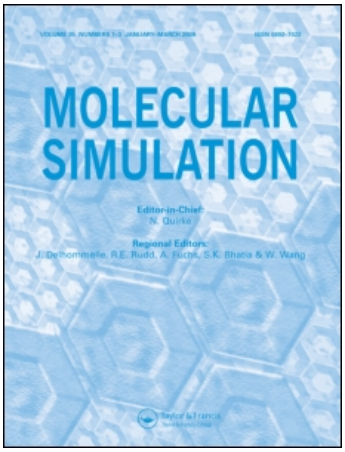

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Mark A. Plummer[a]; Scott W. Cowley[b]
[a] **MP***r&d*, LLC, Centennial, CO, USA [b] Colorado School of Mines, Golden, CO, USA

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Chemical mechanisms in hydrogen sulfide decomposition to hydrogen and sulfur

MARK A. PLUMMER†* and SCOTT W. COWLEY‡

†**MP***r&d*, LLC, Centennial, CO, USA
‡Colorado School of Mines, Golden, CO, USA

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Hydrogen sulfide (H_2S) conversion into hydrogen (H_2) and sulfur was previously investigated using oxidation/reduction chemistry. First, H_2S was reacted with 2-*t*-butylanthraquinone (TBAQ) in a process solvent to form the hydroquinone (HTBAQH) and atomic sulfur. Sulfur was then polymerized into its ring form (S_8) for recovery from the process solvent. These first two reactions were aided by a sulfur complexing agent (SCA). Then, HTBAQH was dehydrogenated using a heterogeneous catalyst. In the current work, computational chemistry using semi empirical methods was used to determine the detailed chemical steps occurring through S_8 formation. It was found that the process solvent stabilizes the diradical form of TBAQ and the SCA splits H_2S into an ion pair. These two mechanisms assisted in the transfer of two electrons and two protons from H_2S to TBAQ to form HTBAQH and atomic sulfur. The sulfur atom was computationally shown to be a diradical stabilized by one or two molecules of the complexing agent. Also, sulfur polymerization was computationally shown to be diradical in nature with the growing polymer chain being terminated by one or two SCA.

Keywords: Hydrogen sulfide decomposition; Sulfur polymerization; Computational chemistry; Diradical sulfur chemistry; Sulfur complexing agent; Hydrogen

1. Introduction

The desulfurization of fuels is generally accomplished by hydrogenation and consequent production of hydrogen sulfide (H_2S) [1–3]. A process to decompose H_2S into hydrogen (H_2) and sulfur (S_8) has been investigated [4–6]. The purpose of this process is to recycle 25–40% of the total hydrogen needed in crude oil refineries for hydrogenation. In commercial technology [2], H_2S is oxidized to sulfur and water thereby losing its hydrogen content for recycle.

This H_2S decomposition process consists of three basic steps (figure 1). First, H_2S is reacted with an anthraquinone, e.g. 2-*t*-butylanthraquinone (TBAQ), in a process solvent. This produces the anthrahydroquinone (HTBAQH) and atomic sulfur (S). Several solvents were previously evaluated for this process [6–7]. Based on TBAQ to HTBAQH conversion rate, *N*-methyl-2-pyrrolidinone (NMP) was selected. Secondly, the atomic sulfur is polymerized into the S_8 ring for removal by precipitation from NMP. These first two basic steps are controlled by a sulfur complexing agent (SCA) dissolved in NMP. In the third step, HTBAQH is dehydrogenated using a heterogeneous catalyst. This dehydrogenation occurs in the presence of the process solvent and the SCA.

In the current work, computational chemistry using semi empirical methods was used to determine the detailed chemical steps occurring through S_8 recovery. The purpose of defining these steps was to aid subsequent work in optimizing the overall process. Semi empirical methods have been successfully used in other investigations of sulfur compounds for calculating formation energies, polarities and ionization potentials [8].

2. Computational methods

AM1 or Zindo_1 equilibrium methods were used to yield minimum energy structures and electron distributions at 0 K for all individual molecules, i.e. TBAQ and its diradical, NMP solvent, SCA and H_2S. Then, single point calculations were made to obtain total molecular energy. Zindo_1 was used only with ionic molecules since AM1 calculations did not yield acceptable results. That is, the

*Corresponding author. Email: mplummer65@msn.com

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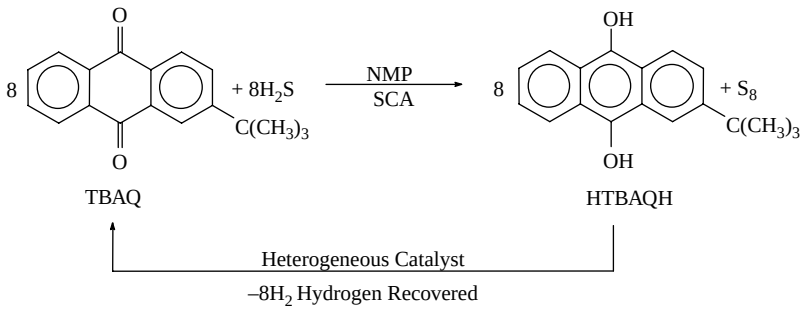

Figure 1. Overall process chemistry to convert H_2S into hydrogen and sulfur.

splitting of H_2S into an ion pair as detailed below could not be achieved using the AM1 method. AM1 was used in all other work since Zindo_1 some times yielded highly strained structures.

For the multi-component structures (complexes, ion pairs and free radical polymers) molecular dynamics (MD) was used to determine minimum energy structures and electron transfer levels between components. Again, AM1 or Zindo_1 methods were used depending on the situation as described above. Most computations were done at 295 or 335 K, which were the optimum temperatures found in previous experimental work for sulfur precipitation from NMP and TBAQ conversion, respectively. Multi-component structures were considered stable if the components did not migrate away from each other during MD calculations.

In the MD work, minimum energies were generally obtained in under 10 picoseconds (ps). After each MD study, the multi component structure was energy minimized at 0 K to obtain its equilibrium energy level. A summation was then made of the 0 K minimum energies of the individual molecules that were used to make up the multi component structure. This energy sum was then subtracted from the energy level of the final multi component structure at 0 K to yield the formation energy of the latter. The semi empirical methods used are well parameterized for organic compounds especially for calculating heats of formation [9]. Hence, formation energies calculated by this procedure should be sufficiently accurate for the discussed mechanisms.

Several initial docking positions were evaluated with multi component structures. Initial docking that yielded the greatest ± charge difference between individual atoms in the docked molecules generally yielded the lowest energy level after MD testing.

For either single or multi-component structures where all electrons were paired, restricted Hartree-Fock (RHF) theory with a spin multiplicity (SM) of one was used. For free radical structures, unrestricted Hartree-Fock (UHF) theory was used with a SM of three to account for the unpaired electrons. In all equilibrium calculations, the Polak-Ribiere algorithm was used to obtain a minimum energy of 0.01 kcal/g-mole.

3. Results and discussion

3.1 Initial evaluation of sulfur polymerization chemistry

It was assumed that sulfur polymerization in this process occurs by the addition of one sulfur atom monomer at a time to form a growing linear chain. This assumption was based on the polymerization of other monomers such as ethylene and styrene [10]. Then after a sufficient number of sulfur atoms had been added, the chain would fold into an S_8 ring. However, the exact chemical mechanism for this polymerization and folding was unknown. The first suggested mechanism [7] was through formation of linear sulfanes, i.e. H—S_X—H. Then, sulfur would fold via

$$H-S_9-H \rightarrow H-S-H + S_8 \downarrow .$$

Linear sulfanes were computationally evaluated with X values from 9 to 18 at polymerization temperatures from 273 to 593 K. This temperature range included the optimum experimental temperatures of 295 and 335 K. Also, pyridine (PY) was used as the SCA with the H—S_9—H case. Sulfur folding was considered to have occurred when the terminals of any sequential 8 sulfur atoms contacted each other within 2.0 ± 0.2 Å. This work used the MD/AM1/SM1 method.

Under these conditions, sulfur folding from a linear polymer to a ring S_8 form was not noted. This result was independent of whether or not PY was used as the SCA. Hence, it was concluded that sulfur polymerization and folding via sulfane formation is not occurring in this process.

The next linear polymers evaluated computationally for folding were sulfur diradicals. It has been shown that sulfur diradicals are formed in the decomposition of sulfur at temperatures > 373 K [11]. Sulfur folding via diradicals would be via

$$S_X^{\bullet\bullet} \rightarrow S_8 \downarrow + S_{X-8}^{\bullet\bullet}.$$

These studies were first performed without PY as the SCA or the NMP solvent. The values of X tested ranged from 8 to 15 for temperatures from 273 to 373 K. Folding occurred only for X values of 9 and 12 using the MD/AM1/SM3 method.

Next sulfur diradicals were tested with PY as the SCA using either 1 or 2 mol PY per polymer chain using the

Table 1. Energy and charge values for individual and complexed molecules.

	Molecular energy kcal/g-mole		*TBAQ charges – ESU*	
	Total	*Formation of complex*	*Oxygen*	*Center ring*
NMP	−29789.6			
TBAQ	−72988.6		−0.578	0.177
$TBAQ^{\bullet\bullet}$	−72944.7		−0.580	0.173
TBAQ → $TBAQ^{\bullet\bullet}$ Formation	43.9			
Complexing one NMP with one TBAQ or one $TBAQ^{\bullet\bullet}$				
NMP—TBAQ	−102778.3	−0.1	−0.580	0.173
NMP—$TBAQ^{\bullet\bullet}$	−102739.5	−5.2	−0.307	0.015

MD/AM1/SM3 method. It was found that PY in all cases formed stable complexes with the sulfur diradicals. Excellent folding was obtained for *X* values of 8 and 9 for both the 1 and 2 PY mole cases over the 273–373 K temperature range investigated, e.g.

$$PY-S_8^{\bullet\bullet}-PY \rightarrow S_8 \downarrow +2PY.$$

Folding was also obtained for higher *X* values over more limited temperature ranges especially for the 2 mol PY case.

Finally, folding was tested with the NMP solvent at 2 mol per mole of the linear $S_8^{\bullet\bullet}$ diradical. It was found that the NMP molecules migrated away from the $S_8^{\bullet\bullet}$ diradical during MD calculations. Therefore, a stable complex with this diradical and 2 NMP molecules will not form over a temperature range of 295–335 K. Based on this result, a larger number of NMP molecules were not evaluated with this diradical.

Based on the above folding results, the detailed mechanisms for the entire process chemistry were computationally evaluated for thermodynamic potential using diradical sulfur formation and diradical polymerization chemistry.

3.2 TBAQ solvation step

The first chemical step is to convert TBAQ to its diradical structure with the transfer of one electron from each carbonyl bond to the center ring making this ring aromatic.

$$TBAQ \leftrightarrow TBAQ^{\bullet\bullet}. \quad (1)$$

The $TBAQ^{\bullet\bullet}$ structure should assist in transferring two electrons and two protons from H_2S to TBAQ to form HTBAQH and a diradical sulfur atom.

The current effort here was to computationally determine if NMP would enhance $TBAQ^{\bullet\bullet}$ formation via forming a stable NMP–$TBAQ^{\bullet\bullet}$ complex. Stable NMP–$TBAQ^{\bullet\bullet}$ complex formation was suggested by previous proton NMR work [7].

First, the difference in AM1 formation energy for $TBAQ^{\bullet\bullet}$ over TBAQ was calculated and found to be +43.9 kcal/g-mole (table 1). Hence, in the absence of NMP, $TBAQ^{\bullet\bullet}$ is not favored over TBAQ.

Next, complexing studies with NMP and TBAQ or $TBAQ^{\bullet\bullet}$ were performed using the MD/AM1 method. TBAQ or $TBAQ^{\bullet\bullet}$ was initially docked with 1 NMP molecule at a distance between molecules of 2.0 Å with overlapping carbonyl groups (figure 2).

NMP complexes with either TBAQ or $TBAQ^{\bullet\bullet}$ were found to be favored over the initial molecules as shown by negative formation energies of −0.1 − 5.2 kcal/g-mole (table 1). Since, the NMP–$TBAQ^{\bullet\bullet}$ complex exhibited the most negative formation energy, this complex would be more favored over the NMP–TBAQ complex.

Essentially no charge transfer from NMP to TBAQ or $TBAQ^{\bullet\bullet}$ was noted in any of the complexes formed. Also, complexing NMP with TBAQ did not affect the charge on the TBAQ oxygen atoms at −0.580 electrostatic units (ESU). In contrast, complexing NMP with $TBAQ^{\bullet\bullet}$ resulted in decreasing the total negative charge on the oxygen atoms, i.e. −0.580 for TBAQ down to −0.307 ESU for $TBAQ^{\bullet\bullet}$ (table 1). This charge reduction was mostly transferred to the $TBAQ^{\bullet\bullet}$ center ring. These charge variations would enhance the transfer of two electrons and two protons from H_2S to $TBAQ^{\bullet\bullet}$.

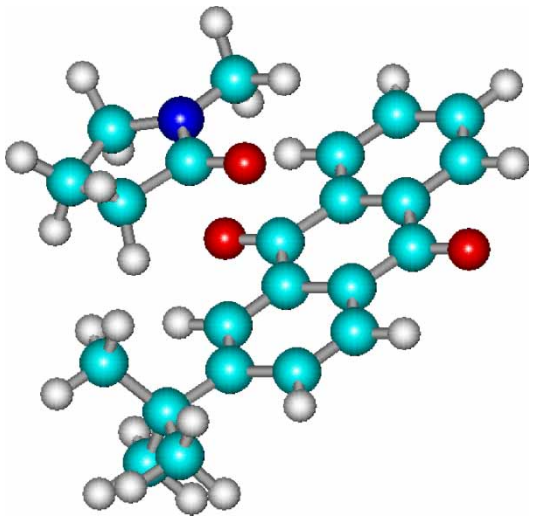

Figure 2. Initial docking of one NMP molecule (top) with $TBAQ^{\bullet\bullet}$ (bottom) carbon–blue, hydrogen–white, oxygen–red and nitrogen–dark blue in online colour version.

Essentially, the same results detailed above were obtained when 2 molecules of NMP were initially docked with either TBAQ or $TBAQ^{\bullet\bullet}$.

3.3 First ion pair formation step

The second chemical step is the reaction of H_2S with the SCA to form an ion pair. Two SCA compounds, diethylmethylamine (DEMA) and PY, were used to evaluate this step, e.g.

$$H_2S + PY \leftrightarrow PYH^+ + HS^-. \quad (2)$$

DEMA or PY was individually docked with H_2S by placing the nitrogen atom of the SCA at 2 Å from one of the hydrogen atoms of H_2S. The existence of a stable complex was obtained using the MD/Zindo_1/SM1 method. During MD calculations, it was noted that the hydrogen atom of H_2S initially docked near the SCA constantly oscillated within bonding distances between the SCA nitrogen atom and the H_2S sulfur atom. This demonstrated stable SCA/H_2S complexes. Next, the $SCAH^+/HS^-$ ion pair was formed by removing the oscillating hydrogen atom as a proton and bonding it with the SCA. The MD procedure was then repeated to obtain the formation energy of the $SCAH^+/HS^-$.

It was found that the complexes and ion pairs were thermodynamically favorable over the individual components with formation energies of −40.5 and −40.7 kcal/g-mole (table 2), respectively, for PY and DEMA in the absence of NMP.

Also, there was no difference in formation energies between each stable complex and the corresponding ion pair (table 2). This says that, in the absence of a solvent, there is an equal likely hood of finding a stable complex and an ion pair in mixtures of H_2S with either DEMA or PY.

The next procedure was to dock PY or DEMA with NMP–H_2S stable complexes containing 1–3 molecules of NMP. Docking was performed by placing the nitrogen atom of the SCA at 2 Å from a hydrogen atom of H_2S in a given NMP–H_2S complex (figure 3).

During MD/Zindo_1/SM1 calculations for the 1 NMP case, the docked hydrogen atom in H_2S constantly oscillated within bonding distances of the nitrogen atom in the SCA and the sulfur atom in H_2S. For the 2 and 3 NMP cases, the docked hydrogen atom migrated to the SCA. This shows that both PY and DEMA are capable of extracting a proton from H_2S complexed with 1, 2 and 3 molecules of NMP to yield $SCAH^+/HS^-$ ion pairs. Hence, the $SCAH^+/HS^-$ ion pair was computationally formed by removing the oscillating or migrating hydrogen atom as a proton from H_2S in the stable complex and bonding it with the SCA. The MD procedure was then repeated to obtain the total energy of the $SCAH^+/HS^-$ ion pair.

It was found that all complexes and ions pairs are thermodynamically favored over individual molecules, i.e. formation energies ranged from −68.3 to −574.5 kcal/g-mole depending on the SCA and the number of NMP molecules in the structure (table 2).

Table 2. Energy values for complexed and ion pair structures.

	Molecular energy kcal/g-mole	
	Total	*Formation*
Initial molecules		
H_2S	−7359.3	
NMP	−41662.0	
PY-H_2S structures		
0 NMP complex	−36503.3	−40.5
0 NMP ion pair	−36503.3	−40.5
Difference		0.0
1 NMP complex	−78196.0	−71.2
1 NMP ion pair	−78196.0	−71.2
Difference		0.0
2 NMP complex	−120210.2	−423.4
2 NMP ion pair	−120210.2	−423.4
Difference		0.0
3 NMP complex	−162022.8	−574.0
3 NMP ion pair	−162023.3	−574.5
Difference		−0.5
PY	−29103.5	
DEMA	−32713.6	
DEMA-H_2S structures		
0 NMP complex	−40113.6	−40.7
0 NMP ion pair	−40113.6	−40.7
Difference		0.0
1 NMP complex	−81803.2	−68.3
1 NMP ion pair	−81806.0	−71.1
Difference		−2.8
2 NMP complex	−123662.0	−265.1
2 NMP ion pair	−123675.8	−278.9
Difference		−13.8
3 NMP complex	−165529.3	−470.4
3 NMP ion pair	−165527.6	−468.7
Difference		1.7

The difference between the ion pair and complexed structures for PY was zero for structures containing 1 and 2 molecules of NMP (table 2). For these cases, the complex and ion pair structures are thermodynamically equal. For the 3 NMP case with PY the difference of −0.5 kcal/g-mole shows a slight thermodynamic advantage for the ion pair over the comparable complex structure.

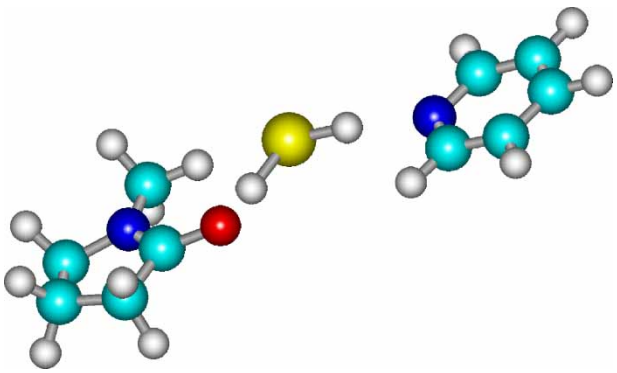

Figure 3. Initial docking of NMP (left), H_2S (middle) and PY (right) carbon–blue, hydrogen–white, oxygen–red, nitrogen–dark blue and sulfur–yellow in online colour version.

For the DEMA structures, the formation energy difference between the ion pair and complex structure exhibited a maximum negative value of − 13.8 kcal/g-mole for the 2 NMP case (table 2). Hence, the ion pair structure would be considerably more favored thermodynamically for this case. The ion pair for the DEMA case with 1 NMP would be slightly more favored over the corresponding complex case with a formation energy difference of − 2.8 kcal/g-mole. With, the 3 NMP case, the complex structure would be more favored with a difference of 1.7 kcal/g-mole. The latter result is probably due to considerable steric hindrance for DEMA to approach and react with H_2S complex with 3 NMP molecules.

The more negative complex to ion formation energy differences for the DEMA cases versus those for PY cases are probably due to the higher basicity (pK_b of 3.5) of DEMA compared to that for PY (pK_b of 8.8). That is, a higher SCA basicity would more easily attract an acidic proton from H_2S.

3.4 First electron and first proton transfer steps

The next two chemical steps consist of an electron transfer followed by a proton transfer from the ion pair to the $TBAQ^{\bullet\bullet}$ diradical. For PY in the presence of NMP, the steps are respectively (molecular complexes are parenthesized):

$$TBAQ^{\bullet\bullet} + (PHY^{+} - HS^{-} - NMP) \leftrightarrow TBAQ^{\bullet -} + (PYH^{+} - HS^{\bullet} - NMP) \quad (3)$$

$$TBAQ^{\bullet -} + (PYH^{+} - HS^{\bullet} - NMP) \leftrightarrow HTBAQ^{\bullet} + (HS^{\bullet} - NMP) + PY. \quad (4)$$

These reactions were studied with the MD/AM1/SM3 method using the initial docked positions in figure 4. These initial positions yield the largest ± atomic charge differences between molecules in the complexed structures.

Formation energies for both steps are thermodynamically favorable with the electron transfer being more favorable at − 140.5 kcal/g-mole than the proton transfer at − 46.8 kcal/g-mole, respectively (table 3). These computer results confirm experimental cyclic voltametry data [7].

3.5 Second ion formation step

In the second ion formation step, the mono $HS^{\bullet}$ radical and PY are converted into an ion pair as follows

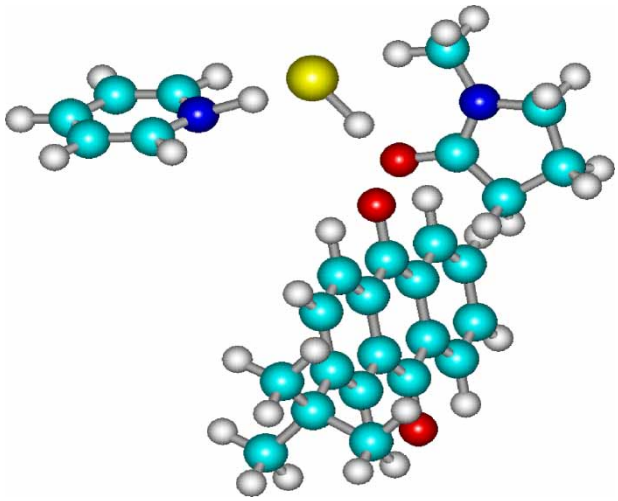

Figure 4. Initial docked positions for the first electron and proton transfer steps: PYH^{+} (left), $HS^{\cdot}$ (middle), NMP (right) and $TBAQ^{\bullet\bullet}$ (bottom).

(parenthesized molecules are stable complexes):

$$PY + (HS^{\bullet} - NMP) \leftrightarrow (PYH^{+} - S^{\bullet -} - NMP). \quad (5)$$

The MD/Zindo_1/SM3 technique was used to evaluate this chemical step. The initial starting positions of the molecules were the same as those in figure 3 with the hydrogen atom of the $HS^{\bullet}$ radical positioned at 2 Å from the nitrogen atom of PY.

The formation energy for this ion formation step is favorable at − 1.0 kcal/g-mole (table 3). This value is more favorable than that for the first ion pair formation step under equivalent conditions.

3.6 Second electron transfer, proton transfer and sulfur diradical removal steps

The next chemical steps consist of first transferring an electron from the product complex in step (5) to the mono radical $HTBAQ^{\bullet}$ generated in step (4) as follows:

$$HTBAQ^{\bullet} + (PHY^{+} - S^{\bullet -} - NMP) \leftrightarrow (HTBAQ^{-} - PYH^{+} - S^{\bullet\bullet} - NMP). \quad (6)$$

The product complex formed was quite stable, i.e. none of the components in the complex migrated away during MD calculations with a duration of 10 ps. Then a second PY molecule was placed at 2 Å from the sulfur diradical and MD calculation were continued. Sulfur removal, as a diradical complexed with 2 PY molecules, occurred

Table 3. Total molecular energy for conversion of TBAQ to HTBAQH—kcal/g-mole.

	Step 3 *First electron transfer*	*Step 4* *First proton transfer*	*Step 5* *Second ion formation*	*Step 6* *Second electron transfer*	*Step 7* *Second proton formation*
Reactants	− 128790.4	− 128930.9	− 55609.1	− 128900.7	− 149981.0
Products	− 128930.9	− 128977.7	− 55610.1	− 128940.4	− 150074.5
Difference	− 140.5	− 46.8	− 1.0	− 39.7	− 93.5

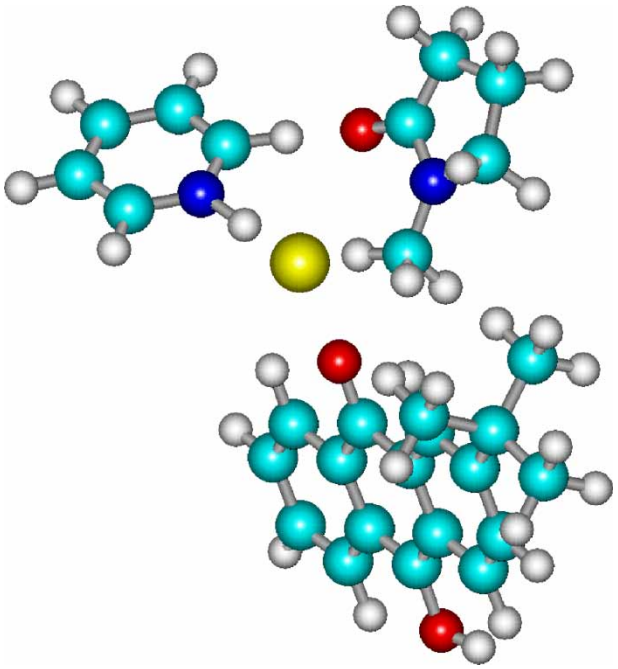

Figure 5. Initial docking for the second electron and proton transfer steps: upper molecules–PYH^+ (left), $S^{\cdot -}$ (middle), NMP (right) lower–$HTBAQ^{\cdot -}$.

in less than 1 ps along with a proton transfer as follows:

$$(HTBAQ^- - PYH^+ - S^{\bullet\bullet} - NMP) + PY \leftrightarrow HTBAQH + (PY - S^{\bullet\bullet} - PY) + NMP. \quad (7)$$

These reactions were evaluated using the MD/AM1/SM3 method with initial docked positions as shown in figure 5.

Formation energies for steps (6) and (7) are thermodynamically favorable with electron transfer at −39.7 kcal/g-mole and proton transfer/S removal at −93.5 kcal/g-mole, respectively (table 3).

Steps (6) and (7) were combined and also studied using the MD/AM1/SM3 method. This approach is not as likely as two separate steps. That is, it would require getting the two reactants of step (6) together simultaneously with a second molecule of PY. However, this approach yields more favorable thermodynamics than the two-step approach. That is, a formation energy of −276.7 kcal/g-mole was calculated for the combined steps versus a total of −133.2 kcal/g-mole for the two-step approach. For the combined case, the S diradical migrates from the reaction site complexed with 1 PY molecule for eventual polymerization as detailed below.

3.7 *Sulfur polymerization steps*

As detailed above, the conversion of TBAQ to HTBAQH yields a diradical sulfur atom complexed with 1 or 2 PY molecules. Hence, these complexes were used as monomers for the polymerization process in which one sulfur diradical was added at a time to a growing polymer chain. The overall mechanism for this sulfur polymerization can be summarized as follows:

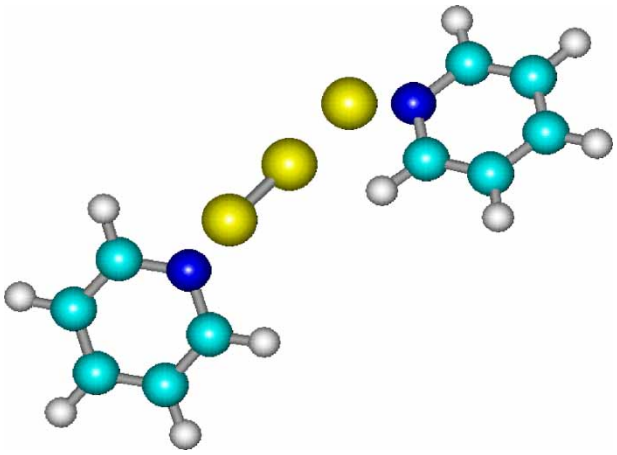

Figure 6. Initial docked positions for making a three-atom sulfur polymer.

$$\text{First}: \quad PY - S_X^{\bullet\bullet} + PY - S^{\bullet\bullet} \rightarrow PY - S_{X+1}^{\bullet\bullet} + PY \quad (8)$$

or

$$PY - S_X^{\bullet\bullet} - PY + PY - S^{\bullet\bullet} - PY \rightarrow PY - S_{X+1}^{\bullet\bullet} - PY + 2PY \quad (9)$$

where X equals 1–7.

$$\text{Then}: \quad PY - S_8^{\bullet\bullet} + PY \rightarrow S_8 \downarrow + 2PY \quad \text{or} \quad (10)$$

$$PY - S_8^{\bullet\bullet} - PY \rightarrow S_8 \downarrow + 2PY. \quad (11)$$

A typical initial docking arrangement to study step (8) is shown in figure 6 where the initially docked sulfur atoms are 2 Å apart.

Less than 2 ps of MD/AM1/SM3 computation time were generally required to add a PY—$S^{\bullet\bullet}$ monomer to the growing polymer chain and to release a PY molecule which migrated away from the polymerization site (step (8)).

In step (10), the linear polymer PY—$S_8^{\bullet\bullet}$ was found to fold in about 5 ps. However, the release of the last complexed PY molecule would not occur for MD times up to 10 ps without the assistance of a free molecule of PY.

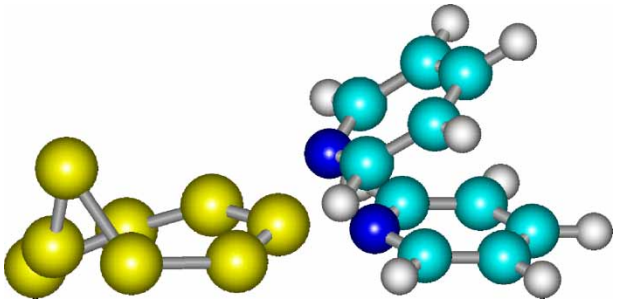

Figure 7. Initial docking of free PY to remove last complexed PY.

Table 4. Total molecular energy values during sulfur polymerization using 1 PY molecule per growing sulfur polymer chain at 335 K—kcal/g-mole.

	Step 8							*Steps 8 and 10*
State	*S to S_1*	*S_1 to S_2*	*S_2 to S_3*	*S_3 to S_4*	*S_4 to S_5*	*S_5 to S_6*	*S_6 to S_7*	*S_7 to S_8*
Reactants	−25530.0	−51117.0	−55638.3	−60110.5	−64604.3	−69103.6	−73580.6	−78027.7
Products	−25558.5	−51184.4	−55687.8	−60167.7	−64685.9	−69176.1	−73611.3	−78127.8
Difference	−28.5	−67.4	−49.5	−57.2	−81.6	−72.5	−30.7	−100.1

After a free PY molecule was docked near the complexed PY molecule (figure 7), both molecules of PY were released from the folded S_8 in about 0.5 ps. Experimentally, 8 molecules of PY per S_8 ring were generally used. Therefore, there was sufficient amount of free PY to accomplish the removal of the complexed PY molecule after PY—$S_8^{\bullet\bullet}$ folding.

Results show favorable energy values of −28.5– to 81.6 kcal/g-mole for the formation of all complexes (step (8)) containing 1–7 sulfur atoms in the PY—$S_X^{\bullet\bullet}$ polymers (table 4). The formation energy for forming the PY—$S_8^{\bullet\bullet}$ polymer, S_8 folding and the release of PY (step (10)) was found to be very favorable at −100.1 kcal/g-mole (table 4). This very favorable S_8 formation energy should limit the production of polymers greater than PY—$S_8^{\bullet\bullet}$. This conclusion was experimentally supported by the fact that the NMP solutions after S_8 precipitation contained essentially no sulfur polymers of any length.

Addition of a PY—$S^{\bullet\bullet}$—PY monomer to the growing polymer chain (step (9)) took < 10 ps and generally < 5 ps of MD/AM1/SM3 time. In some cases, a free PY molecule had to be docked near a second complexed PY molecule before the latter could be released. Then both PY molecules were released in about 1 ps leaving 2 PY molecules to stabilize the growing polymer chain. Again, there were sufficient free PY molecules in the experimental tests to accomplish this step.

Folding of the PY—$S_8^{\bullet\bullet}$—PY polymer and the release of one complexed PY molecule (step (11)) required < 10 ps.

Table 6. Total molecular energy values during sulfur polymerization—kcal/g-mole.

	1 PY per polymer chain at 335 K		*2 PY per polymer chain at 295 K*	
	Step 12	*Step 13*	*Step 14*	*Step 15*
State	S_2 to S_4	S_4 to S_8	S_2 to S_4	S_4 to S_8
Reactants	−60159.6	−78091.6	−102331.2	−120342.6
Products	−60169.6	−78145.4	−102378.9	−120346.0
Difference	−10.0	−53.8	−47.7	−3.4

Again, a free molecule of PY had to be docked as in figure 7 to release the last complexed PY molecule in < 1 ps.

Table 5. Total molecular energy values during sulfur polymerization at 295 K using 2 PY molecules per growing polymer chain—kcal/g-mole.

	Step 9							*Steps 9 and 11*
State	*S to S_1*	*S_1 to S_2*	*S_2 to S_3*	*S_3 to S_4*	*S_4 to S_5*	*S_5 to S_6*	*S_6 to S_7*	*S_7 to S_8*
Reactants	−46638.5	−93366.4	−97848.8	−102353.7	−106854.5	−111345.2	−115857.6	−141355.0
Products	−46683.2	−93382.2	−97887.6	−102388.4	−106882.1	−111390.2	−115884.7	−141433.7
Difference	−44.7	−15.8	−38.8	−34.7	−27.6	−45.0	−27.1	−78.7

Favorable polymerization energies were obtained for the 2 PY monomer case (steps (9) and (11)). However, these formation energies (table 5) are not quite as favorable thermodynamically as those obtained for the 1 PY monomer case.

Two polymerization mechanisms other than addition of one sulfur diradical at a time to a growing polymer chain were also investigated, i.e.

$$2\text{PY}-\text{S}_2^{\bullet\bullet} \rightarrow \text{PY}-\text{S}_4^{\bullet\bullet} + 2\text{PY} \text{ followed by} \quad (12)$$

$$2\text{PY}-\text{S}_4^{\bullet\bullet} \rightarrow \text{S}_8 \downarrow + 2\text{PY} \quad \text{or} \quad (13)$$

$$2\text{PY}-\text{S}_2^{\bullet\bullet}-\text{PY} \rightarrow \text{PY}-\text{S}_4^{\bullet\bullet}-\text{PY} + 2\text{PY} \text{ followed by} \quad (14)$$

$$2\text{PY}-\text{S}_4^{\bullet\bullet}-\text{PY} \rightarrow \text{S}_8^{\bullet\bullet} \downarrow + 4\text{PY}. \quad (15)$$

Favorable formation energies in the range of −10.0 to −53.8 kcal/g-mole were calculated for these cases using the MD/AM1/SM3 method (table 6).

However under equivalent conditions, these energies are less thermodynamically favorable than those via the addition of one sulfur diradical at a time to the growing sulfur polymer chain especially that for S_8 formation and folding.

4. Conclusions

Computational chemistry has been used to determine the sulfur production steps in a process to decompose H_2S into hydrogen and sulfur. Overall, this process is accomplished by converting TBAQ into HTBAQH in the presence of NMP as solvent and a SCA, e.g. PY. Then the sulfur atoms produced are polymerized via a free radical mechanism into the S_8 ring form for recovery.

The detailed sulfur chemistry occurs in three major parts. In the first part, NMP stabilizes TBAQ in its diradical form $TBAQ^{\bullet\bullet}$ and PY splits H_2S into PYH^+ and HS^- ions. Then an electron is transferred from HS^- to $TBAQ^{\bullet\bullet}$ converting the latter to a radical anion $TBAQ^{\bullet -}$. Next, a proton transfer from PYH^+ occurs changing $TBAQ^{\bullet -}$ into the $HTBAQ^{\bullet}$ radical along with yielding a free PY molecule. The $HS^{\bullet}$ free radical produced complexes with NMP and migrates away from the reaction site.

In the second part, the $HS^{\bullet}$—NMP complex reacts with PY to yield a PYH^+ ion and the $S^{\bullet -}$ radical anion. This is followed by an electron transfer from $S^{\bullet -}$ to $HTBAQ^{\bullet}$ yielding the $HTBAQ^-$ ion and the sulfur diradical $S^{\bullet\bullet}$. These two product species are in a stable complex with PY and NMP at the reaction site. When a free PY molecule contacts this product complex, a proton is transferred from PYH^+ to $HTBAQ^-$ producing HTBAQH. At the same time, the $S^{\bullet\bullet}$ diradical is transported away as a PY—$S^{\bullet\bullet}$ or PY—$S^{\bullet\bullet}$—PY complex.

In the third part, either PY—$S^{\bullet\bullet}$ or PY—$S^{\bullet\bullet}$—PY acts as the basic monomer for addition to a growing sulfur polymer which builds to either a PY—$S_8^{\bullet\bullet}$ or PY—$S_8^{\bullet\bullet}$—PY linear chain. Finally, the PY—$S_8^{\bullet\bullet}$ or PY—$S_8^{\bullet\bullet}$—PY linear chain folds into the S_8 product and the released PY molecules migrate away.

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