Oxidation reaction mechanism and kinetics between OH radicals and alkyl substituted aliphatic thiols: H-abstraction pathways

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Electronic Supplementary Information

Table S1. Temperature dependence of the equilibrium constants for the first bimolecular reaction step [R_i +$OH^\bullet$ ⇆ IM_i ; i=1–4] along the pathways **1**–**4** at different temperatures.

$CH_3SH + OH^\bullet \rightarrow [\ CH_3SH\ldots OH^\bullet]$		
T (K)	K_p (bar^{-1})	K_c ($cm^3\ molecule^{-1}$)
254	1.06E-04	3.72E-24
298	4.88E-05	2.01E-24
322	3.52E-05	1.57E-24
375	2.00E-05	1.04E-24
403	1.59E-05	8.85E-25
430	1.31E-05	7.78E-25

$C_2H_5SH + OH^\bullet \rightarrow [\ C_2H_5SH\ldots OH^\bullet]$		
T (K)	K_p (bar^{-1})	K_c ($cm^3\ molecule^{-1}$)
252	2.38E-04	8.28E-24
278	1.31E-04	5.03E-24
298	8.93E-05	3.68E-24
343	4.47E-05	2.12E-24
397	2.43E-05	1.33E-24
425	1.89E-05	1.11E-24

$n\text{-}C_3H_7SH + OH^\bullet \rightarrow [n\text{-}C_3H_7SH\ldots OH^\bullet]$		
T (K)	K_p (bar^{-1})	K_c ($cm^3\ molecule^{-1}$)
257	4.20E-04	1.49E-23
298	2.16E-04	8.89E-24
353	1.40E-04	6.82E-24
419	6.43E-05	3.72E-24

$iso\text{-}C_3H_7SH + OH^\bullet \rightarrow [iso\text{-}C_3H_7SH\ldots OH^\bullet]$		
T (K)	K_p (bar^{-1})	K_c ($cm^3\ molecule^{-1}$)
256	4.09E-04	1.45E-23
299	1.45E-04	5.99E-24
358	5.30E-05	2.62E-24
380	3.97E-05	2.08E-24
429	2.34E-05	1.39E-24

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Table S2. Wigner tunneling factor for the final unimolecular dissociation reaction step at temperatures ranging from 252 to 430 K.

Temperature (K) \ Pathway	Second step			
	IM1 → P1	IM2 → P2	IM3 → P3	IM4 → P4
252		1.289		
254	1.371			
256				1.268
257			1.310	
278		1.238		
298	1.270	1.207	1.231	
299				1.197
322	1.231			
344		1.156		
353			1.164	
358				1.137
375	1.170			
380				1.122
397		1.117		
403	1.148			
419			1.117	
425		1.102		
429				1.096
430	1.130			

Table S3. Expectation value of the $<S^2>$ operator at the reported theoretical levels.

Species / Method	IM1 (0,2)	IM2 (0,2)	TS1 (0,2)	TS2 (0,2)	P1 (0,2)	P2 (0,2)
ωB97XD/aug-cc-pVTZ	0.7579	0.7579	0.7600	0.7600	0.7541	0.7541
M06-2x/aug-cc-pVTZ	0.7584	0.7586	0.7606	0.7608	0.7539	0.7540
HF/6-31+G* (CBS-QB3)	0.7684	0.7683	0.7658	0.7651	0.7652	0.7651

Species / Method	IM3 (0,2)	IM4 (0,2)	TS3 (0,2)	TS4 (0,2)	P3 (0,2)	P4 (0,2)
ωB97XD/aug-cc-pVTZ	0.7578	0.7579	0.7600	0.7601	0.7541	0.7542
M06-2x/aug-cc-pVTZ	0.7586	0.7587	0.7608	0.7609	0.7540	0.7540
HF/6-31+G* (CBS-QB3)	0.7683	0.7698	0.7654	0.7651	0.7651	0.7651

Table S4: Kinetic rate constants for all reaction steps involved in the chemical pathways **1**–**4** at different pressures and temperatures, using the RRKM theory, according to the computed CBS-QB3 energy profiles.

Table S4a:

T (K)	Rate constant (at $P = 10^{-8}$ bar)								Effective rate constant ($cm^3\,molecule^{-1}\,s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff}(**1**) R1+OH$^\bullet$→P1	k_{eff}(**2**) R2+OH$^\bullet$→P2	k_{eff}(**3**) R3+OH$^\bullet$→P3	k_{eff}(**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	4.92E00	1.20E01	1.54E01	1.04E01	2.51E-23	1.29E-22	2.99E-22	1.90E-22
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	6.85E00	1.37E01	1.60E01	1.29E01	1.75E-23	8.91E-23	1.75E-22	9.21E-23
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	7.67E00	1.41E01	1.58E01	1.36E01	1.48E-23	6.59E-23	1.18E-22	3.74E-23
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	8.57E00	1.42E01	1.53E01	1.39E01	1.01E-23	3.59E-23	5.64E-23	3.10E-23
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	9.15E00	1.39E01	1.45E01	1.37E01	9.19E-24	2.07E-23	1.26E-22	1.96E-23
430	3.71E+14			1.78E+14	9.39E00			1.33E01	8.25E-24			3.54E-22

Table S4b:

T (K)	Rate constant (at $P = 10^{-6}$ bar)								Effective rate constant ($cm^3\,molecule^{-1}\,s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff}(**1**) R1+OH$^\bullet$→P1	k_{eff}(**2**) R2+OH$^\bullet$→P2	k_{eff}(**3**) R3+OH$^\bullet$→P3	k_{eff}(**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	4.92E02	1.20E03	1.54E03	1.04E03	2.51E-21	1.29E-20	2.99E-20	1.90E-20
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	6.85E02	1.37E03	1.60E03	1.29E03	1.75E-21	8.91E-21	1.75E-20	9.21E-21
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	7.67E02	1.41E03	1.58E03	1.36E03	1.48E-21	6.59E-21	1.18E-20	3.74E-21
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	8.57E02	1.42E03	1.53E03	1.39E03	1.01E-21	3.59E-21	5.64E-21	3.10E-21
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	9.15E02	1.39E03	1.45E03	1.37E03	9.19E-22	2.07E-21	1.26E-20	1.96E-21
430	3.71E+14			1.78E+14	9.39E02			1.33E03	8.25E-22			3.54E-20

Table S4c:

T (K)	Rate constant (at $P = 10^{-4}$ bar)								Effective rate constant ($cm^3\,molecule^{-1}\,s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff} (**1**) R1+OH$^\bullet$→P1	k_{eff} (**2**) R2+OH$^\bullet$→P2	k_{eff} (**3**) R3+OH$^\bullet$→P3	k_{eff} (**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	4.92E04	1.20E05	1.54E05	1.04E05	2.51E-19	1.29E-18	2.99E-18	1.90E-18
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	6.85E04	1.37E05	1.60E05	1.29E05	1.75E-19	8.91E-19	1.75E-18	9.21E-19
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	7.67E04	1.41E05	1.58E05	1.36E05	1.48E-19	6.59E-19	1.18E-18	3.74E-19
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	8.57E04	1.42E05	1.53E05	1.39E05	1.01E-19	3.59E-19	5.64E-19	3.10E-19
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	9.15E04	1.39E05	1.45E05	1.37E05	9.19E-20	2.07E-19	1.26E-18	1.96E-19
430	3.71E+14			1.78E+14	9.39E04			1.33E05	8.25E-20			3.54E-18

Table S4d:

T (K)	Rate constant (at $P = 10^{-2}$ bar)								Effective rate constant ($cm^3\,molecule^{-1}\,s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff} (**1**) R1+OH$^\bullet$→P1	k_{eff} (**2**) R2+OH$^\bullet$→P2	k_{eff} (**3**) R3+OH$^\bullet$→P3	k_{eff} (**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	4.92E06	1.20E07	1.54E07	1.04E07	2.51E-17	1.29E-16	2.99E-16	1.90E-16
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	6.85E06	1.37E07	1.60E07	1.29E07	1.75E-17	8.91E-17	1.75E-16	9.20E-17
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	7.67E06	1.41E07	1.58E07	1.36E07	1.48E-17	6.59E-17	1.18E-16	3.73E-17
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	8.57E06	1.42E07	1.53E07	1.39E07	1.01E-17	3.59E-17	5.64E-17	3.10E-17
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	9.15E06	1.39E07	1.45E07	1.37E07	9.19E-18	2.07E-17	1.26E-16	1.96E-17
430	3.71E+14			1.78E+14	9.39E06			1.33E07	8.25E-18			3.54E-16

Table S4e:

T (K)	Rate constant (at $P = 10^0$ bar)								Effective rate constant ($cm^3\,molecule^{-1}\,s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff}(**1**) R1+OH$^\bullet$→P1	k_{eff}(**2**) R2+OH$^\bullet$→P2	k_{eff}(**3**) R3+OH$^\bullet$→P3	k_{eff}(**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	4.79E08	1.18E09	1.46E09	9.08E08	2.44E-15	1.27E-14	2.83E-14	1.66E-14
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	6.72E08	1.35E09	1.56E09	1.19E09	1.71E-15	8.78E-15	1.71E-14	8.48E-15
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	7.55E08	1.39E09	1.55E09	1.27E09	1.45E-15	6.50E-15	1.16E-14	3.51E-15
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	8.47E08	1.41E09	1.51E09	1.34E09	9.94E-16	3.56E-15	5.57E-15	2.98E-15
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	9.08E08	1.38E09	1.44E09	1.34E09	9.12E-16	2.05E-15	1.25E-14	1.91E-15
430	3.71E+14			1.78E+14	9.33E08			1.31E09	8.20E-16			3.48E-14

Table S4f:

T (K)	Rate constant (at $P = 10^2$ bar)								Effective rate constant ($cm^3\,molecule^{-1}\,s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff}(**1**) R1+OH$^\bullet$→P1	k_{eff}(**2**) R2+OH$^\bullet$→P2	k_{eff}(**3**) R3+OH$^\bullet$→P3	k_{eff}(**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	1.99E10	6.41E10	6.33E10	2.15E10	1.01E-13	6.87E-13	1.24E-12	3.92E-13
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	3.42E10	8.77E10	8.72E10	4.11E10	8.72E-14	5.71E-13	9.59E-13	2.94E-13
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	4.21E10	9.73E10	9.69E10	5.23E10	8.11E-14	4.55E-13	7.25E-13	1.44E-13
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	5.28E10	1.07E11	1.07E11	6.77E10	6.20E-14	2.70E-13	3.95E-13	1.51E-13
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	6.23E10	1.13E11	1.12E11	8.08E10	6.26E-14	1.68E-13	9.71E-13	1.15E-13
430	3.71E+14			1.78E+14	6.83E10			8.86E10	6.00E-14			2.36E-12

Table S4g:

T (K)	Rate constant (at $P = 10^4$ bar)								Effective rate constant ($cm^3\,molecule^{-1}\,s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff}(**1**) R1+OH$^\bullet$→P1	k_{eff}(**2**) R2+OH$^\bullet$→P2	k_{eff}(**3**) R3+OH$^\bullet$→P3	k_{eff}(**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	5.15E10	2.62E11	1.87E11	3.93E10	2.63E-13	2.81E-12	3.63E-12	7.17E-13
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	1.16E11	5.01E11	3.59E11	9.87E10	2.96E-13	3.26E-12	3.93E-12	7.05E-13
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	1.64E11	6.62E11	4.76E11	1.47E11	3.16E-13	3.09E-12	3.55E-12	4.04E-13
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	2.53E11	9.31E11	6.73E11	2.41E11	2.97E-13	2.35E-12	2.48E-12	5.37E-13
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	3.69E11	1.25E12	9.09E11	3.70E11	3.71E-13	1.86E-12	7.88E-12	5.28E-13
430	3.71E+14			1.78E+14	4.80E11			5.00E11	4.22E-13			1.33E-11

Table S4h:

T (K)	Rate constant (at $P = 10^6$ bar)								Effective rate constant ($cm^3\,molecule^{-1}\,s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff}(**1**) R1+OH$^\bullet$→P1	k_{eff}(**2**) R2+OH$^\bullet$→P2	k_{eff}(**3**) R3+OH$^\bullet$→P3	k_{eff}(**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	5.27E10	2.75E11	1.93E11	3.97E10	2.69E-13	2.95E-12	3.75E-12	7.25E-13
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	1.20E11	5.41E11	3.76E11	1.01E11	3.06E-13	3.52E-12	4.11E-12	7.20E-13
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	1.71E11	7.26E11	5.04E11	1.51E11	3.30E-13	3.39E-12	3.76E-12	4.15E-13
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	2.68E11	1.05E12	7.27E11	2.50E11	3.15E-13	2.65E-12	2.68E-12	5.58E-13
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	3.98E11	1.46E12	1.01E12	3.90E11	4.00E-13	2.17E-12	8.76E-12	5.57E-13
430	3.71E+14			1.78E+14	5.26E11			5.35E11	4.62E-13			1.42E-11

Table S4i:

T (K)	Rate constant (at $P = 10^8$ bar)								Effective rate constant ($cm^3\ molecule^{-1}\ s^{-1}$)			
	IM1→R1+OH$^\bullet$	IM2→R2+OH$^\bullet$	IM3→R3+OH$^\bullet$	IM4→R4+OH$^\bullet$	IM1→P1	IM2→P2	IM3→P3	IM4→P4	k_{eff} (**1**) R1+OH$^\bullet$→P1	k_{eff} (**2**) R2+OH$^\bullet$→P2	k_{eff} (**3**) R3+OH$^\bullet$→P3	k_{eff} (**4**) R4+OH$^\bullet$→P4
254	2.89E+15	1.49E+15	8.63E+14	8.36E+14	5.27E10	2.75E11	1.93E11	3.97E10	2.69E-13	2.95E-12	3.75E-12	7.25E-13
298	1.34E+15	7.60E+14	4.77E+14	4.65E+14	1.20E11	5.41E11	3.77E11	1.01E11	3.06E-13	3.52E-12	4.12E-12	7.20E-13
322	9.67E+14	5.74E+14	3.73E+14	3.64E+14	1.71E11	7.26E11	5.04E11	1.51E11	3.30E-13	3.39E-12	3.76E-12	4.15E-13
358	5.58E+14	4.08E+14	2.77E+14	2.71E+14	2.68E11	1.05E12	7.28E11	2.50E11	3.15E-13	2.65E-12	2.68E-12	5.58E-13
397	4.46E+14	3.05E+14	2.15E+14	2.11E+14	3.98E11	1.46E12	1.01E12	3.91E11	4.00E-13	2.17E-12	8.76E-12	5.57E-13
430	3.71E+14			1.78E+14	5.26E11			5.36E11	4.62E-13			1.42E-11