Technology*, 2002, **36**, 4065-4073.