Electronic Supplementary Material

Theoretical study on the mechanism of sulfur migration to gas in the pyrolysis of benzothiophene

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S1. H_2S generation without S or SH radical involved

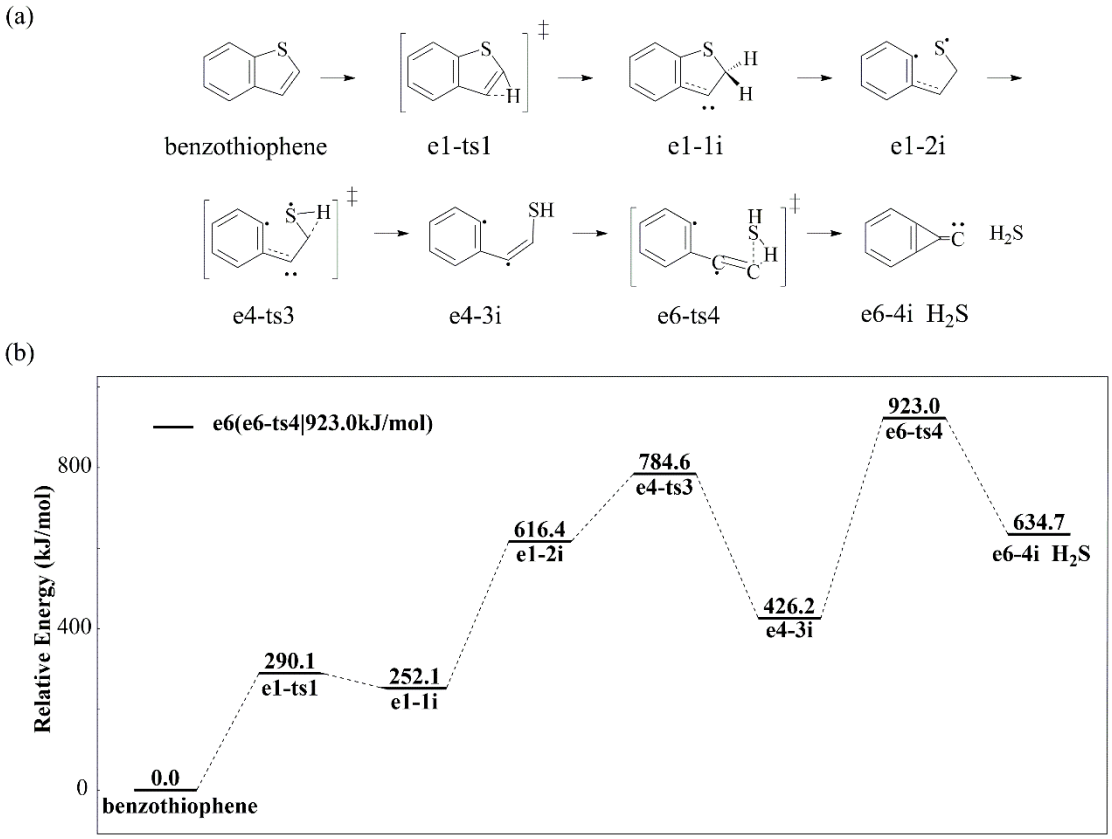

Fig. S1 The H_2S formation pathways (a) and corresponding energy diagrams (b)

H_2S can be generated without S or SH radical involved, as shown in **Fig. S1**. Following Mode E, e1-1i is obtained and transforms into e1-2i via homolysis. Afterward, intermediate e4-3i with a sulfhydryl group is formed through H-transfer from C_1 to S. Finally, H_2S and e6-4i are generated via the synergistic H-transfer reaction, which is the rate-determining step for H_2S formation (923.0 kJ/mol). The high energy barrier indicates that the formation of H_2S without involving S and SH radicals from benzothiophene pyrolysis is really difficult.

S2. Atom coordinates of the optimized structures

2.1 Atom coordinates of benzothiophene and sulfur-containing products

Benzothiophene

C	1.41678600	1.37220900	-0.00009700
C	0.11073800	0.85158500	-0.00021300
C	1.02910800	-1.42631200	-0.00007900

C	2.30724800	-0.88485000	0.00014100
C	2.49950000	0.50761600	0.00008500
H	1.56963900	2.44598700	-0.00015100
H	0.88354700	-2.50024000	-0.00010800
H	3.16679600	-1.54526900	0.00036400
H	3.50731200	0.90669800	0.00025600
C	-0.06182000	-0.55333600	-0.00019800
S	-1.76524600	-0.97913200	0.00004100
C	-1.14929100	1.54815300	0.00000900
C	-2.21588100	0.71135200	0.00000600
H	-1.23835600	2.62683100	0.00058800
H	-3.26333500	0.97360700	0.00047500

S radical

S	0.00000000	0.00000000	0.00000000

SH radical

S	-0.46795100	0.46795300	0.00000000
H	-1.42511000	1.42423100	-0.00012300

CS radical

C	0.00000000	0.00000000	-1.11923600
S	0.00000000	0.00000000	0.41971400

H_2S

S	0.00000000	0.00000000	0.10356600
H	0.00000000	0.97308600	-0.82852600
H	0.00000000	-0.97308600	-0.82852600

2.2 Atom coordinates of the optimized structures for initial steps

A1-1i

C	1.37715800	1.34387600	0.00012000
C	0.06768300	0.84205700	0.00010400
C	1.03747000	-1.42344100	0.00000600
C	2.31045400	-0.89333400	0.00002000
C	2.48091500	0.50120200	0.00007600
H	1.52291100	2.41873000	0.00016700
H	0.88478900	-2.49568700	-0.00003600
H	3.17368300	-1.54845500	-0.00001100

H	3.47946200	0.92369900	0.00008900
C	-0.11503600	-0.58754100	0.00004400
S	-1.66685500	-1.30688500	0.00001500
C	-1.05614800	1.77086400	0.00015300
C	-2.33248100	1.41275400	0.00016100
H	-0.78006800	2.83022000	0.00022900
H	-3.24477400	1.99548400	0.00021800

B1-1i

C	1.31396300	1.28388800	0.00013900
C	0.05143100	0.63216300	0.00009800
C	1.19659200	-1.52586500	-0.00003600
C	2.43253000	-0.85988200	0.00000500
C	2.48360800	0.54073000	0.00009300
H	1.35472600	2.36901400	0.00020900
H	1.16053200	-2.61050200	-0.00010300
H	3.35436900	-1.43286200	-0.00003200
H	3.44351800	1.04388800	0.00012400
C	0.05011200	-0.76756700	0.00001100
S	-2.78251200	-0.82629800	0.00000000
C	-1.16804700	1.37900500	0.00014200
C	-2.44439400	0.81962000	0.00010600
H	-1.09492400	2.46370600	0.00020800
H	-3.28579200	1.50944700	0.00014500

C1-ts1

C	1.39313100	1.36081700	-0.02146000
C	0.08937600	0.84440800	-0.02026600
C	1.01125100	-1.41014300	0.04177400
C	2.29643900	-0.87780400	0.01859700
C	2.48739500	0.50597300	-0.01232400
H	1.53905100	2.43498000	-0.03959800
H	0.86488700	-2.48276900	0.08164000
H	3.15110600	-1.54410200	0.03227100
H	3.49096100	0.91455700	-0.02502700
C	-0.09306500	-0.55490800	0.01427200

S	-1.74353000	-1.18732200	-0.06196800
C	-1.10379700	1.67480100	-0.00147500
C	-2.38039400	1.31035900	0.00846400
H	-1.00372100	2.76376700	0.04050300
H	-2.34781600	-0.21029800	0.73620400
C1-1i			
C	1.39895000	1.36917700	-0.00151400
C	0.10069700	0.84173900	0.00176500
C	1.04555300	-1.42897000	-0.00169300
C	2.32865200	-0.87853200	0.00407000
C	2.49504200	0.50973400	0.00387100
H	1.54517800	2.44334400	-0.01162600
H	0.90319600	-2.50299200	-0.01588600
H	3.19398100	-1.53049200	0.00111100
H	3.49695900	0.92435300	0.00003900
C	-0.03275700	-0.55759100	0.02193500
S	-1.78877800	-0.92421600	-0.09239600
C	-1.17546000	1.55943100	0.00277300
C	-2.37809900	0.92750300	0.01467300
H	-1.17910300	2.64648500	0.03156900
H	-2.03522600	-1.24819000	1.19784900
D1-ts1			
C	-1.40630700	1.36805200	-0.00085900
C	-0.11522900	0.82511900	-0.00472200
C	-1.03875500	-1.43381900	-0.00063600
C	-2.31299700	-0.87935300	0.00152300
C	-2.49901800	0.51222500	0.00161100
H	-1.54717200	2.44351600	-0.00430300
H	-0.90386600	-2.50896500	-0.00037600
H	-3.17818500	-1.53288000	0.00490900
H	-3.50398500	0.91772100	0.00135600
C	0.06011000	-0.57053800	-0.00046700
S	1.79099700	-0.96216800	0.00525700
C	1.17861800	1.50972200	-0.03132500

C	2.34462200	0.68594800	-0.11035400
H	1.25895500	2.58172800	-0.19330100
H	1.95204500	1.38942800	0.97897300

D1-1i

C	1.39421000	1.35879900	-0.00028300
C	0.11021800	0.81709800	0.00018300
C	1.05152000	-1.43647300	0.00034400
C	2.33061400	-0.88005500	0.00008500
C	2.49954100	0.50692900	-0.00034000
H	1.53668800	2.43450600	-0.00072000
H	0.91596800	-2.51183100	0.00021400
H	3.19871900	-1.52938000	0.00005700
H	3.49972100	0.92499500	-0.00060100
C	-0.03735700	-0.57118100	0.00028700
S	-1.80629100	-0.95949700	-0.00018300
C	-1.21944400	1.54068600	0.00043600
C	-2.39324500	0.60055200	-0.00079900
H	-1.33379000	2.20539800	0.86842700
H	-1.33299200	2.21012900	-0.86393900

E1-ts1

C	1.42901200	1.37257900	-0.00651000
C	0.11891100	0.86546800	-0.01784600
C	1.02002200	-1.42204900	0.00407600
C	2.30069900	-0.88310800	0.01281600
C	2.50988700	0.50494500	0.00851600
H	1.56948300	2.44702300	-0.01533400
H	0.87576000	-2.49564900	0.00938800
H	3.15472400	-1.55152000	0.02313600
H	3.52119800	0.89419900	0.01590200
C	-0.06774900	-0.54420100	-0.01674400
S	-1.76578700	-0.98831400	-0.00546300
C	-1.09181400	1.67006900	-0.10583600
C	-2.17874600	0.77892200	-0.00784900
H	-1.89038100	1.43259200	1.00989600

H	-3.21953100	1.03062700	-0.17932200

E1-1i

C	-1.46207800	1.37169400	0.00023300
C	-0.12899100	0.88215000	0.00037200
C	-1.00784500	-1.42356300	-0.00029000
C	-2.28772000	-0.89326400	-0.00025800
C	-2.52644000	0.49825300	0.00015000
H	-1.60663800	2.44546100	0.00000500
H	-0.86099600	-2.49649100	-0.00058500
H	-3.13456500	-1.57189900	-0.00025700
H	-3.54524800	0.86643200	0.00054000
C	0.08675600	-0.54452600	0.00018700
S	1.75391700	-1.00447000	0.00014100
C	1.01962400	1.70061000	-0.00107800
C	2.21022200	0.86458400	0.00007000
H	2.83371200	1.04552600	-0.88147400
H	2.82990100	1.04686600	0.88319900

2.3 Atom coordinates of the optimized structures for key intermediate generation and dominant pathways to generate sulfur-containing radicals

A5-2i

C	1.26061700	1.22490800	0.15167600
C	-0.03562400	0.69170100	0.08329200
C	0.98709600	-1.51946600	-0.25507200
C	2.24570200	-0.96251300	-0.18283900
C	2.38238400	0.42125300	0.02229100
H	1.37385300	2.29128500	0.30978500
H	0.86008000	-2.58312100	-0.41269600
H	3.12525300	-1.58784000	-0.28349500
H	3.37031900	0.86437000	0.07979900
C	-0.18676700	-0.72385400	-0.12644100
S	-1.72172400	-1.49586700	-0.22799400
C	-1.20782200	1.55762900	0.22239200
C	-1.20286000	2.86144000	0.41634100
H	-2.17082900	1.04148800	0.15372700

H	-1.93633500	3.64383100	0.53936400

A5-ts3

C	1.38140800	1.26387900	0.08650600
C	0.03519300	0.77622900	0.08794800
C	0.93856100	-1.52254600	-0.17279600
C	2.21878200	-1.00133600	-0.16245900
C	2.43613700	0.39850900	-0.03288900
H	1.53389000	2.33036100	0.19476600
H	0.78011600	-2.58837500	-0.28393300
H	3.06915500	-1.66533700	-0.26499900
H	3.45210200	0.77706700	-0.01901600
C	-0.16438600	-0.66428800	-0.06137500
S	-1.80487000	-1.20754200	-0.11018600
C	-1.08605800	1.60173400	0.14020300
C	-1.43353100	2.73654600	0.68527500
H	-2.15378100	0.19736000	-0.19654600
H	-2.32300500	3.35145100	0.59963200

A2-ts2

C	1.12013800	1.29883800	-0.02639800
C	-0.11290500	0.64404100	-0.12666500
C	1.07891500	-1.48955800	0.00286700
C	2.29017600	-0.82224200	0.12379500
C	2.30417200	0.57437600	0.10865500
H	1.15727500	2.38221100	-0.05652600
H	1.04088400	-2.57213500	0.00662500
H	3.21419700	-1.37917000	0.22034300
H	3.24394300	1.10826900	0.19523200
C	-0.14082800	-0.79016600	-0.12412300
S	-1.63142200	-1.65203600	-0.28801100
C	-1.34466100	1.37298200	-0.32637600
C	-2.29435800	1.89220700	0.44897300
H	-1.28012200	2.61129600	0.01968900
H	-3.14523900	2.43613300	0.02583700

D2-ts2

C	-1.20849900	1.35714400	-0.23429900
C	0.03241100	0.69269900	-0.14100500
C	-1.07011300	-1.47342200	0.17740700
C	-2.28745600	-0.80257900	0.11546600
C	-2.35321400	0.59251300	-0.08605900
H	-1.26753800	2.42438400	-0.41017300
H	-1.02653900	-2.54943100	0.29686900
H	-3.20935500	-1.36321500	0.22012200
H	-3.32339900	1.07282300	-0.13812800
C	0.08895800	-0.70353400	0.11210500
S	1.80707200	-0.99056200	-0.10520500
C	1.42356700	1.58013900	0.58371000
C	1.54920400	0.81846300	-0.58421200
H	1.11422200	2.61773300	0.47530700
H	1.75030400	1.27815900	1.58059000

A2-2i

C	1.24562500	1.40685300	0.16873900
C	-0.01459200	0.75592600	0.14904200
C	1.18787600	-1.37755600	-0.00500900
C	2.42256400	-0.70628600	0.01634500
C	2.43674100	0.68090600	0.10317300
H	1.27137500	2.48753100	0.23609000
H	1.15888300	-2.45847800	-0.07234900
H	3.34710000	-1.26785400	-0.03445300
H	3.38056600	1.21467900	0.12082400
C	-0.02748100	-0.69461600	0.05830100
S	-1.52623200	-1.58045600	0.02802000
C	-1.17228100	1.49626700	0.21474100
C	-2.22174200	2.25289000	0.28027400
H	-2.68278400	2.52227500	1.23180800
H	-2.71449500	2.63819700	-0.61373900

A3-ts3

C	-1.36561100	1.35568600	-0.00241800
C	-0.05618500	0.81754200	0.07095900

C	-1.03052300	-1.42533700	0.01728400
C	-2.28751900	-0.86087500	0.01386800
C	-2.46815500	0.53778400	-0.00183000
H	-1.47139800	2.43319000	-0.02764200
H	-0.92604100	-2.50216700	0.00193600
H	-3.15549200	-1.51140400	0.00703900
H	-3.46572600	0.95887900	-0.02698200
C	0.15047700	-0.63655000	0.08278600
S	1.69139900	-1.39259400	0.03127000
C	1.10850400	1.55836300	-0.02994100
C	2.34987700	1.33061600	-0.20969700
H	3.28716600	1.68551100	0.18569900
H	2.37735300	0.23025500	-0.70812600

A3-3i

C	1.50032300	1.22624600	-0.15650300
C	0.11317300	0.81929700	0.03920200
C	0.89073500	-1.56397500	-0.04888600
C	2.20808700	-1.12198700	-0.04113600
C	2.49069600	0.30582500	-0.16721700
H	1.71455800	2.28481500	-0.24089600
H	0.67876500	-2.62799900	-0.07679800
H	3.02540400	-1.82972500	-0.00269500
H	3.52105500	0.62506300	-0.27893600
C	-0.16734300	-0.66415800	-0.07385400
S	-1.77316400	-1.22314200	-0.47529100
C	-0.85428200	1.71656800	0.39903700
C	-1.73071300	2.53334800	0.67654800
H	-2.43788900	-0.12632500	-0.04465600
H	-2.46523600	3.23609700	0.98629100

A3-ts4

C	1.45732200	1.17133000	-0.07085300
C	0.16055400	0.72323300	0.15757900
C	1.03146400	-1.59606300	0.15656800
C	2.30194500	-1.12626800	-0.10718400

C	2.50213400	0.25438600	-0.23359800
H	1.65234500	2.23415300	-0.13645800
H	0.83416000	-2.65190400	0.28856000
H	3.13670100	-1.80872900	-0.20815800
H	3.49907700	0.63095900	-0.43627600
C	-0.09501400	-0.70628900	0.19316600
S	-1.44370200	-1.40963300	-1.04968500
C	-0.90131500	1.64118300	0.32379800
C	-1.79275300	2.43798300	0.47733400
H	-0.85162700	-0.99900900	0.94154200
H	-2.59421800	3.12522700	0.60275300

A3-4i

C	1.16512300	1.20827600	-0.06926100
C	-0.09667600	0.93872800	0.36359300
C	0.47723200	-1.54214100	0.33440800
C	1.82449900	-1.13968200	-0.08269700
C	2.13020800	0.15919700	-0.29192300
H	1.46472100	2.23836800	-0.21996400
H	0.40203100	-2.43575900	0.94333700
H	2.57268600	-1.91489800	-0.20222000
H	3.12946200	0.43786300	-0.60627700
C	-0.53044600	-0.46712700	0.56164800
S	-0.89990900	-1.49925300	-0.94974400
C	-1.03503900	1.96304100	0.65464000
C	-1.85985900	2.80365700	0.91581100
H	-1.27348700	-0.62153200	1.33515900
H	-2.58091800	3.55218700	1.13702000

A3-5i

C	-0.11926700	-1.21092000	-0.00010400
C	0.59376700	-0.00002500	-0.00002100
C	-1.50988600	1.20656300	-0.00037000
C	-2.20958500	0.00005000	0.00005300
C	-1.51001500	-1.20654900	0.00011200
H	0.42685200	-2.14644400	-0.00023400

H	-2.04895200	2.14718100	-0.00036100
H	-3.29363600	0.00013900	0.00027000
H	-2.04907100	-2.14715800	0.00019100
C	-0.11922700	1.21087000	0.00037200
C	2.02197000	0.00002900	-0.00006200
C	3.22697200	0.00003000	-0.00003400
H	0.42703700	2.14632200	0.00032900
H	4.28940100	-0.00032700	0.00012600

A6-4i

C	-1.46467500	-0.20646600	-0.00007800
C	-2.65049000	-0.97514700	-0.00009800
C	-1.27066800	-3.01072600	-0.00017700
C	-0.11218100	-2.21947600	-0.00018000
C	-0.21963100	-0.82762000	-0.00012400
H	-1.54359800	0.87484000	-0.00002800
H	-1.20981500	-4.09330200	-0.00021100
H	0.86347300	-2.69338900	-0.00021400
H	0.67754900	-0.21954200	-0.00011400
C	-2.47155100	-2.34964000	-0.00013200
C	-3.93952500	-0.36417000	-0.00000700
C	-5.02202500	0.16355000	0.00000500
H	-5.97956300	0.62399300	-0.00041100

C3-ts2

C	1.40347700	1.36533500	0.03752200
C	0.09601900	0.82923100	0.02453700
C	1.08371300	-1.45018400	-0.02446100
C	2.34441600	-0.88006900	-0.04702800
C	2.49802100	0.52187300	-0.00577300
H	1.53812200	2.44111200	0.05805100
H	0.95154600	-2.52532400	-0.04315700
H	3.21998000	-1.51664400	-0.09982300
H	3.49721900	0.94238000	-0.01651900
C	-0.01614700	-0.58071700	0.03157400
S	-1.90574500	-0.86688500	-0.04076000

C	-1.16345900	1.52893100	-0.03513000
C	-2.34026200	0.81542600	-0.03098800
H	-1.17661600	2.61503600	-0.05661400
H	-0.97300500	-0.98536300	1.10869800
C3-2i			
C	1.44539000	1.34995400	0.12883000
C	0.10559800	0.84910100	0.19996200
C	1.03832100	-1.47735500	0.01605900
C	2.25527200	-0.93688500	-0.22563500
C	2.47175400	0.48586500	-0.11630800
H	1.61174900	2.42138600	0.13594400
H	0.89406600	-2.55199400	0.01817800
H	3.09509300	-1.57590600	-0.47363600
H	3.47266300	0.87200000	-0.27464800
C	-0.08555500	-0.60928100	0.41116400
S	-1.95140900	-0.82129800	-0.09823200
C	-1.05390500	1.55533800	-0.07691700
C	-2.26184600	0.80863000	-0.18204700
H	-1.03919600	2.62783200	-0.24224900
H	-0.30200600	-0.80474400	1.47747200
C4-3i			
C	1.54990300	1.27727900	-0.07827900
C	0.37705700	0.52111100	0.07524900
C	1.74954200	-1.45302300	0.40973100
C	2.90938300	-0.69160300	0.25550000
C	2.80193900	0.67611200	0.01112900
H	1.47611400	2.34273400	-0.26882300
H	1.82189400	-2.51809800	0.60019000
H	3.88410200	-1.16027700	0.32524900
H	3.69503500	1.27890500	-0.11061400
C	0.49729500	-0.85722000	0.32127100
S	-3.52177600	-0.02056100	0.23286200
C	-0.92455000	1.19171600	-0.02578000
C	-2.11045400	0.63357600	0.09314400

H	-0.92690000	2.26298900	-0.21891500
H	-0.39421200	-1.46240000	0.44332900
C5-4i			
C	-1.40361900	0.81718200	-0.00432300
C	-2.59949800	0.06387300	0.14899500
C	-1.23281500	-1.93474500	0.48808000
C	-0.07875200	-1.16245800	0.33198900
C	-0.15948200	0.21297900	0.08581800
H	-1.48275300	1.88240200	-0.19474400
H	-1.15050400	-2.99858400	0.67819400
H	0.89524900	-1.63524800	0.40251500
H	0.74731300	0.79518100	-0.03240400
C	-2.47712400	-1.32759600	0.39743200
C	-3.92422000	0.61506300	0.06967100
H	-3.81257900	1.70115100	-0.12727200
H	-3.39399800	-1.89361200	0.51291300