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

Supplementary Information for

Unravelling the Impact of Hydrocarbon Structure on the Fumarate Addition Mechanism – a Gas Phase *ab-initio* Study

*Vivek S. Bharadwaj[‡],Shubham Vyas[‡,#], Stephanie M. Villano[‡], C. Mark Maupin[‡], Anthony M. Dean[‡]**

[‡]Chemical and Biological Engineering Department, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401

[#]Department of Chemistry and Geochemistry, Colorado School of Mines, 1500 Illinois Street, Golden CO 80401

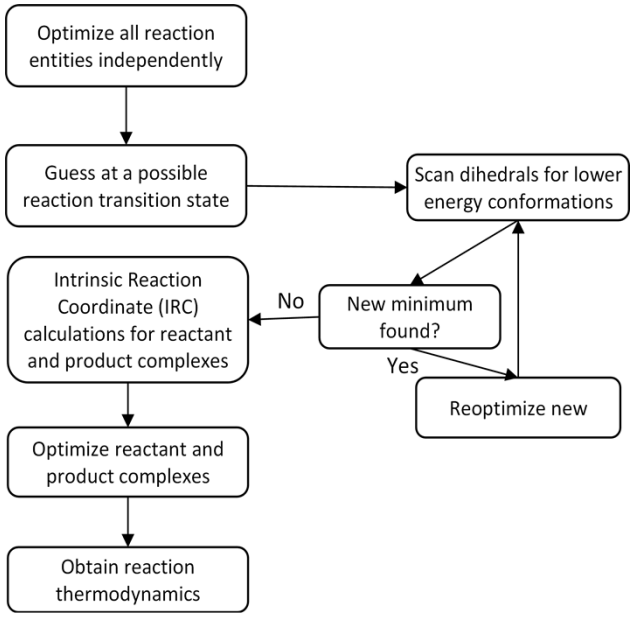
Corresponding Author

* To whom correspondence should be addressed: AMD, email: amdean@mines.edu, PHONE: 303-273-3643, FAX: 303-273-3730;

Funding Sources

ONR MURI Grant N00014-10-1-0946

Section 1: Potential Energy Surfaces



Scheme 1: Workflow for electronic structure calculations.

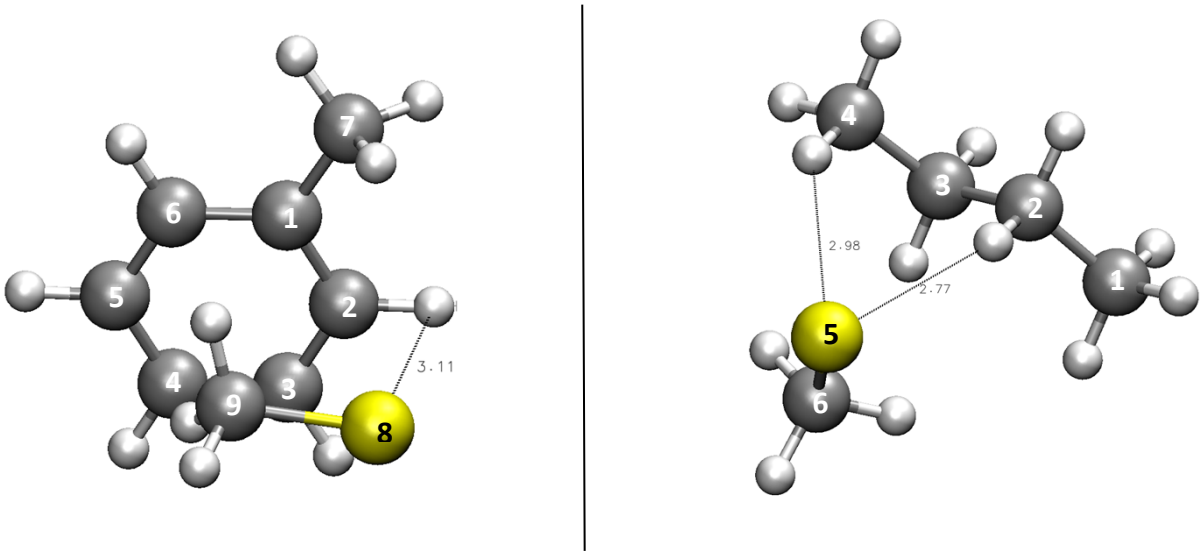


Figure S1: Reactant complex structures for step 1 (Initial H-Abstraction) in the case of toluene (left) and butane (right). Potential non-covalent interactions between the sulfur atom and hydrogen atoms of the hydrocarbon are indicated with dashed lines. The atomic indexes correspond to the heavy atoms as listed in Section S1.1 for toluene (Table S1) and butane (Table S2)

S 1.1 Resonance stabilization in radicals from Mulliken density analysis

Table S1: Mulliken spin densities for atoms in the Initial H-abstraction step for Toluene. The radical centers are indicated in Red.

Atom #	Atom	Spin Density		Difference
		RC	PC	Abs(RC)-Abs(PC)
1	C	-0.13	-0.23	-0.10
2	C	0.14	0.24	-0.09
3	C	-0.08	-0.12	-0.05
4	C	0.15	0.25	-0.10
5	C	-0.08	-0.12	-0.05
6	C	0.15	0.23	-0.09
7	C	0.60	0.86	-0.26
8	S	0.36	0.01	0.35
9	C	-0.01	0.00	0.01
10	H	0.01	0.00	0.01
11	H	0.00	0.00	0.00
12	H	0.00	0.00	0.00
13	H	-0.07	-0.01	0.06
14	H	-0.02	-0.04	-0.02
15	H	-0.01	-0.01	-0.01
16	H	0.00	0.00	0.00
17	H	-0.01	-0.01	-0.01
18	H	0.00	0.00	0.00
19	H	-0.01	-0.01	0.00
20	H	-0.02	-0.04	-0.02

The table above lists the Mulliken spin densities for all the atoms in the reactant complex and the product complex for step 1 (Initial H-abstraction) in the case of toluene. The right most column indicated the difference in the spin densities between the product and reactant complex. A negative sign indicates a gain in spin density while a positive sign indicates a loss in spin density. It is to be noted that of the spin density that is lost by the sulfur atom only 75% is retained by the carbon center of benzyl radical, while the rest is delocalized amongst the carbons of the aromatic ring.

In the case of butane, Table S2, almost all of the spin density transferred from the sulfur centered radical in the reactant complex ends up on the carbon centered radical on the butyl radical. This the lack of spin delocalization indicates a less stabilized product complex in the case of butane.

Table S2: Mulliken spin densities for atoms in the Initial H-abstraction step for Butane. The radical centers are indicated in Red.

Atom #	Atom	Spin Density		Difference
		RC	PC	Abs(RC)-Abs(PC)
1	C	-0.05	-0.08	-0.04
2	C	0.79	1.05	-0.26
3	C	-0.05	-0.08	-0.03
4	C	0.01	0.01	0.00
5	S	0.29	0.01	0.27
6	C	-0.01	0.00	0.00
7	H	0.00	0.00	0.00
8	H	0.00	0.00	0.00
9	H	0.00	0.00	0.00
10	H	-0.06	0.00	0.06
11	H	-0.03	-0.06	-0.02
12	H	0.01	0.01	-0.01
13	H	0.01	0.01	0.00
14	H	0.04	0.05	-0.01
15	H	0.00	0.00	0.00
16	H	0.00	0.00	0.00
17	H	0.00	0.00	0.00
18	H	0.04	0.05	-0.01
19	H	0.01	0.01	0.00

Section 2: Kinetic Modelling

Table S3: The A-factors and Activation energies for all the reactions of the Fumarate Addition Mechanism along with the specific reaction numbers as listed in the CHEMKIN Mechanism input file. RC denotes Reactant Complex and PC denotes Product Complex.

Reaction #	Reaction	A-Factor (mole-cm-sec-K)	Activation Energy (cal/mol)
Step 1 : Initial H-abstraction			
Toluene			
1	C_7H_8+CH_3S => R1_tol_RC	1.36E+14	0
2	R1_tol_RC => C_7H_8+CH_3S	8.27E+16	6100
3	R1_tol_RC => R1_tol_PC	1.79E+12	14490
4	R1_tol_PC => R1_tol_RC	2.16E+13	8160
5	R1_tol_PC => C_7H_7+CH_3SH	6.62E+17	4240
6	C_7H_7+CH_3SH => R1_tol_PC	1.36E+14	0
Butane			
7	C_4H_{10}+ CH_3S => R1_but_RC	1.49E+14	0
8	R1_but_RC => C_4H_{10}+ CH_3S	1.81E+16	3390
9	R1_but_RC => R1_but_PC	5.94E+11	15180
10	R1_but_PC => R1_but_RC	1.61E+11	2580
11	R1_but_PC => C_4H_9+ CH_3SH	9.28E+16	3140
12	C_4H_9+ CH_3SH => R1_but_PC	1.49E+14	0
Step 2 : Fumarate Addition			
Toluene			
13	C_7H_7+$C_4H_4O_4$=> R2_tol_RC_R	1.06E+14	0
14	C_7H_7+$C_4H_4O_4$=> R2_tol_RC_S	1.06E+14	0
15	R2_tol_RC_R => C_7H_7+$C_4H_4O_4$	5.22E+16	6870
16	R2_tol_RC_S => C_7H_7+$C_4H_4O_4$	3.89E+17	6020
17	R2_tol_RC_R => $C_{11}H_{11}O_4$_R	9.82E+10	7050
18	R2_tol_RC_S => $C_{11}H_{11}O_4$_S	1.63E+12	6790
19	$C_{11}H_{11}O_4$_R => R2_tol_RC_R	9.40E+12	22110
20	$C_{11}H_{11}O_4$_S => R2_tol_RC_S	1.76E+13	21650
Butane			
21	C_4H_9+$C_4H_4O_4$=> R2_but_RC_RR	1.23E+14	0
22	C_4H_9+$C_4H_4O_4$=> R2_but_RC_RS	1.23E+14	0
23	C_4H_9+$C_4H_4O_4$=> R2_but_RC_SR	1.23E+14	0
24	C_4H_9+$C_4H_4O_4$=> R2_but_RC_SS	1.23E+14	0
25	R2_but_RC_RR => C_4H_9+$C_4H_4O_4$	2.04E+18	7240
26	R2_but_RC_RS => C_4H_9+$C_4H_4O_4$	7.33E+17	7340
27	R2_but_RC_SR => C_4H_9+$C_4H_4O_4$	1.55E+18	6310
28	R2_but_RC_SS => C_4H_9+$C_4H_4O_4$	2.12E+18	6180
29	R2_but_RC_RR => $C_8H_{13}O_4$_RR	3.71E+11	2120
30	R2_but_RC_RS => $C_8H_{13}O_4$_RS	1.40E+11	2410

Reaction #	Reaction	A-Factor (mole-cm-sec-K)	Activation Energy (cal/mol)
31	R2_but_RC_SR => $C_8H_{13}O_4$_SR	1.18E+11	1680
32	R2_but_RC_SS => $C_8H_{13}O_4$_SS	1.69E+11	1930
33	$C_8H_{13}O_4$_RR => R2_but_RC_RR	1.25E+14	25590
34	$C_8H_{13}O_4$_RS = > R2_but_RC_RS	6.25E+13	26990
35	$C_8H_{13}O_4$_SR => R2_but_RC_SR	6.01E+13	25450
36	$C_8H_{13}O_4$_SS => R2_but_RC_SS	5.17E+13	25390
Step 3 : Thiyl Radical Regeneration			
Toluene			
37	$C_{11}H_{11}O_4$_R+CH_3SH => R3_tol_RC_R	1.22E+14	0
38	R3_tol_RC_R => $C_{11}H_{11}O_4$_R+CH_3SH	1.11E+18	5190
39	R3_tol_RC_R => R3_tol_PC_R	6.89E+11	9040
40	R3_tol_PC_R => R3_tol_RC_R	5.35E+11	17450
41	R3_tol_PC_R => $C_{11}H_{12}O_4$_R+CH_3S	1.23E+16	6460
42	$C_{11}H_{12}O_4$_R+CH_3S => R3_tol_PC_R	1.23E+14	0
43	$C_{11}H_{11}O_4$_S+CH_3SH => R3_tol_RC_S	1.22E+14	0
44	R3_tol_RC_S => $C_{11}H_{11}O_4$_S+CH_3SH	2.30E+18	5280
45	R3_tol_RC_S => R3_tol_PC_S	1.46E+13	8610
46	R3_tol_PC_S => R3_tol_RC_S	1.79E+12	17800
47	R3_tol_PC_S => $C_{11}H_{12}O_4$_S+CH_3S	1.66E+15	7550
48	$C_{11}H_{12}O_4$_S+CH_3S => R3_tol_PC_S	1.23E+14	0
Butane			
49	$C_8H_{13}O_4$_RR+CH_3SH => R3_but_RC_RR	1.24E+14	0
50	$C_8H_{13}O_4$_RS+CH_3SH => R3_but_RC_RS	1.24E+14	0
51	$C_8H_{13}O_4$_SR+CH_3SH => R3_but_RC_SR	1.24E+14	0
52	$C_8H_{13}O_4$_SS+CH_3SH => R3_but_RC_SS	1.24E+14	0
53	R3_but_RC_RR => $C_8H_{13}O_4$_RR+CH_3SH	1.81E+16	4800
54	R3_but_RC_RS => $C_8H_{13}O_4$_RS+CH_3SH	1.48E+17	5870
55	R3_but_RC_SR => $C_8H_{13}O_4$_SR+CH_3SH	2.24E+17	5670
56	R3_but_RC_SS => $C_8H_{13}O_4$_SS+ CH_3SH	3.58E+16	3940
57	R3_but_RC_RR => R3_but_PC_RR	5.91E+10	8570
58	R3_but_RC_RS => R3_but_PC_RS	3.82E+11	8910
59	R3_but_RC_SR => R3_but_PC_SR	8.47E+12	9280
60	R3_but_RC_SS => R3_but_PC_SS	1.42E+11	7370
61	R3_but_PC_RR => R3_but_RC_RR	1.98E+12	16990
62	R3_but_PC_RS => R3_but_RC_RS	2.28E+11	14680
63	R3_but_PC_SR => R3_but_RC_SR	4.62E+13	15750
64	R3_but_PC_SS => R3_but_RC_SS	1.93E+12	14610
65	R3_but_PC_RR => $C_8H_{14}O_4$_RR+CH_3S	2.45E+17	5860
66	R3_but_PC_RS => $C_8H_{14}O_4$_RS+CH_3S	2.87E+16	5030
67	R3_but_PC_SR => $C_8H_{14}O_4$_SR+CH_3S	3.04E+17	5100
68	R3_but_PC_SS => $C_8H_{14}O_4$_SS+CH_3S	1.71E+16	3790

Reaction #	Reaction	A-Factor (mole-cm-sec-K)	Activation Energy (cal/mol)
69	$C_8H_{14}O_4$_RR+CH_3S => R3_but_PC_RR	1.25E+14	0
70	$C_8H_{14}O_4$_RS+CH_3S => R3_but_PC_RS	1.25E+14	0
71	$C_8H_{14}O_4$_SR+CH_3S => R3_but_PC_SR	1.25E+14	0
72	$C_8H_{14}O_4$_SS+CH_3S => R3_but_PC_SS	1.25E+14	0

Table S4: The matrix of equilibrium constants that constitute the reaction mechanism for toluene and butane.

	K_{eq}^{RC} (mol/cm^3)	K_{eq}^{TST}	K_{eq}^{PC} (cm^3/mol)
Step 1	Initial H-abstraction		
Toluene	4.86E+01	1.89E-06	3.81E+00
Butane	2.54E+00	2.15E-09	3.11E+00
Step 2	Fumarate Addition		
Toluene R	2.22E+02	1.15E+09	
Toluene S	7.13E+00	7.29E+09	
Butane RR	1.23E+01	4.81E+14	
Butane RS	4.04E+01	2.31E+15	
Butane SR	3.33E+00	5.23E+14	
Butane SS	1.96E+00	5.13E+14	
Step 3	Thiyl Radical Regeneration		
Toluene R	7.04E-01	1.88E+06	9.30E-02
Toluene S	3.94E-01	4.43E+07	4.23E-03
Butane RR	2.28E+01	4.44E+04	9.96E-02
Butane RS	1.69E+01	2.84E+04	4.70E-02
Butane SR	7.90E+00	1.02E+04	4.46E-01
Butane SS	2.68E+00	1.49E+04	1.84E+00