Supplementary data

Thermochemistry and Kinetics for 2-butanone-1yl Radical ($\text{CH}_2\bullet\text{C}(=\text{O})\text{CH}_2\text{CH}_3$) Reactions with O_2

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Data for tables collected by Mara Pfeffinger – KIT student

SM1: Calculated Thermochemical Properties of Radicals and Stable Species^a

	Species		$\Delta_f H_{298}^0$ ^b	S_{298}^0 ^b	Cp (T) cal mole ⁻¹ K ⁻¹						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CH ₃ CH=C=O	TVR ^c		64.02	14.06	17.13	19.99	22.51	26.61	29.73	34.66
	C—CH ₃	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	Total		-24.50	68.54	16.15	19.19	21.92	24.29	28.16	31.12	35.85
CH ₃ C(=O)CH ₂ CH ₃	TVR ^c		64.71	12.49	17.16	21.99	26.44	33.85	39.54	48.60
	C—CH ₃	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	CH ₃ —CH ₂	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	Total		-57.02	79.85	19.95	23.97	28.05	31.87	38.45	43.64	52.11
CH ₃ CC(=O)CH ₂ (OH)	TVR ^c	3.03	65.75	10.95	14.65	18.57	22.16	28.04	32.47	39.46
CH ₃ CH ₂ YC(O•)CH ₂ OO	TVR ^c		82.02	29.29	36.71	42.98	48.06	55.62	60.94	68.87
	CH ₃ —CH ₂	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	CH ₃ CH ₂ —C(=O)	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	Total		-6.95	92.64	34.66	41.46	47.11	51.71	58.67	63.65	71.19
CH ₂ =CHC(=O)CH ₂ (OH)	TVR ^c		69.62	17.92	23.12	27.94	32.10	38.61	43.37	50.78
	CH—C(=O)	IR		3.79	2.83	3.07	3.08	2.97	2.62	2.28	1.72
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	CH ₂ —OH	IR		2.64	2.68	2.45	2.25	2.08	1.81	1.61	1.33
	Total		-64.94	87.76	28.81	33.52	37.68	41.2	46.55	50.39	56.43
CH ₂ •C(=O)CH ₂ CH ₃	TVR ^c		71.73	21.76	27.46	32.47	36.68	43.21	48.00	55.39
	CH ₃ —CH ₂	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	CH ₂ —C(=O)	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	C(=O)—CH ₂ •	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	Total		-13.45	88.45	30.41	34.9	38.8	42.2	47.76	52.03	58.84
CH•(OOH)C(=O)CH ₂ CH ₃	TVR ^c		79.93	25.81	31.87	37.40	42.15	49.55	54.95	63.32
	CH ₃ —CH ₂	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	CH ₂ —C(=O)	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	C(=O)—CH	IR		Barrier > 3.5 not considered							
	CH•—OOH	IR		Barrier > 3.5 not considered							
	O—OH	IR		Barrier > 3.5 not considered							
	Total		-39.13	90.55	31.18	36.62	41.53	45.8	52.6	57.66	65.64
CH ₂ (OO•)C(=O)CH ₂ CH ₃	TVR ^c		88.49	29.58	36.33	42.31	47.31	54.96	60.43	68.60
	CH ₃ —CH ₂	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	CH ₂ —C(=O)	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	CH ₂ —OO•	IR		5.61	2.10	2.19	2.21	2.18	2.01	1.81	1.47
	Total		-40.52	110.82	40.33	45.96	50.85	55.01	61.52	66.27	73.52

^aThermodynamic properties are referred to a standard state of an ideal gas at 1 atm; torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, a more exact contribution from hindered rotations is included; ^b ΔH_{f298}^0 in kcal mol⁻¹; S_{298}^0 in cal mol⁻¹ K⁻¹; ^cDFT at B3LYP/6-311G(d,p) ^fThe sum of contributions from translations, external rotations, and Vibrations. ^dContribution from internal rotation about the corresponding bonds.

SM1 (con't): Calculated Thermochemical Properties of Radicals and Stable Species^a

	Species		$\Delta_f H_{298}^0$ ^b	S_{298}^0 ^b	Cp (T) cal mole ⁻¹ K ⁻¹						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CH ₂ (OOH)C(OH)=CHCH ₃	TVR ^c		82.61	27.99	34.09	39.43	43.89	50.72	55.67	63.49
	CH ₃ —CH	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	C—OH	IR		2.64	2.68	2.45	2.25	2.08	1.81	1.61	1.33
	C—CH• (OOH)	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	C—OOH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	O—OH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	Total		-28.35	89.77	32.76	38.6	43.61	47.75	54.08	58.67	66.01
CH ₂ =C=C=O	TVR ^c	18.68	67.30	14.74	16.75	18.53	20.07	22.58	24.49	27.52
CH ₂ (OOH)C(=O)CH ₂ CH ₃	TVR ^c		76.96	23.62	30.04	36.07	41.36	49.74	55.93	65.56
	CH ₃ —CH ₂	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	CH ₂ —C(=O)	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	CH ₂ —OOH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	O—OH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	Total		-75.33	93.68	32.27	37.48	42.4	46.88	54.29	59.96	69.01
CH ₂ (OOH)C(=O)CH ₂ CH ₂ •	TVR ^c		77.64	25.92	32.70	38.44	43.12	50.18	55.22	62.90
	HOO—CH ₂	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	CH ₂ —C(=O)	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	CH ₂ —CH ₂ •	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	O—OH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	Total		-26.96	94.36	34.57	40.14	44.77	48.64	54.73	59.25	66.35
CH ₂ (OOH)C(=O)CH•CH ₃	TVR ^c		78.93	25.41	32.04	37.80	42.56	49.77	54.91	62.71
	CH ₃ —CH•	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	CH•—C(=O)	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	CH ₂ —OOH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	O—OH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	Total		-37.67	95.65	34.06	39.48	44.13	48.08	54.32	58.94	66.16
CH ₃ YCHOCH ₂ C(=O)	TVR ^c		71.51	19.49	25.09	30.32	34.85	41.92	47.06	54.86
	CH ₃ —C	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	Total		-50.68	76.03	21.58	27.15	32.25	36.63	43.47	48.45	56.05
CH ₂ (O•)C(=O)CH=CH ₂	TVR ^c		71.93	20.40	25.80	30.39	34.15	39.80	43.80	49.74
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	C(=O)—CH	IR		Barrier > 3.5 not considered							
	Total		-5.89	78.03	23.68	28.49	32.59	36.02	41.30	45.12	50.87

^aThermodynamic properties are referred to a standard state of an ideal gas at 1 atm; torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, a more exact contribution from hindered rotations is included; ^b ΔH_{f298}^0 in kcal mol⁻¹; S_{298}^0 in cal mol⁻¹ K⁻¹; ^cDFT at B3LYP/6-311G(d,p) ^fThe sum of contributions from translations, external rotations, and Vibrations. ^dContribution from internal rotation about the corresponding bonds.

SM1 (con't): Calculated Thermochemical Properties of Radicals and Stable Species^a

	Species		$\Delta_f H_{298}^0$ ^b	S_{298}^0 ^b	Cp (T) cal mole ⁻¹ K ⁻¹						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CH ₂ (O•)C(=O)CH ₂ CH ₃	TVR ^c		73.18	20.94	26.59	31.86	36.48	43.84	49.30	57.74
	CH ₂ (O•)—C(=O)	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	CH ₂ —CH ₃	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	Total		-40.94	83.8	26.31	31.34	35.99	40.13	46.89	52.01	60.06
CH ₂ (OO•)C(OH)=CHCH ₃	TVR ^c		77.13	24.51	31.23	37.09	41.95	49.31	54.57	62.52
	CH ₃ —CH	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	C—OH	IR		2.64	2.68	2.45	2.25	2.08	1.81	1.61	1.33
	C(OH)—CH ₂ OO•	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	CH ₂ —OO•	IR		5.61	2.10	2.19	2.21	2.18	2.01	1.81	1.47
	Total		-28.63	89.9	31.38	37.93	43.48	47.99	54.68	59.38	66.51
CH ₃ YCHOCH ₂ C(=O)	TVR ^c		71.51	19.49	25.09	30.32	34.85	41.92	47.06	54.86
	CH ₃ —C	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	Total		-50.68	76.03	21.58	27.15	32.25	36.63	43.47	48.45	56.05
(O=)CHC(=O)CH ₂ CH ₃	TVR ^c		72.62	21.14	26.56	31.47	35.67	42.24	47.01	54.15
	C(=O)—CH(=O)	IR		Barrier > 3.5 Kcal mol ⁻¹ – not considered							
	C(=O)—CH ₂	IR		6.10	3.28	2.69	2.20	1.87	1.50	1.32	1.13
	CH ₂ —CH ₃	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	Total		-70.97	83.24	26.51	31.31	35.6	39.32	45.29	49.72	56.47
(O=)CHC(OH)=CHCH ₃	TVR ^c		72.98	21.98	27.45	32.28	36.35	42.62	47.16	54.05
	CH ₃ —CH	IR		4.52	2.09	2.06	1.93	1.78	1.55	1.39	1.19
	C—OH	IR		2.64	2.68	2.45	2.25	2.08	1.81	1.61	1.33
	C(OH)—CH(=O)	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	Total		-66.36	80.14	26.75	31.96	36.46	40.21	45.98	50.16	56.57
(O=)Y(CCH ₂ CH ₂ OCH ₂)	TVR ^c	-69.13	70.71	19.76	25.70	31.23	35.99	43.38	48.70	56.69
CH ₂ (OOH)C(OH)=CHCH ₂ • ≡ CH ₂ (OOH)C•(OH)CH=CH ₂	TVR ^c	78.76	26.50	33.23	38.89	43.47	50.27	55.13	62.62	78.76
	C—OH	IR		2.64	2.68	2.45	2.25	2.08	1.81	1.61	1.33
	CH ₂ —OOH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	O—OH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	Total		-29.58
CH ₂ (OOH)C(=O)CH=CH ₂	TVR ^c		76.96	23.62	30.04	36.07	41.36	49.74		
	CH ₂ —C(=O)	IR		6.10	3.28	2.69	2.20	1.87	1.50		
	C(=O)—CH=CH ₂	IR		3.79	2.83	3.07	3.08	2.97	2.62		
	CH ₂ —OOH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	O—OH	IR		Barrier > 3.5 kcal mol ⁻¹ – not considered							
	Total		-75.33								

^aThermodynamic properties are referred to a standard state of an ideal gas at 1 atm; torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, a more exact contribution from hindered rotations is included; ^b $\Delta_f H_{298}^0$ in kcal mol⁻¹; S_{298}^0 in cal mol⁻¹ K⁻¹; ^cDFT at B3LYP/6-311G(d,p) ^dThe sum of contributions from translations, external rotations, and Vibrations. ^dContribution from internal rotation about the corresponding bonds.

SM2: Calculated Thermochemical Properties of Transition State Structures^a

	Species		$\Delta_f H_{298}^0$ ^b	S_{298}^0 ^b	Cp (T) cal mol ⁻¹ K						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
TS0	TVR^c	36.93	73.48	22.60	28.52	33.64	37.88	44.36	49.03	56.06
TS01	TVR^c	44.77	83.47	26.46	31.45	35.69	39.20	44.68	48.84	55.55
TS02a	TVR^c	48.30	76.22	22.71	28.35	33.38	37.64	44.22	48.96	56.08
TS02	TVR^c	47.19	79.13	25.93	30.93	35.16	38.69	44.28	48.52	55.38
TS03	TVR^c	69.12	77.57	25.71	31.29	35.79	39.41	44.95	49.10	55.76
TS04	TVR^c	18.67	80.42	25.25	30.36	34.75	38.43	44.24	48.63	55.61
TS1	TVR^c	-17.09	82.85	28.50	35.63	41.79	46.86	54.43	59.72	67.44
TS1-1	TVR^c	-15.76	88.79	30.81	37.19	42.69	47.22	54.12	59.11	66.75
TS1-2	TVR^c	-3.23	81.54	25.55	30.04	34.23	37.93	43.90	48.39	55.45
TS1-3	TVR^c	13.95	92.44	33.25	40.09	45.68	50.13	56.67	61.24	68.08
TS1-3B	TVR^c	-13.11	82.60	30.35	37.76	43.77	48.55	55.54	60.41	67.63
TS1-4	TVR^c	5.19	78.42	23.22	28.23	32.92	37.02	43.51	48.23	55.44
TS1-5	TVR^c	31.92	81.51	24.70	29.74	34.25	38.09	44.11	48.52	55.42
TS1-6	TVR^c	10.21	90.12	31.24	37.09	42.23	46.54	53.15	57.97	65.63

SM2 (con't): Calculated Thermochemical Properties of Transition State Structures^a

	Species		$\Delta_f H_{298}^0$ ^b	S_{298}^0 ^b	Cp (T) cal mol ⁻¹ K						
					300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
TS1-7	TVR^c	-28.34	90.12	31.24	37.09	42.23	46.54	53.15	57.97	65.63
TS1-8	TVR^c	-5.49	79.52	28.51	36.08	42.39	47.46	54.86	59.95	67.43
TS1-9	TVR^c	-8.80	92.30	32.06	38.56	43.92	48.24	54.71	59.38	66.69
TS1-10	TVR^c	12.68	90.42	32.56	39.23	44.82	49.34	56.02	60.70	67.74
TS2	TVR^c	-8.93	82.14	28.13	35.51	41.80	46.93	54.53	59.81	67.49
TS2-1	TVR^c	-7.52	92.79	30.84	36.46	41.55	45.90	52.70	57.73	65.66
TS2-2	TVR^c	-2.65	81.64	27.36	33.83	39.28	43.72	50.44	55.30	62.82
TS2-3	TVR^c	-6.78	69.99	17.32	20.14	22.48	24.39	27.30	29.43	32.79
TS3	TVR^c	-0.36	90.17	30.06	37.06	43.03	47.92	55.22	60.33	67.80
TS3-1	TVR^c	-36.14	88.50	29.31	35.20	40.54	45.10	52.23	57.44	65.57
TS4	TVR^c	5.21	89.39	30.14	36.50	42.09	46.78	54.00	59.21	67.05
TS4-1	TVR^c	-35.60	86.53	26.76	32.18	37.16	41.47	48.33	53.40	61.14
TS5	TVR^c	-9.10	80.90	27.89	34.89	40.93	45.89	53.38	58.71	66.71
TS5-1	TVR^c	-7.71	83.17	27.94	34.03	39.59	44.38	51.86	57.32	65.71

^aThermodynamic properties are referred to a standard state of an ideal gas at 1 atm; ^b $\Delta_f H_{298}^0$ in kcal mol⁻¹; S_{298}^0 in cal mol⁻¹ K⁻¹; ^cDensity Functional Theory at B3LYP/6-311G(d,p);

SM 3: Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

$CH_2\bullet C(=O)CH_2CH_3$	$CH_2(OO\bullet)C(=O)CH_2CH_3$	$CH_2(OOH)C(=O)CH_2CH_3$
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0	H,3,r93,4,a934,2,d9342,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
H,3,r123,2,a1232,1,d12321,0	H,3,r123,2,a1232,1,d12321,0	H,4,r124,3,a1243,2,d12432,0
Variables:	O,1,r131,2,a1312,3,d13123,0	O,1,r131,2,a1312,3,d13123,0
r21=1.43917616	O,13,r1413,1,a14131,2,d141312,0	O,13,r1413,1,a14131,2,d141312,0
r32=1.52706038	Variables:	H,14,r1514,13,a151413,1,d1514131,0
r43=1.52559669	r21=1.53778141	Variables:
r52=1.23285102	r32=1.51133556	r21=1.5346521
r61=1.08267885	r43=1.52532346	r32=1.51366503
r71=1.08403548	r52=1.20711668	r43=1.52562377
r83=1.09728289	r61=1.0906898	r52=1.20941267
r94=1.09253153	r71=1.09143483	r61=1.0963943
r104=1.09156449	r83=1.09761192	r71=1.09414314
r114=1.09159438	r94=1.09196921	r83=1.09580031
r123=1.09723829	r104=1.09167448	r93=1.09727194
a321=118.01543034	r114=1.09141285	r104=1.09239585
a432=113.45335182	r123=1.0966188	r114=1.09155657
a521=120.38467498	r131=1.4460642	r124=1.09198348
a612=118.46827447	r1413=1.32204969	r131=1.41634581
a712=122.22321547	a321=118.69776284	r1413=1.45757359
a832=108.00697558	a432=113.29070409	r1514=0.96718197
a943=110.68853643	a521=117.09925629	a321=117.80753734
a1043=110.94821885	a612=109.23668523	a432=113.38288922
a1143=110.95354825	a712=108.83215836	a521=118.39697379
a1232=108.03522875	a832=107.57174833	a612=107.78220372
d4321=179.85708222	a943=110.38824474	a712=108.92047802
d5213=179.98898866	a1043=111.13723832	a832=107.17929378
d6123=179.97943952	a1143=111.00721203	a934=111.87563701
d7123=-0.02108331	a1232=107.54986408	a1043=110.53999003
d8321=-56.86535282	a1312=114.63524062	a1143=110.9336336
d9432=179.94208582	a14131=111.6437403	a1243=111.21872038
d10432=59.43096146	d4321=-178.07927175	a1312=115.68327429
d11432=-59.55315802	d5213=-179.66379984	a14131=106.77059213
d12321=56.54100364	d6123=-120.86088714	a151413=100.09230752
	d7123=118.90229521	d4321=175.36584462
	d8321=-53.9045236	d5213=178.20270805
	d9432=-179.93048996	d6123=-99.90021056
	d10432=59.71074797	d7123=142.4121848
	d11432=-59.69598513	d8321=-60.82788664
	d12321=58.02075098	d9342=122.07325787
	d13123=1.30976767	d10432=179.15132075
	d141312=-80.41896416	d11432=58.86571443
		d12432=-60.4098628
		d13123=15.76045313
		d141312=69.65381036
		d1514131=118.58726446

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6-311G(d,p) level of theory.

SM 3 (con't): Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

<i>CH₂(OOH)C(=O)CH•CH₃</i>	<i>CH₂(OOH)C(=O)CH₂CH₂•</i>	<i>CH₂(OO•)C(OH)=CHCH₃</i>
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,4,a834,2,d8342,0	H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0	H,3,r93,4,a934,2,d9342,0	H,5,r95,2,a952,1,d9521,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
O,1,r121,2,a1212,3,d12123,0	O,1,r121,2,a1212,3,d12123,0	H,4,r124,3,a1243,2,d12432,0
O,12,r1312,1,a13121,2,d131212,0	O,12,r1312,1,a13121,2,d131212,0	O,1,r131,2,a1312,3,d13123,0
H,13,r1413,12,a141312,1,d1413121,0	H,13,r1413,12,a141312,1,d1413121,0	O,13,r1413,1,a14131,2,d141312,0
Variables:	Variables:	Variables:
r21=1.53188087	r21=1.52844626	r21=1.5054403
r32=1.43282995	r32=1.52192644	r32=1.33338659
r43=1.48214677	r43=1.48439535	r43=1.50172191
r52=1.23575163	r52=1.21093952	r52=1.37074317
r61=1.09554634	r61=1.09556053	r61=1.09294153
r71=1.09433568	r71=1.09899509	r71=1.09195461
r83=1.08342304	r83=1.10606601	r83=1.08197739
r94=1.09768704	r93=1.10021937	r95=0.96303802
r104=1.08979337	r104=1.08147191	r104=1.09476209
r114=1.09739777	r114=1.08058108	r114=1.09520925
r121=1.41776796	r121=1.40795678	r124=1.09529128
r1312=1.45868053	r1312=1.44965784	r131=1.44544874
r1413=0.96714145	r1413=0.97267107	r1413=1.32209528
a321=119.43267457	a321=116.2312402	a321=125.5514186
a432=121.75484109	a432=114.41367356	a432=125.98746484
a521=117.58494527	a521=120.95156036	a521=107.78733366
a612=108.373001	a612=110.176705	a612=109.96370348
a712=108.75337176	a712=109.01154613	a712=111.10981917
a834=119.91341323	a832=105.80054629	a832=117.07092646
a943=110.67480463	a934=112.06330662	a952=109.32032199
a1043=110.8172878	a1043=120.2724493	a1043=111.04099742
a1143=110.82872373	a1143=119.80476404	a1143=111.21429473
a1212=115.91269631	a1212=113.01012512	a1243=113.65742434
a13121=106.99956296	a13121=107.52601075	a1312=112.57155391
a141312=99.85419217	a141312=99.69839892	a14131=111.71036138
d4321=179.53486198	d4321=167.00229203	d4321=-179.92646206
d5213=178.7108125	d5213=-179.98153293	d5213=179.76695053
d6123=-107.68692881	d6123=48.00695314	d6123=-122.59477548
d7123=134.56472653	d7123=-70.5585065	d7123=115.84610668
d8342=-178.81163272	d8321=-70.05932151	d8321=-0.50378723
d9432=119.73782615	d9342=124.51115348	d9521=179.21400592
d10432=-1.48269168	d10432=-172.18047097	d10432=-123.93077579
d11432=-123.0110273	d11432=11.66034011	d11432=117.0317914
d12123=8.50425019	d12123=165.49326381	d12432=-3.63100229
d131212=71.11019451	d131212=69.65274781	d13123=-5.69003857
d1413121=118.94277974	d1413121=-81.37761214	d141312=87.42253594

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3 (con't): Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

<i>O=CHC(=O)CH₂CH₃</i>	<i>O=CHC(OH)=CHCH₃</i>	<i>CH₃CH₂Y(C(O•)CH₂OO)</i>
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,3,r73,2,a732,1,d7321,0	H,3,r73,2,a732,1,d7321,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,4,a834,2,d8342,0	H,5,r85,2,a852,1,d8521,0	H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
O,1,r121,2,a1212,3,d12123,0	O,1,r121,2,a1212,3,d12123,0	H,3,r123,2,a1232,1,d12321,0
Variables:	Variables:	O,1,r131,2,a1312,3,d13123,0
r21=1.53929757	r21=1.48792718	O,13,r1413,1,a14131,2,d141312,0
r32=1.50815722	r32=1.33999913	Variables:
r43=1.52530528	r43=1.49579913	r21=1.58287136
r52=1.20980477	r52=1.36931786	r32=1.58104081
r61=1.10954444	r61=1.10901411	r43=1.52231928
r73=1.09707882	r73=1.08454238	r52=1.26801905
r83=1.0970821	r85=0.96260493	r61=1.0909456
r94=1.0919283	r94=1.09535356	r71=1.09040013
r104=1.09182805	r104=1.0953044	r83=1.09196157
r114=1.09182572	r114=1.0944725	r94=1.09340082
r121=1.20224815	r121=1.20782401	r104=1.09371997
a321=117.33452336	a321=121.53263712	r114=1.09032641
a432=113.61668041	a432=126.93227445	r123=1.09144669
a521=117.52696601	a521=111.09027745	r131=1.42020722
a612=112.81283913	a612=113.36336687	r1413=1.47233264
a732=107.3370232	a732=114.90927584	a321=111.44292436
a834=111.91268342	a852=109.76995461	a432=113.04701922
a943=110.53888328	a943=110.93163942	a521=120.99914376
a1043=111.082599	a1043=110.9194964	a612=109.50555577
a1143=111.0814428	a1143=113.56800976	a712=118.50838581
a1212=123.67014326	a1212=124.68431419	a832=105.46290364
d4321=-179.98949144	d4321=179.99231055	a943=109.64554805
d5213=179.99917648	d5213=-179.99207188	a1043=111.905446
d6123=-179.99811299	d6123=179.99918707	a1143=111.22934098
d7321=-55.70840628	d7321=0.01972368	a1232=105.47318745
d8342=121.76364887	d8521=179.97700869	a1312=88.46065925
d9432=-179.98903276	d9432=-120.62086907	a14131=91.58905187
d10432=59.70582044	d10432=120.9803128	d4321=-81.63703999
d11432=-59.68370821	d11432=0.18975139	d5213=-135.02300314
d12123=0.00394956	d12123=-0.01524574	d6123=159.47947732
		d7123=28.0786355
		d8321=41.78759548
		d9432=179.65317338
		d10432=60.56044496
		d11432=-60.48846895
		d12321=156.11774747
		d13123=-87.03375503
		d141312=-18.6645157

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3 (con't): Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

<i>CH₃Y(CHOCH₂C(=O))</i>	<i>CH₃C••C(=O)CH₂OH</i>	<i>CH₂=CHC(=O)CH₂OH</i>
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,4,r54,3,a543,2,d5432,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,2,r62,1,a621,3,d6213,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,1,r81,2,a812,3,d8123,0	O,1,r81,2,a812,3,d8123,0	O,1,r81,2,a812,3,d8123,0
H,1,r91,2,a912,3,d9123,0	H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0
O,3,r103,2,a1032,1,d10321,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r124,3,a1243,2,d12432,0	H,4,r114,3,a1143,2,d11432,0	H,3,r113,2,a1132,1,d11321,0
H,4,r134,3,a1343,2,d13432,0	H,8,r128,1,a1281,2,d12812,0	H,8,r128,1,a1281,2,d12812,0
Variables:	Variables:	Variables:
r21=1.51599195	r21=1.54176395	r21=1.51960991
r32=1.53624322	r32=1.40571263	r32=1.48487226
r43=1.53073309	r43=1.45099925	r43=1.33267746
r54=1.44633951	r52=1.23758048	r52=1.21762709
r62=1.09769144	r61=1.09999089	r61=1.10159247
r71=1.09328248	r71=1.09594235	r71=1.10160592
r81=1.09239767	r81=1.40068606	r81=1.39856935
r91=1.09220512	r94=1.09020356	r94=1.08345713
r103=1.19275085	r104=1.09778406	r104=1.08457533
r124=1.09588397	r114=1.11419089	r113=1.08626478
r134=1.09505582	r128=0.97244874	r128=0.97064366
a321=117.96766842	a321=118.82420174	a321=117.35146769
a432=87.69096514	a432=121.4731007	a432=121.49300744
a543=89.41624196	a521=118.89397237	a521=119.1965953
a621=111.25789248	a612=107.13098362	a612=107.96591602
a712=109.93961376	a712=111.32336539	a712=107.96721484
a812=110.07663919	a812=108.5848763	a812=111.80026654
a912=110.93705962	a943=115.48067393	a943=121.95165422
a1032=135.83764918	a1043=117.34243737	a1043=119.98917041
a1243=114.79510096	a1143=97.1947367	a1132=117.2828599
a1343=115.60414125	a1281=105.10751527	a1281=105.1888069
d4321=-118.45856054	d4321=-110.52185977	d4321=-179.926341
d5432=1.91872715	d5213=172.7248851	d5213=179.98833511
d6213=132.02055712	d6123=-72.47305073	d6123=-57.40027927
d7123=-73.59209522	d7123=44.95207261	d7123=57.37020237
d8123=166.85536571	d8123=165.94082575	d8123=179.98330047
d9123=46.78838409	d9432=170.7453597	d9432=179.98744745
d10321=59.92816737	d10432=34.58144007	d10432=-0.00684224
d12432=-113.33228415	d11432=-76.58126803	d11321=0.05266816
d13432=117.30933434	d12812=23.915864	d12812=0.04440193

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6-311G(d,p) level of theory.

SM 3 (con't): Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

<i>CH₂=C=C=O</i>	<i>CH₃CH=C=O</i>	<i>O=Y(CCH₂CH₂OCH₂)</i>
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
O,3,r43,2,a432,1,d4321,0	O,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
H,1,r51,2,a512,3,d5123,0	H,1,r51,2,a512,3,d5123,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
Variables:	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
r21=1.31515379	H,2,r82,3,a823,4,d8234,0	H,3,r83,2,a832,1,d8321,0
r32=1.27336377	Variables:	H,3,r93,4,a934,2,d9342,0
r43=1.17386008	r21=1.51305155	H,4,r104,3,a1043,2,d10432,0
r51=1.0903007	r32=1.31015048	H,4,r114,3,a1143,2,d11432,0
r61=1.09060533	r43=1.16528956	O,1,r121,2,a1212,3,d12123,0
a321=179.77637483	r51=1.09403478	Variables:
a432=179.92290136	r61=1.09403829	r21=1.53171299
a512=122.13831378	r71=1.09131986	r32=1.52886023
a612=122.15526664	r82=1.08396358	r43=1.52946527
d4321=160.42140809	a321=123.86111172	r52=1.20194367
d5123=16.39648093	a432=179.88012314	r61=1.09162311
d6123=-163.60605836	a512=111.02859984	r71=1.10177121
	a612=111.02016492	r83=1.09522801
	a712=111.40349066	r93=1.09036654
	a823=115.84511673	r104=1.09954213
	d4321=-21.09584348	r114=1.08915558
	d5123=-120.04008929	r121=1.41788243
	d6123=119.97784659	a321=105.90919193
	d7123=-0.02809548	a432=102.13356391
	d8234=158.84553484	a521=126.31829356
		a612=111.60858424
		a712=108.74266712
		a832=107.96444643
		a934=115.63448571
		a1043=110.88381808
		a1143=114.52455216
		a1212=106.13640225
		d4321=-14.55834871
		d5213=-179.2827814
		d6123=-126.640137
		d7123=113.656865
		d8321=102.67636361
		d9342=120.89190835
		d10432=-87.63682474
		d11432=148.92834485
		d12123=-7.17512985

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3 (cont): Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

CH₂(O•)C(=O)CH₂CH₃

C
C,1,r21
C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0
H,3,r123,2,a1232,1,d12321,0
O,1,r131,2,a1312,3,d13123,0
Variables:
r21=1.42770632
r32=1.53235599
r43=1.52756772
r52=1.23705121
r61=1.08155562
r71=1.90784176
r83=1.09955872
r94=1.09241715
r104=1.09101608
r114=1.09101461
r123=1.09955175
r131=1.34561894
a321=118.17784433
a432=112.76198691
a521=119.94095096
a612=120.76959382
a712=96.87547664
a832=108.95762899
a943=110.66586241
a1043=110.74571359
a1143=110.74346406
a1232=108.95901554
a1312=125.23694747
d4321=-179.99983884
d5213=179.99934793
d6123=-179.99559957
d7123=0.00819322
d8321=-57.74444575
d9432=-179.98488585
d10432=59.42768702
d11432=-59.39712094
d12321=57.74314851
d13123=0.00271522

CH•(OOH)C(=O)CH₂CH₃

C
C,1,r21
C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0
H,3,r93,4,a934,2,d9342,0
H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0
H,4,r124,3,a1243,2,d12432,0
O,1,r131,2,a1312,3,d13123,0
O,13,r1413,1,a14131,2,d141312,0
H,14,r1514,13,a151413,1,d1514131,0
Variables:
r21=1.53538268
r32=1.51593018
r43=1.52720002
r52=1.21588967
r61=1.09919094
r71=1.09662935
r83=1.09830292
r93=1.09970577
r104=1.09483841
r114=1.09397497
r124=1.09450326
r131=1.41730027
r1413=1.45873697
r1514=0.97459516
a321=117.82299556
a432=113.14788765
a521=118.50632691
a612=108.11507357
a712=109.15681635
a832=107.39661149
a934=111.73858761
a1043=110.50236735
a1143=110.91317146
a1243=111.19430895
a1312=115.35708411
a14131=106.44880732
a151413=99.83278254
d4321=174.14028872
d5213=177.81043439
d6123=-95.64767027
d7123=146.53083799
d8321=-62.3031483
d9342=122.13081387
d10432=179.14579913
d11432=58.84466399
d12432=-60.43717206
d13123=19.70191607
d141312=68.1840569
d1514131=113.84298665

CH•(OOH)C(OH)=CHCH₃

C
C,1,r21
C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0
H,3,r73,2,a732,1,d7321,0
H,5,r85,2,a852,1,d8521,0
H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0
O,1,r121,2,a1212,3,d12123,0
O,12,r1312,1,a13121,2,d131212,0
H,13,r1413,12,a141312,1,d1413121,0
Variables:
r21=1.48001252
r32=1.34246229
r43=1.49498204
r52=1.37092505
r61=1.10622165
r73=1.08474883
r85=0.9624549
r94=1.09510393
r104=1.09512986
r114=1.0941917
r121=1.21461
r1312=2.86725454
r1413=0.98439578
a321=122.5412172
a432=126.47386998
a521=110.37530981
a612=113.33622264
a732=116.46316371
a852=109.79680151
a943=110.56142718
a1043=110.56274137
a1143=114.02965505
a1212=126.05952408
a13121=130.19360288
a141312=7.83524293
d4321=179.99338659
d5213=-179.99894574
d6123=-179.99087719
d7321=-0.01297011
d8521=-179.99355103
d9432=-121.2262236
d10432=120.99356838
d11432=-0.11717113
d12123=0.01418143
d131212=-0.05253832
d1413121=-178.71898188

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3 (cont): Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)		
$\text{CH}_2\bullet\text{C}(\text{OH})=\text{CHCH}_3$	$\text{CH}_2(\text{OOH})\text{C}(\text{OH})=\text{CHCH}_2\bullet$	$\text{CH}_2(\text{OOH})\text{C}(\text{OH})\text{CH}=\text{CH}_2$
C C,1,r21 C,2,r32,1,a321 C,3,r43,2,a432,1,d4321,0 O,2,r52,1,a521,3,d5213,0 H,1,r61,2,a612,3,d6123,0 H,3,r73,2,a732,1,d7321,0 H,5,r85,2,a852,1,d8521,0 H,4,r94,3,a943,2,d9432,0 H,4,r104,3,a1043,2,d10432,0 H,4,r114,3,a1143,2,d11432,0 H,1,r121,2,a1212,3,d12123,0 Variables: r21=1.38645365 r32=1.3951439 r43=1.5001638 r52=1.37777165 r61=1.08322897 r73=1.08463583 r85=0.96876317 r94=1.09326147 r104=1.10236029 r114=1.10235774 r121=1.082945 a321=123.65685827 a432=123.8203921 a521=115.71190624 a612=120.74528762 a732=117.2301658 a852=109.10775745 a943=111.03109995 a1043=112.55766894 a1143=112.55697739 a1212=120.31571117 d4321=179.99881966 d5213=179.99888587 d6123=179.99981299 d7321=-0.00271972 d8521=179.99230776 d9432=-179.98331645 d10432=60.41758496 d11432=-60.38414671 d12123=-0.00108988	C C,1,r21 C,2,r32,1,a321 C,3,r43,2,a432,1,d4321,0 O,2,r52,1,a521,3,d5213,0 H,1,r61,2,a612,3,d6123,0 H,1,r71,2,a712,3,d7123,0 H,3,r83,2,a832,1,d8321,0 H,5,r95,2,a952,1,d9521,0 H,4,r104,3,a1043,2,d10432,0 H,4,r114,3,a1143,2,d11432,0 O,1,r121,2,a1212,3,d12123,0 O,12,r1312,1,a13121,2,d131212,0 H,13,r1413,12,a141312,1,d1413121,0 Variables: r21=1.50149264 r32=1.38629276 r43=1.3806085 r52=1.36282205 r61=1.09885587 r71=1.09697791 r83=1.08373101 r95=0.96366425 r104=1.0811208 r114=1.0861527 r121=1.41480842 r1312=1.45948451 r1413=0.96704443 a321=125.20450766 a432=126.37405961 a521=110.4658361 a612=110.51829298 a712=109.7256634 a832=114.76805061 a952=109.31426904 a1043=120.9179429 a1143=123.25665246 a1212=114.35448581 a13121=107.31602561 a141312=99.40369369 d4321=178.61854393 d5213=178.18555442 d6123=-104.35560571 d7123=136.91428443 d8321=-2.18413354 d9521=-177.49218867 d10432=179.32795846 d11432=-0.20205871 d12123=11.79066704 d131212=73.01959687 d1413121=122.18182055	C C,1,r21 C,2,r32,1,a321 C,3,r43,2,a432,1,d4321,0 O,2,r52,1,a521,3,d5213,0 H,1,r61,2,a612,3,d6123,0 H,1,r71,2,a712,3,d7123,0 H,3,r83,2,a832,1,d8321,0 H,5,r95,2,a952,1,d9521,0 H,4,r104,3,a1043,2,d10432,0 H,4,r114,3,a1143,2,d11432,0 O,1,r121,2,a1212,3,d12123,0 O,12,r1312,1,a13121,2,d131212,0 H,13,r1413,12,a141312,1,d1413121,0 Variables: r21=1.50149264 r32=1.38629276 r43=1.3806085 r52=1.36282205 r61=1.09885587 r71=1.09697791 r83=1.08373101 r95=0.96366425 r104=1.0811208 r114=1.0861527 r121=1.41480842 r1312=1.45948451 r1413=0.96704443 a321=125.20450766 a432=126.37405961 a521=110.4658361 a612=110.51829298 a712=109.7256634 a832=114.76805061 a952=109.31426904 a1043=120.9179429 a1143=123.25665246 a1212=114.35448581 a13121=107.31602561 a141312=99.40369369 d4321=178.61854393 d5213=178.18555442 d6123=-104.35560571 d7123=136.91428443 d8321=-2.18413354 d9521=-177.49218867 d10432=179.32795846 d11432=-0.20205871 d12123=11.79066704 d131212=73.01959687 d1413121=122.18182055

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6-311G(d,p) level of theory.

SM 3 (cont): Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

CH₂(OOH)C(=O)CH•CH₃	CH₂(OO•)C(OH)=CHCH₃	CH₂(OOH)C(=O)CH=CH₂
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,4,a834,2,d8342,0	H,3,r83,4,a834,2,d8342,0	H,3,r83,4,a834,2,d8342,0
H,4,r94,3,a943,2,d9432,0	H,5,r95,2,a952,1,d9521,0	H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	O,1,r111,2,a1112,3,d11123,0
O,1,r121,2,a1212,3,d12123,0	H,4,r124,3,a1243,2,d12432,0	O,11,r1211,1,a12111,2,d121112,0
O,12,r1312,1,a13121,2,d131212,0	O,1,r131,2,a1312,3,d13123,0	H,12,r1312,11,a131211,1,d1312111,0
H,13,r1413,12,a141312,1,d1413121,0	O,13,r1413,1,a14131,2,d141312,0	Variables:
Variables:	Variables:	r21=1.53319453
r21=1.53188087	r21=1.5054403	r32=1.48816828
r32=1.43282995	r32=1.33338659	r43=1.33304544
r43=1.48214677	r43=1.50172191	r52=1.21362373
r52=1.23575163	r52=1.37074317	r61=1.0964793
r61=1.09554634	r61=1.09294153	r71=1.0942295
r71=1.09433568	r71=1.09195461	r83=1.08278415
r83=1.08342304	r83=1.08197739	r94=1.08363345
r94=1.09768704	r95=0.96303802	r104=1.08488275
r104=1.08979337	r104=1.09476209	r111=1.41566216
r114=1.09739777	r114=1.09520925	r1211=1.45784416
r121=1.41776796	r124=1.09529128	r1312=0.96731704
r1312=1.45868053	r131=1.44544874	a321=118.03250642
r1413=0.96714145	r1413=1.32209528	a432=120.5501564
a321=119.43267457	a321=125.5514186	a521=118.31423956
a432=121.75484109	a432=125.98746484	a612=107.86414765
a521=117.58494527	a521=107.78733366	a712=108.64752961
a612=108.373001	a612=109.96370348	a834=122.02057078
a712=108.75337176	a712=111.10981917	a943=121.8301035
a834=119.91341323	a832=117.07092646	a1043=120.11048205
a943=110.67480463	a952=109.32032199	a1112=115.83758384
a1043=110.8172878	a1043=111.04099742	a12111=106.7112666
a1143=110.82872373	a1143=111.21429473	a131211=100.06386255
a1212=115.91269631	a1243=113.65742434	d4321=177.72853825
a13121=106.99956296	a1312=112.57155391	d5213=177.80904834
a141312=99.85419217	a14131=111.71036138	d6123=-99.17446747
d4321=179.53486198	d4321=-179.92646206	d7123=143.18124827
d5213=178.7108125	d5213=179.76695053	d8342=-179.56022248
d6123=-107.68692881	d6123=-122.59477548	d9432=-179.99140621
d7123=134.56472653	d7123=115.84610668	d10432=0.17917991
d8342=-178.81163272	d8321=-0.50378723	d11123=16.61627515
d9432=119.73782615	d9521=179.21400592	d121112=68.06903235
d10432=-1.48269168	d10432=-123.93077579	d1312111=116.93761111
d11432=-123.0110273	d11432=117.0317914	
d12123=8.50425019	d12432=-3.63100229	
d131212=71.11019451	d13123=-5.69003857	
d1413121=118.94277974	d141312=87.42253594	

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3 (cont): Geometry Parameters for radicals and stable species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

CH₂(O●)C(=O)CH=CH₂	CH●=C(OH)CH₂CH₃
C	C
C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,3,r73,2,a732,1,d7321,0
H,3,r83,4,a834,2,d8342,0	H,5,r85,2,a852,1,d8521,0
H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
O,1,r111,2,a1112,3,d11123,0	H,4,r114,3,a1143,2,d11432,0
Variables:	H,3,r123,2,a1232,1,d12321,0
r21=1.58845877	Variables:
r32=1.48144983	r21=1.3153466
r43=1.33329901	r32=1.51004944
r52=1.20237743	r43=1.53756375
r61=1.11266338	r52=1.38602565
r71=1.10027065	r61=1.0764495
r83=1.08308297	r73=1.09132474
r94=1.08365097	r85=0.96337686
r104=1.08461544	r94=1.09274801
r111=1.33463916	r104=1.09232914
a321=115.77722144	r114=1.09318768
a432=120.93150076	r123=1.09981954
a521=118.42557602	a321=123.47560653
a612=99.43462564	a432=113.26391229
a712=107.50420939	a521=120.58000275
a834=122.88548749	a612=140.08835872
a943=121.54218069	a732=108.56778689
a1043=120.64969448	a852=108.60623526
a1112=112.31410577	a943=110.68505325
d4321=177.97734812	a1043=110.53326706
d5213=178.85900957	a1143=111.78438548
d6123=-82.79194824	a1232=108.51848695
d7123=163.59973804	d4321=-115.43772575
d8342=-179.11748953	d5213=-177.88538443
d9432=-179.94545867	d6123=177.97430803
d10432=0.23147324	d7321=7.27187499
d11123=34.03678562	d8521=-163.36297832
	d9432=-178.54817175
	d10432=61.40508381
	d11432=-58.38683318
	d12321=122.58000283

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6-311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)		
TS0	TS01	TS02
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,3,r73,2,a732,1,d7321,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0	H,5,r85,2,a852,1,d8521,0	H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
H,3,r123,2,a1232,1,d12321,0	H,1,r121,2,a1212,3,d12123,0	H,3,r123,2,a1232,1,d12321,0
Variables:	Variables:	Variables:
r21=1.32756129	r21=1.2990463	r21=1.22039151
r32=1.48349068	r32=1.31771857	r32=1.46604218
r43=1.50497931	r43=1.48104152	r43=1.53678021
r52=1.37427075	r52=2.25224405	r52=2.09057229
r61=1.08226261	r61=1.08693988	r61=2.61078845
r71=1.08145298	r73=1.09729936	r71=1.06297282
r83=1.09024191	r85=0.93857449	r83=1.09569388
r94=1.09188062	r94=1.09826584	r94=1.09267824
r104=1.09775622	r104=1.09728126	r104=1.09220893
r114=1.09224214	r114=1.09865824	r114=1.08940826
r123=1.36505247	r121=1.08714216	r123=1.0931693
a321=136.71990292	a321=171.57495542	a321=163.14801384
a432=120.62658201	a432=122.8687838	a432=112.94995252
a521=128.89699965	a521=101.94404947	a521=97.05805202
a612=121.22169185	a612=122.9991208	a612=66.18403314
a712=120.20721983	a732=119.54631761	a712=172.48058462
a832=115.14388355	a852=105.43489174	a832=107.8905333
a943=111.76496342	a943=110.20307523	a943=110.01851941
a1043=109.66314111	a1043=112.92873022	a1043=110.93759191
a1143=111.16628682	a1143=110.56815027	a1143=109.82898623
a1232=77.17157449	a1212=121.57436603	a1232=108.30631452
d4321=-69.05078916	d4321=-88.4430863	d4321=-109.36447679
d5213=-178.92532111	d5213=175.57387514	d5213=-174.90628195
d6123=179.22102083	d6123=179.4760966	d6123=-164.0246146
d7123=-0.8660239	d7321=90.99881294	d7123=168.58484378
d8321=82.16378257	d8521=153.06619347	d8321=13.01681
d9432=-163.20180538	d9432=121.08731529	d9432=-179.03898698
d10432=77.11709517	d10432=0.60859556	d10432=61.06791729
d11432=-41.21774044	d11432=-120.13664775	d11432=-59.00317849
d12321=-178.77634427	d12123=-0.81821536	d12321=128.97170853

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

TS02a	TS03	TS04
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	O,2,r42,1,a421,3,d4213,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	H,1,r51,2,a512,3,d5123,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,3,r73,2,a732,1,d7321,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0	H,3,r83,4,a834,2,d8342,0	H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0	Variables:	H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0	r21=1.43963393	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	r32=1.35138881	H,4,r114,3,a1143,2,d11432,0
H,3,r123,2,a1232,1,d12321,0	r42=1.25569274	H,3,r123,2,a1232,1,d12321,0
Variables:	r51=1.07853409	Variables:
r21=1.39366291	r61=1.07307673	r21=1.33571364
r32=1.49558964	r73=1.07449564	r32=2.15797971
r43=1.5345231	r83=1.07371217	r43=1.48934966
r52=1.31367249	a321=119.86721749	r52=1.18638704
r61=1.50144811	a421=103.70190718	r61=1.07553099
r71=1.09116252	a512=125.27045724	r71=1.08437967
r83=1.09810806	a612=116.27849388	r83=1.08682952
r94=1.0921896	a732=119.80445318	r94=1.1000951
r104=1.09092447	a834=100.85327099	r104=1.0911904
r114=1.09270673	d4213=-179.62340472	r114=1.09244942
r123=1.0929198	d5123=-58.41479611	r123=1.08347421
a321=134.89660477	d6123=132.8936621	a321=102.14048771
a432=113.79827206	d7321=12.50199815	a432=106.45745852
a521=104.70511502	d8342=-172.32180315	a521=154.4420929
a612=69.73326712		a612=123.08927613
a712=123.50417818		a712=117.06226212
a832=106.81290311		a832=91.56736921
a943=110.48219766		a943=109.82702416
a1043=110.61928042		a1043=111.53225876
a1143=111.02482925		a1143=111.72316071
a1232=108.70893341		a1232=101.93115239
d4321=140.14562943		d4321=148.56923473
d5213=-179.35009158		d5213=177.13078823
d6123=-177.65891812		d6123=15.80650394
d7123=22.79343531		d7123=-159.40206777
d8321=-98.74996546		d8321=-91.50984082
d9432=176.94641409		d9432=170.81395009
d10432=56.72192577		d10432=51.44496611
d11432=-63.14946611		d11432=-70.29978185
d12321=15.62408446		d12321=24.42966684

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6-311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

TS1	TS1-10	TS1-1
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0	H,3,r83,4,a834,2,d8342,0
H,4,r94,3,a943,2,d9432,0	H,5,r95,2,a952,1,d9521,0	H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
H,3,r123,2,a1232,1,d12321,0	O,1,r121,2,a1212,3,d12123,0	O,1,r121,2,a1212,3,d12123,0
O,1,r131,2,a1312,3,d13123,0	O,12,r1312,1,a13121,2,d131212,0	O,12,r1312,1,a13121,2,d131212,0
O,13,r1413,1,a14131,2,d141312,0	H,13,r1413,12,a141312,1,d1413121,0	H,13,r1413,12,a141312,1,d1413121,0
Variables:	Variables:	Variables:
r21=1.53589029	r21=1.51921849	r21=1.51169889
r32=1.49063692	r32=1.46155164	r32=1.4834587
r43=1.50023638	r43=1.34095239	r43=1.48430428
r52=1.21248831	r52=1.25670409	r52=1.2090235
r61=1.09453969	r61=1.10707621	r61=1.09613673
r71=1.09240158	r71=1.10798779	r71=1.09119489
r83=1.09309293	r83=1.09548175	r83=1.08462005
r94=1.09123188	r95=1.48717019	r94=1.09034087
r104=1.0974871	r104=1.0845631	r104=1.09913636
r114=1.09169978	r114=1.09783083	r114=1.09344863
r123=1.3664248	r121=1.39383921	r121=1.43429668
r131=1.42817194	r1312=1.52544973	r1312=1.73839346
r1413=1.40674119	r1413=0.94250064	r1413=0.96778612
a321=114.9543567	a321=119.62510804	a321=102.59398572
a432=117.88671362	a432=120.60451726	a432=121.74874558
a521=120.68587082	a521=119.06698193	a521=129.71428024
a612=108.37622558	a612=109.66921393	a612=114.76268704
a712=110.85372073	a712=111.63476055	a712=113.31411148
a832=113.14464357	a832=117.15695624	a834=118.17170938
a943=111.57173778	a952=107.58012411	a943=111.63280241
a1043=109.75810887	a1043=123.21616685	a1043=109.72158457
a1143=111.39302273	a1143=121.43837634	a1143=110.80593019
a1232=94.95717017	a1212=114.54154889	a1212=93.84832088
a1312=110.67128186	a13121=107.64459494	a13121=102.24579203
a14131=106.86721611	a141312=94.71812569	a141312=93.46973731
d4321=161.24835499	d4321=-154.28255107	d4321=-135.85729151
d5213=175.11085034	d5213=-177.47654811	d5213=-166.71846614
d6123=-124.37710789	d6123=-75.92486716	d6123=-90.31324025
d7123=115.04557931	d7123=163.75966079	d7123=141.8498599
d8321=-56.95172954	d8321=22.96903117	d8342=160.27073454
d9432=-172.64994405	d9521=129.40903597	d9432=24.07048571
d10432=67.63575494	d10432=178.27045816	d10432=-95.46949419
d11432=-50.29585346	d11432=0.06264522	d11432=146.84586657
d12321=37.91971514	d12123=35.90426683	d12123=25.35898389
d13123=-2.21787936	d131212=77.25035321	d131212=-177.45427617
d141312=-54.35293824	d1413121=-179.8055739	d1413121=-148.77482593

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6-311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

TS1-2	TS1-3	TS1-3B
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,3,a523,4,d5234,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,2,r62,1,a621,3,d6213,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,1,r81,2,a812,3,d8123,0	H,3,r83,4,a834,2,d8342,0	H,3,r83,4,a834,2,d8342,0
H,1,r91,2,a912,3,d9123,0	H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0
O,3,r103,2,a1032,1,d10321,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r124,3,a1243,2,d12432,0	H,4,r114,3,a1143,2,d11432,0	O,1,r111,2,a1112,3,d11123,0
H,4,r134,3,a1343,2,d13432,0	O,1,r121,2,a1212,3,d12123,0	Variables:
Variables:	O,12,r1312,1,a13121,2,d131212,0	r21=2.20045806
r21=1.4789873	H,13,r1413,12,a141312,1,d1413121,0	r32=1.46971323
r32=1.42614631	Variables:	r43=1.33478091
r43=1.64662587	r21=1.53540399	r52=1.17979975
r52=2.41465534	r32=1.46675786	r61=1.10768428
r62=1.09252664	r43=1.44969581	r71=1.10770219
r71=1.0989202	r52=1.21962061	r83=1.08278973
r81=1.09794248	r61=1.10698838	r94=1.0845477
r91=1.084977	r71=1.10629871	r104=1.08465485
r103=1.20625535	r83=1.09339214	r111=1.23116733
r124=1.09536938	r94=1.09281248	a321=107.28646777
r134=1.10143137	r104=1.29302257	a432=120.81235134
a321=129.37877146	r114=1.09248449	a521=119.73169527
a432=109.98231152	r121=1.39687672	a612=89.18077409
a523=57.48038581	r1312=1.80364631	a712=89.17203072
a621=115.19752919	r1413=0.93770203	a834=124.15312034
a712=110.6012783	a321=117.39389892	a943=121.14484536
a812=107.80409084	a432=118.65329055	a1043=121.33251877
a912=113.92455114	a521=120.82516955	a1112=105.49920334
a1032=128.60351179	a612=108.98332187	d4321=-179.98827453
a1243=103.99226014	a712=111.11920026	d5213=-179.96079315
a1343=113.7345264	a834=120.80169278	d6123=-122.82088817
d4321=-21.27353135	a943=114.71071582	d7123=122.86926949
d5234=33.15563144	a1043=107.24823503	d8342=179.98912991
d6213=158.86770257	a1143=114.75061112	d9432=-179.98605386
d7123=-106.75611575	a1212=113.20037623	d10432=0.0124341
d8123=138.35653363	a13121=108.20903167	d11123=0.02716174
d9123=18.71094992	a141312=91.62080601	
d10321=169.09314518	d4321=-7.55472843	
d12432=-175.5155059	d5213=178.53709206	
d13432=61.15224737	d6123=-99.83226153	
	d7123=141.34071468	
	d8342=178.97064149	
	d9432=113.15328989	
	d10432=-1.15684242	
	d11432=-115.96499041	
	d12123=21.56559014	
	d131212=164.71588951	
	d1413121=-166.61221656	

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)		
TS1-4	TS1-5	TS1-6
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
O,1,r81,2,a812,3,d8123,0	O,1,r81,2,a812,3,d8123,0	H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0	H,5,r95,2,a952,1,d9521,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
H,8,r128,1,a1281,2,d12812,0	H,8,r128,1,a1281,2,d12812,0	H,4,r124,3,a1243,2,d12432,0
Variables:	Variables:	O,1,r131,2,a1312,3,d13123,0
r21=1.53352247	r21=2.40632969	O,13,r1413,1,a14131,2,d141312,0
r32=1.44016968	r32=1.38095195	Variables:
r43=1.38368298	r43=1.30455566	r21=1.45946127
r52=1.22836697	r52=1.22279909	r32=1.35140111
r61=1.09934417	r61=1.08607408	r43=1.49613816
r71=1.09917792	r71=1.07735907	r52=1.36686851
r81=1.40144021	r81=1.3356216	r61=1.09248167
r94=1.09008659	r94=1.08868975	r71=1.29874927
r104=1.09690112	r104=3.06798108	r83=1.08265244
r114=1.28259884	r114=1.09105155	r95=0.96268413
r128=0.97228932	r128=0.96516197	r104=1.09409062
a321=117.01557984	a321=90.49377208	r114=1.09679508
a432=120.07031028	a432=154.4693933	r124=1.09483556
a521=119.04965947	a521=113.08354446	r131=1.38562459
a612=108.00690011	a612=86.15152633	r1413=1.48954601
a712=109.41744826	a712=90.71375948	a321=122.76200965
a812=109.95871811	a812=123.39744198	a432=125.85959363
a943=120.08833034	a943=121.50157734	a521=111.4670981
a1043=124.46919705	a1043=27.69267393	a612=116.68446404
a1143=59.6864147	a1143=122.70082222	a712=113.61999901
a1281=104.90590805	a1281=110.66629412	a832=115.79620633
d4321=-105.35871105	d4321=-126.61977968	a952=109.53917337
d5213=174.79297669	d5213=142.23523986	a1043=110.71560301
d6123=-61.27347117	d6123=-171.82390781	a1143=111.3543779
d7123=54.98120783	d7123=-53.64810257	a1243=113.3960169
d8123=176.55265695	d8123=64.66847384	a1312=117.21086256
d9432=-176.57889949	d9432=174.39652438	a14131=90.63461241
d10432=9.62777892	d10432=50.99598614	d4321=178.9955688
d11432=-95.59851784	d11432=-6.50006436	d5213=-179.19369764
d12812=10.1330355	d12812=79.04484445	d6123=-152.50636602
		d7123=87.8729953
		d8321=-1.31653756
		d9521=169.9815519
		d10432=-133.03872988
		d11432=108.46284021
		d12432=-12.95361748
		d13123=-10.77895641
		d141312=118.91766079

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

TS1-7	TS1-8	TS1-9
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0
H,5,r95,2,a952,1,d9521,0	H,5,r95,2,a952,1,d9521,0	H,5,r95,2,a952,1,d9521,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
H,4,r124,3,a1243,2,d12432,0	H,4,r124,3,a1243,2,d12432,0	O,1,r121,2,a1212,3,d12123,0
O,1,r131,2,a1312,3,d13123,0	O,1,r131,2,a1312,3,d13123,0	O,12,r1312,1,a13121,2,d131212,0
O,13,r1413,1,a14131,2,d141312,0	O,13,r1413,1,a14131,2,d141312,0	H,13,r1413,12,a141312,1,d1413121,0
Variables:	Variables:	Variables:
r21=1.40463372	r21=1.50830643	r21=1.38987365
r32=1.38332655	r32=1.35331984	r32=1.44547529
r43=1.5032595	r43=1.45689291	r43=1.34893931
r52=1.36423596	r52=1.36210587	r52=1.36579859
r61=1.07309613	r61=1.09455643	r61=1.08980298
r71=2.69782462	r71=1.09700296	r71=1.08978281
r83=1.07338038	r83=1.08930874	r83=1.09701554
r95=0.94613245	r95=0.96438203	r95=0.95360684
r104=1.08401669	r104=1.08684455	r104=1.08427568
r114=1.08544988	r114=1.09126639	r114=1.09028384
r124=1.0894237	r124=1.310183	r121=2.06751933
r131=1.34123948	r131=1.42179457	r1312=1.30161755
r1413=1.48037023	r1413=1.40436091	r1413=0.95330442
a321=124.31999422	a321=127.36164835	a321=122.42501798
a432=124.33619419	a432=124.2602825	a432=123.27833756
a521=113.53488708	a521=108.90030177	a521=115.88646382
a612=121.49936506	a612=110.32603498	a612=119.85654342
a712=100.53613049	a712=107.45128822	a712=121.05912897
a832=117.18592629	a832=117.05671751	a832=115.97110241
a952=110.81592336	a952=109.43081523	a952=107.51608459
a1043=110.55365768	a1043=115.2536527	a1043=122.80539647
a1143=111.90586494	a1143=116.82749923	a1143=122.19616826
a1243=111.93725172	a1243=102.52991942	a1212=104.02208379
a1312=120.59368351	a1312=116.2011141	a13121=115.74242388
a14131=108.53538282	a14131=110.29741214	a141312=105.53664467
d4321=-178.36175804	d4321=2.47138349	d4321=-177.69899843
d5213=-179.74891645	d5213=-175.70968884	d5213=-178.79777341
d6123=178.72276265	d6123=-116.53235859	d6123=-13.34848574
d7123=42.33110897	d7123=125.7073937	d7123=-170.9714927
d8321=4.73739907	d8321=-170.35135419	d8321=1.70852942
d9521=-149.26381255	d9521=177.27391598	d9521=173.45670353
d10432=152.12662601	d10432=-167.10774293	d10432=179.82859624
d11432=32.42756283	d11432=56.6277061	d11432=0.09448345
d12432=-88.84037034	d12432=-43.54010011	d12123=84.29979126
d13123=4.17029582	d13123=1.9260593	d131212=-60.22233646
d141312=100.19920751	d141312=58.3148855	d1413121=85.512361

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)		
TS2	TS2-1	TS2-2
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0	H,3,r93,4,a934,2,d9342,0	H,3,r93,4,a934,2,d9342,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
H,3,r123,2,a1232,1,d12321,0	O,1,r121,2,a1212,3,d12123,0	O,1,r121,2,a1212,3,d12123,0
O,1,r131,2,a1312,3,d13123,0	O,12,r1312,1,a13121,2,d131212,0	O,12,r1312,1,a13121,2,d131212,0
O,13,r1413,1,a14131,2,d141312,0	H,13,r1413,12,a141312,1,d1413121,0	H,13,r1413,12,a141312,1,d1413121,0
Variables:	Variables:	Variables:
r21=1.53590303	r21=1.52657365	r21=1.52704522
r32=1.52937834	r32=1.51895974	r32=2.21883524
r43=1.51117227	r43=1.47550489	r43=1.36352196
r52=1.20903563	r52=1.2131452	r52=1.18600584
r61=1.09705383	r61=1.10755442	r61=1.09383982
r71=1.09072495	r71=1.10670213	r71=1.09470913
r83=1.09716392	r83=1.10827407	r83=1.08362956
r94=1.08782912	r93=1.10875877	r93=1.08494073
r104=1.39224214	r104=1.08770683	r104=1.0842091
r114=1.08886056	r114=1.08883993	r114=1.08373227
r123=1.09784432	r121=1.39997115	r121=1.41094294
r131=1.42734499	r1312=1.64008992	r1312=1.44663431
r1413=1.41260501	r1413=0.93923208	r1413=0.97136599
a321=120.28871912	a321=115.78237621	a321=112.60900944
a432=116.77948056	a432=109.90572456	a432=106.36295399
a521=118.91641665	a521=121.72781885	a521=125.82508744
a612=109.25379899	a612=110.03980962	a612=109.14978551
a712=107.68647446	a712=111.05588612	a712=107.69621555
a832=106.15182095	a832=108.27458409	a832=87.32666225
a943=115.78490301	a934=110.64057923	a934=120.25570377
a1043=102.34367306	a1043=119.95296345	a1043=121.64647986
a1143=116.76142996	a1143=119.50432504	a1143=121.378273
a1232=106.55749277	a1212=108.41317754	a1212=113.35844179
a1312=115.41103012	a13121=106.01353661	a13121=107.56928465
a14131=109.20052306	a141312=91.52257713	a141312=100.51362091
d4321=-50.68981944	d4321=-19.48911691	d4321=61.05446199
d5213=175.31087561	d5213=179.47699942	d5213=157.954116
d6123=-77.45487566	d6123=-112.58572089	d6123=73.93579491
d7123=163.65604451	d7123=128.38445981	d7123=-44.6257025
d8321=-174.96125785	d8321=102.55343219	d8321=-177.93481805
d9432=170.46929032	d9342=122.39843612	d9342=106.01127679
d10432=56.11047273	d10432=122.45777734	d10432=-93.27538636
d11432=-51.05757059	d11432=-84.43709973	d11432=82.85597745
d12321=71.59538898	d12123=8.13436105	d12123=-169.03082606
d13123=46.51551765	d131212=-169.37924068	d131212=68.47203551
d141312=-74.97535586	d1413121=-176.79787233	d1413121=-88.41494501

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)		
TS2-3	TS3	TS3-1
C	C	C
C,1,r21	C,1,r21	C,1,r21
O,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
H,1,r41,2,a412,3,d4123,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
H,1,r51,2,a512,3,d5123,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
O,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
O,6,r76,1,a761,2,d7612,0	H,1,r71,2,a712,3,d7123,0	H,3,r73,2,a732,1,d7321,0
H,7,r87,6,a876,1,d8761,0	H,3,r83,2,a832,1,d8321,0	H,3,r83,4,a834,2,d8342,0
Variables:	H,4,r94,3,a943,2,d9432,0	H,4,r94,3,a943,2,d9432,0
r21=2.21634755	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
r32=1.14771171	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
r41=1.08440367	H,3,r123,2,a1232,1,d12321,0	O,1,r121,2,a1212,3,d12123,0
r51=1.08506955	O,1,r131,2,a1312,3,d13123,0	O,12,r1312,1,a13121,2,d131212,0
r61=1.35660643	O,13,r1413,1,a14131,2,d141312,0	H,13,r1413,12,a141312,1,d1413121,0
r76=1.44885773	Variables:	Variables:
r87=0.97082886	r21=1.5209813	r21=1.43869658
a321=108.74672318	r32=1.50727764	r32=1.51291252
a412=102.63790326	r43=1.51046816	r43=1.53410381
a512=99.377009	r52=1.2150266	r52=1.22514561
a612=104.90265932	r61=1.38449582	r61=1.07414473
a761=108.89671587	r71=1.1022941	r73=1.08373329
a876=100.14941986	r83=1.10942959	r83=1.08332929
d4123=-133.02866365	r94=1.09760551	r94=1.08456657
d5123=103.09294189	r104=1.09789527	r104=1.08473503
d6123=-17.84032387	r114=1.09780476	r114=1.08483048
d7612=75.22882366	r123=1.10928083	r121=1.33275976
d8761=-96.06002686	r131=1.35749767	r1312=1.48109701
	r1413=1.58062344	r1413=0.95161248
	a321=117.37743028	a321=120.61232995
	a432=114.23494073	a432=111.93614076
	a521=118.16523216	a521=117.480854
	a612=108.26008346	a612=120.91314273
	a712=116.89475892	a732=109.90784613
	a832=107.8106146	a834=109.98587769
	a943=110.70643473	a943=110.32086372
	a1043=111.84506558	a1043=111.26018012
	a1143=111.78552607	a1143=110.84671161
	a1232=108.28463932	a1212=120.7257175
	a1312=117.7377496	a13121=108.10955985
	a14131=88.85603858	a141312=99.1970347
	d4321=173.33971402	d4321=-83.91609458
	d5213=179.59003309	d5213=-178.08604551
	d6123=-78.3297726	d6123=-175.73203151
	d7123=165.31753903	d7321=38.35767423
	d8321=-63.75899176	d8342=118.62857891
	d9432=179.84069122	d9432=-177.72903658
	d10432=59.97049927	d10432=62.56465343
	d11432=-60.33237581	d11432=-58.0706748
	d12321=50.0352401	d12123=2.07744334
	d13123=25.12821207	d131212=-115.31347541
	d141312=-110.35935143	d1413121=-132.09917813

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)		
TS4	TS4-1	TS5
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0	O,2,r52,1,a521,3,d5213,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0
H,4,r94,3,a943,2,d9432,0	H,5,r95,2,a952,1,d9521,0	H,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
H,3,r123,2,a1232,1,d12321,0	H,4,r124,3,a1243,2,d12432,0	H,3,r123,2,a1232,1,d12321,0
O,1,r131,2,a1312,3,d13123,0	O,1,r131,2,a1312,3,d13123,0	O,1,r131,2,a1312,3,d13123,0
O,13,r1413,1,a14131,2,d141312,0	O,13,r1413,1,a14131,2,d141312,0	O,13,r1413,1,a14131,2,d141312,0
Variables:	Variables:	Variables:
r21=1.49588782	r21=1.45946127	r21=1.55000224
r32=1.41487313	r32=1.35140111	r32=1.51247865
r43=1.5124609	r43=1.49613816	r43=1.51292606
r52=1.28813501	r52=1.36686851	r52=1.26238472
r61=1.0921221	r61=1.09248167	r61=1.10174497
r71=1.09229985	r71=1.29874927	r71=1.10252504
r83=1.09367416	r83=1.08265244	r83=1.10822022
r94=1.09552315	r95=0.96268413	r94=1.09748507
r104=1.09273185	r104=1.09409062	r104=1.09859399
r114=1.0919004	r114=1.09679508	r114=1.09779625
r123=1.50286335	r124=1.09483556	r123=1.10826626
r131=1.45254495	r131=1.38562459	r131=1.41874938
r1413=1.31983854	r1413=1.48954601	r1413=1.52272136
a321=132.06523114	a321=122.76200965	a321=118.48623365
a432=126.61080264	a432=125.85959363	a432=110.4576331
a521=117.31933415	a521=111.4670981	a521=118.35321655
a612=111.66073979	a612=116.68446404	a612=115.03176298
a712=108.27511496	a712=113.61999901	a712=114.37838452
a832=109.46751457	a832=115.79620633	a832=109.12721915
a943=112.94166182	a952=109.53917337	a943=110.77922726
a1043=109.58624464	a1043=110.71560301	a1043=111.71238674
a1143=111.7360215	a1143=111.3543779	a1143=111.81875849
a1232=66.53723187	a1243=113.3960169	a1232=110.46923942
a1312=112.15090004	a1312=117.21086256	a1312=97.77335863
a14131=112.10020561	a14131=90.63461241	a14131=95.06973359
d4321=24.54000244	d4321=178.9955688	d4321=-73.26880984
d5213=176.84540793	d5213=-179.19369764	d5213=-170.67693169
d6123=-91.76542036	d6123=-152.50636602	d6123=126.84655346
d7123=147.14286436	d7123=87.8729953	d7123=-0.80705443
d8321=-120.80306625	d8321=-1.31653756	d8321=48.35196359
d9432=-81.53782826	d9521=169.9815519	d9432=178.48761105
d10432=158.71733633	d10432=-133.03872988	d10432=58.77125451
d11432=39.88887617	d11432=108.46284021	d11432=-61.79247689
d12321=166.77549344	d12432=-12.95361748	d12321=164.40616068
d13123=29.29516916	d13123=-10.77895641	d13123=-116.9701387
d141312=-103.44816336	d141312=118.91766079	d141312=1.65283865

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6- 311G(d,p) level of theory.

SM 3(cont): Geometry Parameters for transition state species^a

Z-Matrix Structure: Bond length (angstrom) - Bond angle: (degree) - Dihedral angle: (degree)

TS5-1

C

C,1,r21

C,2,r32,1,a321

C,3,r43,2,a432,1,d4321,0

O,2,r52,1,a521,3,d5213,0

H,1,r61,2,a612,3,d6123,0

H,1,r71,2,a712,3,d7123,0

H,3,r83,2,a832,1,d8321,0

H,4,r94,3,a943,2,d9432,0

H,4,r104,3,a1043,2,d10432,0

H,4,r114,3,a1143,2,d11432,0

H,3,r123,2,a1232,1,d12321,0

O,1,r131,2,a1312,3,d13123,0

O,13,r1413,1,a14131,2,d141312,0

Variables:

r21=1.80966259

r32=1.54821367

r43=1.52534924

r52=1.22126818

r61=1.08790925

r71=1.08840278

r83=1.09044942

r94=1.09265113

r104=1.09382058

r114=1.09071993

r123=1.09444434

r131=1.37479551

r1413=1.4612292

a321=106.6709228

a432=112.2462356

a521=117.24816936

a612=101.04070286

a712=120.62506688

a832=109.07294504

a943=110.13131211

a1043=111.6474071

a1143=110.81024333

a1232=104.53175027

a1312=85.08101414

a14131=94.86810829

d4321=-87.63593771

d5213=-139.65146799

d6123=162.70881321

d7123=32.03254777

d8321=37.5838864

d9432=-175.06689456

d10432=65.37531769

d11432=-55.02906198

d12321=152.21413415

d13123=-82.55606582

d141312=-23.43529049

^aDistances in angstroms and angles in degrees. Geometry parameters optimized at the B3LYP/6-311G(d,p) level of theory.

SM 4: Vibrational Frequencies^a (cm⁻¹) for radicals

Molecules	Frequencies ν ^a							
CH₂•C(=O)CH₂CH₃	52.9882, 740.3193, 1282.7792, 1640.2922, 3338.2016,	244.7079, 837.9800, 1404.3348, 1646.1994, 3448.2933,	268.9315, 864.4409, 1530.9654, 3195.1392,	435.4581, 1063.9967, 1559.6836, 3218.9610,	439.0600, 1080.4821, 1577.2078, 3221.9599,	537.0215, 1185.0884, 1620.4926, 3281.1670,	625.5188, 1188.1703, 1629.1148, 3295.5297,	
CH₂(OO•)C(=O)CH₂CH₃	50.5443, 548.0356, 1113.3085, 1433.6356, 3074.0432,	92.2513, 589.9844, 1150.4290, 1449.0031, 3112.0503,	103.5812, 748.2783, 1155.3554, 1495.1211, 3114.5068,	189.8522, 758.7536, 1265.2209, 1502.5517, 3136.9475,	196.4004, 914.3824, 1294.1143, 1801.7521, 3021.1566,	287.1065, 962.3303, 1334.4017, 3045.1024,	400.4821, 1000.2250, 1382.1170, 3046.0030,	459.1376, 1070.7926, 1420.9049,
CH₂(OOH)C(=O)CH₂CH₃	68.2697,78.4365,234.0879,138.4991,205.9225,247.6948,321.1978,437.9433,505.7604,585.3528,670.7347,814.5498,827.2992,1009.6902,1070.0870,1086.1414,1183.1607,1240.5273,1248.3228,1295.4029,1399.5536,1425.5446,1509.9549,1537.7355,1566.2697,1574.0730,1602.5313,1606.4035,1640.1867,1643.9204,2016.8312,3209.6651,3220.2962,3242.5151, 3254.9178,3282.4798,3297.3049,3304.0499,4081.5229							
CH₂(OOH)C(=O)CH•CH₃	59.5324,126.4390,173.0006,169.2267,99.3665,216.3989,311.0762,390.5395,516.4410,536.6101,629.3392,690.2230,788.8609,866.9638,976.4102,1009.2291,1041.4405,1064.3309,1122.4541,1208.9503,1274.9943,1347.9694,1377.1070,1389.5969,1429.3310,1438.3273,1476.1634,1491.4486,1582.2592,2999.1406,3033.0488,3033.1686,3083.0317,3126.1322,3196.4678,3773.4237							
CH₂(OOH)C(=O)CH₂CH₂•	58.3011,173.5009,240.5804,159.6767,75.4428,318.2216,355.6099,425.6569,467.7658,488.3243,526.1995,665.0233,771.4381,846.5366,883.2843,989.4055,1011.7013,1038.7840,1088.2222,1132.4486,1180.4811,1282.6835,1357.8639,1389.4508,1421.0889,1422.8504,1430.1374,1440.4597,1790.6794,2920.9416,2987.9626,3000.5768,3067.1600,3158.3456,3271.8034,3682.3204							
CH₂(OO•)C(OH)=CHCH₃	76.4557,83.6415,346.3721, 54.4619,203.7632,214.3137,310.1600,393.0573,529.8078,562.1311,622.6253,806.132,814.8868,948.3507,1028.9518,1048.6907,1061.0747,1073.1675,1152.8440,1163.2925,1273.2789,1325.9757,1343.5170,1402.8230,1434.8917,1466.9124,1476.5933,1504.9700,1757.2408,3010.4312,3055.6787,3061.0814,3064.5665,3108.6240,3199.7406,3825.7367							
O=CHC(=O)CH₂CH₃	48.7327,181.7332,126.6168,190.4168,292.6754,458.4268,506.4350,647.8485,750.9807,759.2739,959.0360,998.7842,1082.7160,1104.1067,1171.0831,1268.0406,1355.8417,1383.5656,1419.8643,1444.0890,1494.8402,1501.3531,1789.9939,1809.3891,2918.9491,3024.9740,3043.5906,3043.7164,3110.3425,3110.6113							
O=CHC(OH)=CHCH₃	73.2245,315.7071,164.5534,207.7641,211.2191,323.2768,500.0370,560.0817,680.7343,820.1582,837.3709,1027.3685,1031.0358,1049.9779,1077.9433,1161.3263,1318.6525,1351.4103,1412.2619,1440.3672,1473.9017,1497.6917,1702.4264,1802.4201,2917.0091,3012.2983,3060.7514,3071.0582,3179.1413,3832.8408							
CH₃CH₂Y(C(O•)CH₂OO)	88.6350,113.9800,210.6316,250.9065,353.1887,379.2360,469.4727,571.5162,735.1578,856.0579,945.3639,1030.3117,1068.2779,1097.7658,1102.3191,1141.2771,1177.2193,1244.6209,1253.8587,1319.6188,1357.0191,1450.4853,1491.9946,1506.8612,1572.2377,1630.6613,1642.9195,1649.3886,1670.8477,3211.8235,3231.9850,3259.1873,3267.2396,3279.1246,3298.5093,3319.8883							
CH₃Y(CHOCH₂C(=O))	130.7667,218.7116,228.8160,408.0157,496.8209, 600.7520,762.1988,852.7897,969.6471,1010.5658,1137.9896,1146.1057,1200.5454,1226.0636,1241.8079,1265.7863,1410.3978,1464.6419,1503.1934,1559.9161,1627.3272,1637.4766,1645.0035,2121.8294,3215.9341,3230.4911,3239.3480,3288.8251,3290.0027,3292.0572							
CH₃C••C(=O)CH₂OH	1321.8049,794.4970,890.3760,1093.9653,1104.7846,1205.4254,1244.4789,1370.1728,1456.8636,1493.0213,1560.0298,1598.0440,1647.3370,1652.0824,1902.8396,3133.0692,3194.7955,3221.2025,3244.0998,3307.5620,4043.2533							
CH₂=CHC(=O)CH₂OH	80.0353,121.6658,231.5202,343.0991,378.1620,461.5100,501.4187,723.5728,730.2892,911.5133,1120.4504,1129.6476,1155.0045,1175.0710,1185.5110,1273.0840,1373.3350,1420.5219,1453.1088,1572.7095,1612.7811,1648.6294,1849.7137,1989.3038,3185.3774,3211.3280,3347.4003,3364.4483,3443.3491,4044.5235							
CH₂=C=C=O	31.3979,240.4665,526.3725,728.3317,1004.9224,1154.5194,1165.5246,1617.7374,1959.7223,2489.0325,3299.4547,3375.1732							
CH₃CH=C=O	159.3581,235.1798,576.4356,640.2429,710.9413,966.3235,1162.8042,1192.4247,1254.8740,1555.0840,1574.5307,1627.5333,1657.9952,2368.5223,3207.3317,3263.3529,3281.5169,3382.3680							
O=Y(CCH₂CH₂OCH₂)	123.2880,240.5518,492.0683,503.7395,646.1731,707.6639,827.3148,922.9898,996.9665,1035.2153,1070.3917,1207.8856,1244.3000,1302.9745,1333.1107,1336.0996,1385.5675,1433.1617,1475.8847,1541.6041,1600.3657,1637.0393,1678.6227,2059.9705,3195.0460,3201.7470,3230.2094,3299.5242,3301.0488,3315.0042							
CH₂(O•)C(=O)CH₂CH₃	51.4260,87.4331,151.1262,236.8423,343.9330,457.9592,476.3209,573.4187,669.5958,783.7833,861.3171,934.1274,979.7479,1052.1095,1073.3004,1153.8112,1191.4525,1208.7856,1324.0168,1365.2429,1370.9097,1388.0659,1447.8344,1464.4535,1477.0192,1796.9082,2883.5132,2942.5686,3013.4286,3027.1056,3075.1939,3083.8114,3140.8076							

^aFrequencies are calculated at B3LYP/6-311 level of theory.

SM 4: Vibrational Frequencies^a (cm⁻¹) for radicals

Molecules	Frequencies v ^a					
CH•(OOH)C(=O)CH₂CH₃	41.6995,53.6112,181.8510,193.7150,239.8896,252.7937,270.5456,409.5336,541.9426,581.7615,606.6085,716.3260,863.0192,876.1174,1060.0062,1149.0730,1158.8365,1183.6382,1300.1975,1346.4400,1417.4029,1491.5422,1540.1965,1559.4614,1598.1787,1622.3335,1630.9620,1644.0767,1655.1088,3209.5813,3236.1353,3267.6388,3278.4949,3292.0678,3448.0247,4081.4426					
CH•(OOH)C(OH)=CHCH₃	67.0237,171.3244,42.5917,149.8014,202.3216,210.4852,251.1876,328.1750,439.8000,537.3777,583.0927,664.4967,669.4611,724.6913,876.7315,987.4188,1109.7346,1123.7783,1180.8093,1224.7144,1291.8202,1403.0107,1428.5947,1548.7267,1555.6440,1582.8680,1618.2011,1641.6107,1645.8203,3172.1600,3237.2692,3276.6102,3400.7995,3410.2504,4087.7504,4129.6507					
CH₂•C(OH)=CHCH₃	-56.7172,161.4026,251.4549,279.9636,426.5379,533.2041,582.1820,619.1649,649.0609,727.3331,846.0515,961.8432,1012.6620,1052.4890,1113.7522,1176.7807,1333.4831,1385.5433,1416.4582,1457.7921,1484.5496,1488.8058,1514.9959,2970.2170,2999.0989,3106.9847,3167.1541,3194.2091,3269.5738,3844.1565					
CH₂(OOH)C(OH)=CHCH₂•	51.5139,98.6200,139.4425,176.8547,215.7345,280.1465,313.8906,378.9103,429.7923,514.7187,569.5592,638.0075,711.7651,797.7786,865.3939,944.0267,1004.5171,1044.9995,1063.1873,1138.7223,1227.8304,1266.8230,1327.5406,1360.9833,1375.9532,1433.1559,1453.1462,1517.4884,1546.1231,2994.9098,3032.1456,3124.7650,3184.1968,3228.9628,3774.1807,3817.3778					
CH₂(OOH)C•(OH)CH=CH₂	51.5139,98.6200,139.4425,176.8547,215.7345,280.1465,313.8906,378.9103,429.7923,514.7187,569.5592,638.0075,711.7651,797.7786,865.3939,944.0267,1004.5171,1044.9995,1063.1873,1138.7223,1227.8304,1266.8230,1327.5406,1360.9833,1375.9532,1433.1559,1453.1462,1517.4884,1546.1231,2994.9098,3032.1456,3124.7650,3184.1968,3228.9628,3774.1807,3817.3778					
CH₂(OOH)C(=O)CH•CH₃	59.5324	99.3665	126.4390	169.2267	173.0006	216.3989
	311.0762	390.5395	516.4410	536.6101	629.3392	690.2230
	788.8609	866.9638	976.4102	1009.2291	1041.4405	1064.3309
	1122.4541	1208.9503	1274.9943	1347.9694	1377.1070	1389.5969
	1429.3310	1438.3273	1476.1634	1491.4486	1582.2592	2999.1406
	3033.0488	3033.1686	3083.0317	3126.1322	3196.4678	3773.4237
CH₂(OO•)C(OH)=CHCH₃	54.4619	76.4557	83.6415	203.7632	214.3137	310.1600
	346.3721	393.0573	529.8078	562.1311	622.6253	806.1327
	814.8868	948.3507	1028.9518	1048.6907	1061.0747	1073.1675
	1152.8440	1163.2925	1273.2789	1325.9757	1343.5170	1402.8230
	1434.8917	1466.9124	1476.5933	1504.9700	1757.2408	3010.4312
	3055.6787	3061.0814	3064.5665	3108.6240	3199.7406	3825.7367
CH₂(OOH)C(=O)CH=CH₂	54.1556	83.1364	130.3286	174.2696	226.5501	321.2323
	393.2930	463.8836	536.0304	626.1010	682.1170	768.7706
	872.4291	1003.4113	1015.4454	1036.6161	1062.4347	1086.7308
	1164.1340	1275.4452	1325.2467	1346.7544	1377.2483	1430.5354
	1437.3762	1667.1963	1774.2211	3029.7462	3081.8466	3138.5645
	3196.6406	3232.5852	3771.1159			
CH₂(O•)C(=O)CH=CH₂	99.0800	105.0381	209.6707	316.5519	415.4596	488.6663
	694.6702	727.8620	845.5454	929.3744	1021.1358	1041.3998
	1118.5630	1206.5791	1268.0351	1313.6116	1435.8227	1451.3800
	1801.7691	2847.8275	2987.8642	3141.6224	3196.4244	3234.4723
CH•C(OH)=CH₂CH₃	52.5720	69.9820	97.5085	159.8932	170.7574	213.2620
	321.6752	326.0423	466.8508	505.3978	558.4813	622.4531
	824.2111	870.2119	1033.7279	1034.9924	1054.7856	1083.9328
	1330.3123	1367.5359	1412.3492	1446.0118	1471.8880	1496.4537
	1781.3353	2951.5181	3015.0339	3065.2221	3075.4908	3176.2047
	3838.2974					3544.7085

^aFrequencies are calculated at B3LYP/6-311 level of theory.

SM4: Vibrational Frequencies^a (cm⁻¹) for TST

Molecules	Frequencies ν^a					
TS0	-1969.4046, 148.5948, 190.8300, 238.7271, 398.3043, 570.6661, 640.2680, 700.4063, 783.2089, 815.1680, 826.1515, 932.8499, 1038.8508, 1076.8583, 1097.9436, 1116.7818, 1231.3786, 1326.6508, 1406.7630, 1425.5328, 1480.0129, 1485.5055, 1699.8670, 1960.4568, 3005.1342, 3074.6358, 3101.0989, 3116.5451, 3156.9774, 3245.4433					
TS01	-293.6725, 76.0107, 87.7786, 107.8722, 150.2293, 224.0066, 295.7774, 513.4193, 568.0195, 593.1824, 830.0333, 908.9310, 934.9348, 982.5786, 990.3090, 1071.5182, 1147.8389, 1251.5847, 1362.8095, 1392.4984, 1394.2684, 1476.2700, 2161.8220, 3033.7095, 3067.9998, 3081.9767, 3112.4184, 3123.3440, 3170.8126, 3978.1787					
TS02	-295.3910, 90.4991, 157.4301, 221.2474, 227.6216, 274.7684, 338.2501, 523.7914, 584.4915, 655.5684, 711.4407, 789.5996, 840.7328, 1017.0259, 1089.2215, 1106.5852, 1290.7753, 1350.1940, 1407.1636, 1467.7586, 1495.2968, 1513.8207, 2088.7861, 3030.1132, 3041.1490, 3071.5622, 3105.2738, 3136.6410, 3464.0789, 3766.5586					
TS02a	-2084.5492	41.0093	216.4977	232.6731	380.1388	404.6342
	531.8958	690.5379	785.0528	870.5761	956.8203	1016.8708
	1074.5062	1091.9560	1116.2724	1267.9002	1294.8511	1372.0331
	1415.8468	1435.2247	1466.3999	1498.7735	1510.1605	2015.9297
	3012.4354	3040.0702	3072.9056	3103.8966	3115.9885	3120.3079
TS03	-848.8065	354.0037	447.1707	671.5059	725.6923	904.0032
	982.1189	1076.8778	1124.9762	1214.3814	1406.1289	1596.6886
	1619.4787	1732.5724	3335.1438	3345.8470	3442.5409	3466.5290
TS04	-506.1453	37.3210	153.4108	185.2592	209.3436	332.4975
	432.0237	525.2463	618.4095	636.1269	826.2861	845.7776
	951.4664	1038.8910	1083.5208	1128.7441	1221.3313	1396.0212
	1432.8153	1468.9614	1473.9018	1492.0549	1981.1240	2985.2690
	3070.0320	3114.7273	3116.2088	3151.6516	3216.5805	3282.3397
TS1	-1950.7216,	96.0348,	129.3994,	191.3284,	229.1355,	329.0201,
	478.6854,	526.0569,	562.4994,	663.9995,	758.2249,	781.3668,
	961.5322,	1026.4512,	1043.2223,	1066.9653,	1104.4310,	1156.6283,
	1261.1149,	1350.2300,	1372.1950,	1430.2505,	1473.2302,	1502.8941,
	1606.7865,	1775.7470,	3032.9812,	3064.4453,	3104.0031,	3107.9213,
						3126.2466,
						3146.8654
TS1-1	-753.4312, 90.6779, 115.3888, 134.0402, 156.3864, 171.9966, 227.1287, 276.8761, 387.4455, 448.0932, 582.9940, 650.0853, 795.0440, 829.2872, 956.5588, 972.5148, 999.1775, 1047.3764, 1072.6375, 1137.7305, 1172.4097, 1182.7818, 1310.1287, 1399.6073, 1419.2287, 1497.7834, 1511.4646, 1520.8158, 1805.4715, 3023.1703, 3046.3862, 3092.4652, 3123.1167, 3150.2735, 3197.4930, 3726.4525					
TS1-2	-449.2143, 113.7699, 154.8468, 172.6297, 203.6905, 239.4548, 298.6450, 388.1103, 441.6075, 651.1129, 834.9900, 932.6635, 1046.9193, 1158.4977, 1213.4552, 1281.9993, 1356.7532, 1411.2773, 1536.4025, 1613.8755, 1621.3448, 1631.4282, 1838.9275, 1876.5287, 3221.6123, 3237.3201, 3293.2280, 3316.4840, 3320.9826, 3392.6652					
TS1-3	-1386.4570	46.1045	93.9023	103.5282	147.3178	165.1933
	184.8245,	391.0078,	459.6710,	472.0559,	510.2941,	543.7588,
	556.5777,	656.6255,	700.4007,	761.0626,	943.5774,	951.9268,
	1000.1354,	1048.6188,	1061.8839,	1150.0405,	1212.7989,	1237.5809,
	1310.9802,	1331.9124,	1418.0012,	1488.1552,	1544.2265,	1607.0515,
	3008.2424,	3040.8754,	3086.2525,	3110.7085	3137.6401	3763.3184
TS1-3B	-159.9005	38.8329	66.5816	141.8033	274.2915	277.2987
	338.8506	535.0412	641.4735	665.7903	895.5211	1023.0259
	1039.0020	1086.7992	1094.5597	1236.0263	1303.3081	1429.2437
	1479.4250	1632.2094	1647.2650	1918.2265	2876.4639	2917.4365
	3137.0011	3200.9260	3229.3428			
TS1-4	-1271.9122, 82.5528, 127.0364, 246.1495, 290.9571, 387.5668, 415.8011, 601.1066, 652.9832, 794.4271, 939.2723, 1118.8012, 1185.9967, 1193.9543, 1233.1717, 1269.8186, 1361.8839, 1434.6165, 1453.6424, 1574.1623, 1611.7686, 1650.8187, 1709.7924, 1941.6898, 2364.3106, 3196.2597, 3230.9065, 3246.5357, 3356.2589, 4039.4838					
TS1-5	-847.0877, 54.6933, 134.5735, 197.3313, 264.6021, 273.5644, 407.0484, 564.4999, 639.0336, 676.9540, 779.3770, 993.5733, 1029.4692, 1073.3056, 1120.5567, 1191.5156, 1272.0434, 1391.8595, 1475.1739, 1505.6207, 1573.5734, 1662.0018, 1723.2569, 2096.6874, 2514.3014, 3279.0805, 3344.1048, 3383.5598, 3548.3655, 4070.5240					
TS1-6	-1792.4319	84.2838	100.5555	121.5465	199.6688	238.8800
	308.0587	344.1763	450.6666	561.2482	604.5522	680.9307
	800.4191	834.8204	847.6706	929.1267	1028.6182	1041.1676
	1081.0358	1120.9784	1161.2039	1185.4937	1304.5328	1327.0842
	1407.9397	1444.7315	1474.1225	1496.9332	1625.0138	1963.7210
	3006.5563	3054.9403	3075.0033	3082.5207	3199.4607	3832.1764

TS1-7	-780.6721 218.5842 676.0763 1182.1495 1549.2028 3241.2326	76.2314 264.4117 735.7178 1235.2656 1585.6461 3276.4356	82.8542 341.6565 751.3016 1283.6444 1606.6993 3387.8923	135.8660 460.5098 872.6664 1406.7130 1641.4931 3400.3867	173.5238 558.5219 1108.5143 1430.6994 1645.6517 4075.6399	194.4124 569.2331 1124.8292 1440.0174 3177.3961 4128.1795
TS1-8	-1820.9371, 412.2277, 813.9678, 1060.8029, 1365.4142, 3016.2485,	121.7403, 466.3280, 831.6068, 1171.9175, 1438.3254, 3070.6491,	268.6367, 479.5209, 916.6610, 1192.6360, 1448.2112, 3073.1705,	283.0475, 605.3205, 998.2907, 1241.2228, 1470.9814, 3109.5608,	358.2142, 614.5786, 1024.4229, 1264.9302, 1599.2852, 3164.5592,	380.4606, 674.4037, 1026.9474, 1275.9900, 1636.4152, 3807.2195
TS1-9	-471.6771, 27.1205, 74.4673, 89.0645, 149.4164, 235.4945, 340.2078, 358.4851, 383.9321, 450.2562, 464.7338, 590.8967, 642.4939, 714.5475, 880.7903, 893.2313, 911.6745, 959.0623, 963.6330, 1056.8382, 1068.5751, 1199.4102, 1294.6084, 1343.8740, 1376.1475, 1509.2489, 1549.2709, 1616.2336, 1657.3106, 3042.1081, 3092.6464, 3099.2654, 3123.3539, 3155.3336, 3830.2485, 3919.8041					
TS1-10	-2149.9219, 31.8364, 75.9549, 124.4555, 151.8882, 238.7901, 343.9130, 396.1929, 446.0165, 508.8155, 528.1071, 580.8811, 696.1531, 736.2267, 815.3969, 902.2064, 917.1192, 970.4781, 1013.1342, 1067.8593, 1103.3501, 1128.6454, 1168.4924, 1311.3166, 1342.1032, 1376.2843, 1422.4459, 1467.6361, 1624.0242, 1726.7100, 2948.0691, 3015.4408, 3016.8448, 3058.8372, 3147.1256, 3988.0883					
TS2	-1572.9592,65.2993,134.7774,236.8891,305.3436,357.4324,453.1366,492.3865,527.8230,613.1767,649.6229, 778.3795,782.6203,911.2952,923.0554,1001.6159,1025.4032,1043.9977,1116.1536,1178.2832,1240.1690,1275.3902, 1294.5328,1348.7851,1374.9109,1464.3588,1472.5853,1482.3139,1519.6751,1810.7710,3021.8738,3039.8802, 3060.8238,3118.8964,3139.1142,3208.0016					
TS2-1	-772.8500, 54.5822, 78.2245, 81.0941, 135.7177, 174.0619, 179.8493, 263.1294, 345.3815, 462.8563, 493.3981, 560.9463, 676.4602, 852.7061, 870.8255, 1056.3534, 1119.8140, 1163.5600, 1198.9710, 1299.6031, 1312.8795, 1362.8952, 1402.2792, 1438.4950, 1506.1856, 1592.3979, 1618.7990, 1644.1289, 2014.6863, 3232.6268, 3238.4044, 3285.3373, 3304.0636, 3332.3436, 3444.0094, 4077.1249					
TS2-2	-363.3680, 37.1545, 56.2211, 131.3716, 146.7607, 195.6185, 277.8686, 383.1324, 419.8922, 434.8278, 442.3755, 673.4266, 811.7815, 822.0458, 852.1762, 871.0928, 947.5720, 964.8289, 1026.0730, 1041.6365, 1237.3855, 1264.4380, 1286.4475, 1333.2023, 1410.8438, 1420.9981, 1464.8429, 1564.4679, 1873.8780, 3041.1535, 3202.0285, 3230.1106, 3707.2928					
TS2-3	-251.1828, 97.8970, 124.6452, 195.8736, 316.2867, 354.4157, 465.2863, 579.4617, 868.5869, 924.7380, 1141.1980, 1207.4849, 1397.3880, 1436.2876, 2026.9018, 3106.7301, 3240.1161, 3726.3274					
TS3	-2196.6451, 30.3553, 43.3854,142.9462, 167.7883, 224.6284, 320.5958, 442.8532, 502.1525, 587.4236, 598.6323, 637.1674, 785.9366, 843.5741, 862.3930, 933.5625, 1029.7889, 1041.1607, 1121.5858, 1125.5134, 1134.5065, 1171.5898, 1350.9758, 1364.4810, 1396.3899, 1400.9046, 1408.8829, 1427.5710, 1561.5407, 1967.3020, 2945.5033, 2953.6298, 3026.2823, 3084.2604, 3086.5388, 3183.5357					
TS3-1	-777.2737, 50.2841, 86.7373, 137.8623, 200.2849, 224.9562, 247.4860, 319.4147, 444.6802, 545.7932, 583.5919, 662.3602, 750.0085, 853.8565, 869.8429, 1056.1358, 1151.4835, 1180.5322, 1268.2497, 1337.2627, 1420.6335, 1462.0504, 1489.3155, 1507.6486, 1559.5649, 1614.7188, 1629.8390, 1644.1989, 1654.3532, 3210.7606, 3239.7235, 3270.7171, 3279.5495, 3294.8046, 3393.6135, 4081.1053					
TS4	-2615.9043,60.8586,85.1354,171.6588,181.6997,287.3950,333.4329,453.5522,489.9733,606.3390,701.5563, 722.8838,847.6415,1047.7783,1094.8080,1156.2651,1180.6192,1245.0525,1284.5408,1295.4614,1411.5570, 1422.8340,1498.1052,1567.2925,1585.9348,1591.4171,1639.0131,1652.6256,1687.6886,2081.5668,3196.1842, 3241.6877,3252.7004,3266.9207,3272.1581,3326.1249					
TS4-1	-780.6721,76.2310,82.8542,135.8660,173.5238,194.4124,218.5842,264.4117,341.6565,460.5098,558.5219,569.2331, 676.0763,735.7178,751.3016,872.6664,1108.5143,1124.8292,1182.1494,1235.2656,1283.6444,1406.7130,1430.6994, 1440.0174,1549.2027,1585.6461,1606.6992,1641.4931,1645.6516,3177.3960,3241.2326,3276.4356,3387.8923, 3400.3868,4075.6399,4128.1794					
TS5	-631.7155, 110.3019, 206.2015, 212.5258, 276.4760, 322.2805, 354.7025, 431.9992, 506.8756, 645.5127, 755.2788, 763.1130, 812.7363, 913.3716, 997.1965, 1025.9629, 1046.4651, 1084.7307, 1102.4471, 1197.6391, 1270.6821, 1288.2423, 1322.7383, 1434.0091, 1483.7665, 1507.8866, 1517.8792, 1525.2774, 1532.2106, 3054.8257, 3086.5310, 3089.0021, 3113.7782, 3138.1976, 3154.5935, 3163.9442					
TS5-1	-1055.9547,105.8924,128.3505,223.5765,243.3296,282.6652,315.6838,356.7996,435.6841,522.1450,606.1985, 802.6435,869.7409,928.3372,1063.1020,1144.6368,1171.2283,1226.8343,1251.5114,1344.3045,1375.7382, 1406.5380, 1423.6543,1520.5497,1570.9190,1634.0901,1643.5181,1653.3500,1685.1179,3224.3060,3230.2627, 3250.1379,3283.3363,3289.6110,3306.4815,3340.9302					

^aFrequencies are calculated at the B3LYP/6-311g(d,p) level of theory.

SM5: Moment of Inertia^a for radicals

	Ia b	Ib	Ic
$CH_2\bullet C(=O)CH_2CH_3$	10.20	3.79	2.86
$CH_2(OO\bullet)C(=O)CH_2CH_3$	4.40	1.73	1.34
$CH_2(OOH)C(=O)CH_2CH_3$	4.41	1.69	1.40
$CH_2(OOH)C(=O)CH\bullet CH_3$	4.19	1.75	1.37
$CH_2(OOH)C(=O)CH_2CH_2\bullet$	6.91	1.45	1.28
$CH_2(OO\bullet)C(OH)=CHCH_3$	4.24	1.72	1.30
$O=CHC(=O)CH_2CH_3$	6.72	2.47	1.85
$O=CHC(OH)=CHCH_3$	6.13	2.55	1.82
$CH_3CH_2Y(C(O\bullet)CH_2OO)$	4.92	2.08	1.94
$CH_3Y(CHOCH_2C(=O))$	5.24	3.97	2.51
$CH_3C\bullet C(=O)CH_2OH$	7.71	2.27	1.98
$CH_2=CHC(=O)CH_2OH$	10.34	2.18	1.82
$CH_2=C=C=O$	299.57	4.26	4.20
$CH_3CH=C=O$	39.67	4.54	4.18
$O=Y(CCH_2CH_2OCH_2)$	7.27	3.55	2.54
$CH_2(O\bullet)C(=O)CH_2CH_3$	6.29	2.47	1.83
$CH\bullet(OOH)C(=O)CH_2CH_3$	4.17	1.67	1.28
$CH\bullet(OOH)C(OH)=CHCH_3$	5.16	1.46	1.19
$CH_2\bullet C(OH)=CHCH_3$	9.67	3.87	2.81
$CH_2(OOH)C\bullet(OH)CH=CH_2$	4.14593	1.76318	1.37743
$CH_2(OOH)C(=O)CH\bullet CH_3$	4.18647	1.74811	1.37048
$CH_2(OO\bullet)C(OH)=CHCH_3$	4.23947	1.71520	1.30493
$CH_2(OOH)C(=O)CH=CH_2$	4.28071	1.84957	1.45870
$CH_2(O\bullet)C(=O)CH=CH_2$	6.28533	2.73767	1.96865
$CH_2\bullet C(OH)=CHCH_3$	9.67275	3.87357	2.81437
$CH_2(OOH)C(OH)=CHCH_2\bullet$	4.15	1.76	1.38

^aOptimized at the B3LYP/6-311g(d,p) level of theory. ^bUnits in GHz

SM5: Moment of Inertia^a for TST

	I _a ^b	I _b	I _c
TS0	8.27243	3.97974	3.00441
TS01	6.03499	3.81644	2.60675
TS02	6.79144	3.71199	2.76247
TS02a	10.26164	3.67561	2.93559
TS03	12.98877	9.71615	5.69487
TS04	8.29303	3.41798	2.57978
TS1	3.85605	2.20593	1.54221
TS1-10	3.99332	1.73124	1.49129
TS1-1	4.09563	1.80809	1.33401
TS1-2	4.92858	3.00390	2.05138
TS1-3	3.85280	1.59247	1.14910
TS1-3B	5.66633	2.34202	1.67629
TS1-4	8.09515	2.31065	1.97954
TS1-5	4.19129	2.50302	1.63384
TS1-6	4.75897	1.57418	1.28266
TS1-7	4.60860	1.55938	1.27060
TS1-8	3.82766	2.37159	1.62337
TS1-9	4.18445	1.42484	1.36833
TS2	3.63389	2.41986	1.59265
TS2-1	4.03464	1.72218	1.29990
TS2-2	4.57688	1.36816	1.27364
TS2-3	8.79744	3.70570	2.85483
TS3	4.65184	1.61421	1.32970
TS3-1	3.89470	1.75924	1.35842
TS4	3.47336	2.23274	1.45509
TS4-1	4.60860	1.55938	1.27060
TS5	4.38454	2.13682	1.91423
TS5-1	2.94937	2.61044	1.98579

^aOptimized at the B3LYP/6-311g(d,p) level of theory. ^bUnits in GHz

SM 6: Input file for QRRK with master code analysis (CHEMASTER)

```
Kfit (uncomment if want modified Arrhenius fits)

Temp
9 500. 700. 900. 1100. 1300. 1500. 1900. 2100. 2400.

Pres
6 0.01 0.1 1.0 10. 50. 100.

PARAMETERS (mass), sigma(A), e/k(K)
123. 6.32 657.2
COLLIDER (mass), sigma(A), e/k(K)
28. 3.62 97.5
Delta (E)
900. 0.
EHEAD integration stops at Ehead + highest barrier, def. 75 kcal
75.
INT (integration interval in kcal)
1.0

Chemact
Dissoc

INPUT (A, n ,alpha, E kcal k=AT^nexp(-alpha*T)exp(-E/RT) )
3.5e12 0.0 0.0 0.0
# CJCDOCC + O2 => TS0 from jwb ccj + o2

WELL 1
CQJCDOCC
FREQ
3 367.9 12.160
1257.8 16.452
2977.1 7.388
REACTANT
CJCDOCC+O2
9.7802E+14 .065437 0.0 35.1
# CQJC(DO)CC => TS0 jwb est ccooj - ccj o2
ISOMER
CQCDOCJC
1.5211E+15 -2.87864 0.0 24.7
# CQJC(DO)CC => TS1
ISOMER
CQCDOCCJ
8.2687E+14 -2.84812 0.0 31.57
# CQJC(DO)CC => TS2
PRODUCT
CCC(DO)CHDO+OH
8.2507E+17 -3.57748 0.0 44.55
# CQJCDOCC => TS3
PRODUCT
COJCDOCC+O
9.4217E+16 -2.96554 0.0 47.78
# CQJCDOCC => TS4
PRODUCT
CCCOJDO+CH2O
1.3444E+16 -3.34482 0.0 34.46
# CQJCDOCC => TS5
END

WELL 2
CQCDOCJC
FREQ
3 363.4 16.039
1415.8 12.030
3210.3 6.431
ISOMER
CQJCDOCC
7.7496E+07 .75003 0.0 19.27
# CQCDOCJC => TS1
PRODUCT
CYCOCCDO+OH
2.1368E+09 .75750 0.0 30.39
```

```

# CQCDOCJC => TS1*1
  PRODUCT
  COJCDOCDC+H2O
  1.5608E+06      1.34487      0.0      23.60
# CQCDOCJC => TS1*3B
  PRODUCT
  CCDCDO+CDO+OH
  1.4012E+08      1.23011      0.0      28.11
# CQCDOCJC => TS1*4
  ISOMER
  CQJCOHDCC
  11.0869E+08      .70604      0.0      23.79
# CQCDOCJC => TS1*5
END

```

```

WELL 3
  CQJCOHDCC
  FREQ
  3      360.4      13.210
        1235.0      14.980
        3181.3      6.310
  ISOMER
  CQCDOCJC
  2.8154E+09      .70772      0.0      15.85
# CQJCOHDCC => TS1*5
  PRODUCT
  CCDC(OH)CDO+OH
  1.8292E+11      .68990      0.0      40.58
# CQJCOHDCC => TS1*6
  PRODUCT
  CQCJOHCDC
  9.2089E+07      .96123      0.0      21.64
# CQJCOHDCC => TS1*8
END

```

```

WELL 4
  CQCDOCCJ
  FREQ
  3      373.1      16.553
        1392.2      11.268
        3150.5      6.680
  ISOMER
  CQJCDOCC
  3.1708E+08      .56973      0.0      15.88
# CQCDOCCJ => TS2
  PRODUCT
  ODYCCOCC+OH
  9.2243E+12      -.08020      0.0      17.72
# COOHCDOCCJ => TS2*1
  PRODUCT
  CQCJDO+CDC
  2.4052E+10      .70894      0.0      25.52
# COOHCDOCCJ => TS2*2
END

```


SM 7: CJCCDO.DAT file of NASA Polynomials for use in CHEMKIN modeling

THERMO

```

300.000 1500.000 5000.000
CCDCDO req B3LYP C 3H 4O 1 OG 300.000 5000.000 1391.000 11
8.10276570E+00 1.10218663E-02-3.72435485E-06 5.73368026E-10-3.30660495E-14 2
-1.61343529E+04-1.67013777E+01 2.12139662E+00 2.38964541E-02-1.42743205E-05 3
4.53575951E-09-6.15020094E-13-1.39073230E+04 1.58782128E+01 4
CJCDOCC requences B3LYC 4H 7O 1 OG 300.000 5000.000 1376.000 11
1.62976486E+01 1.49509296E-02-5.23628917E-06 8.25867705E-10-4.84417455E-14 2
-1.39250568E+04-5.59579571E+01 6.83195941E+00 3.32613287E-02-1.81865766E-05 3
4.87469821E-09-5.38764034E-13-1.01330102E+04-3.56193864E+00 4
CCDOCC his molecule iC 4H 8O 1 OG 300.000 5000.000 1393.000 01
8.94026867E+00 1.76293853E-02-5.09830991E-06 7.54101809E-10-4.42459184E-14 2
-3.33341496E+04-1.83208388E+01 5.42426617E-01 3.66543402E-02-2.18425750E-05 3
7.62224781E-09-1.15371905E-12-3.03089623E+04 2.70729620E+01 4
CCJJCDOCO his molecule iC 4H 6O 2 OG 300.000 5000.000 1406.000 01
6.10615702E+00 1.47479729E-02-5.06219080E-06 1.00577155E-09-7.40896439E-14 2
-2.45983865E+03-9.02939895E+00-3.87152538E+00 3.69182788E-02-2.44857987E-05 3
9.07066149E-09-1.40792871E-12 1.23737580E+03 4.51522509E+01 4
CCYCOJCOO his molecule fC 4H 7O 3 OG 300.000 5000.000 1385.000 01
2.12102830E+01 1.64479315E-02-5.78836084E-06 9.15980773E-10-5.38551812E-14 2
-1.28281372E+04-8.37020595E+01 3.74428949E+00 5.90425305E-02-4.68514780E-05 3
1.95028671E-08-3.35304917E-12-6.86137903E+03 9.60278799E+00 4
CDCCDOCOH his molecule fC 4H 6O 2 OG 300.000 5000.000 1393.000 31
1.56801492E+01 1.41942323E-02-4.87872500E-06 7.59923967E-10-4.41898471E-14 2
-3.95467359E+04-5.25147844E+01 4.36677443E+00 3.99607927E-02-2.72721626E-05 3
9.63020749E-09-1.39944512E-12-3.55379441E+04 8.50250085E+00 4
CJQCDOCC requences fromC 4H 7O 3 OG 300.000 5000.000 1393.000 21
1.63254700E+01 1.84629904E-02-6.19899205E-06 9.50419203E-10-5.46591376E-14 2
-2.70347084E+04-5.62164977E+01 4.62714263E+00 4.43747622E-02-2.78104434E-05 3
9.04095085E-09-1.20461735E-12-2.28165002E+04 7.13587542E+00 4
CQJCDOCC requences fromC 4H 7O 3 OG 300.000 5000.000 1363.000 01
2.43308119E+01 1.40917303E-02-5.04519685E-06 8.07586991E-10-4.78629549E-14 2
-3.07065677E+04-9.19507702E+01 9.04709755E+00 4.43626649E-02-2.57767151E-05 3
6.21567767E-09-3.82521447E-13-2.48460921E+04-7.91945181E+00 4
CJQCOHDCC requences fromC 4H 7O 3 OG 300.000 5000.000 1405.000 21
1.77875132E+01 1.69331115E-02-5.60940576E-06 8.52088082E-10-4.86829218E-14 2
-2.18740850E+04-6.43615402E+01 3.83504600E+00 5.34948050E-02-4.29484101E-05 3
1.83460617E-08-3.18671234E-12-1.74441399E+04 9.13177254E+00 4
CDCDCDO his molecule fC 3H 2O 1 OG 300.000 5000.000 1391.000 01
7.54780108E+00 7.02873410E-03-2.39199765E-06 3.70035503E-10-2.14126233E-14 2
6.22209077E+03-1.24307684E+01 3.42369427E+00 1.59533010E-02-9.75502252E-06 3
3.15779806E-09-4.34456424E-13 7.75140853E+03 1.00133897E+01 4
CQCDOCC requences fromC 4H 8O 3 OG 300.000 5000.000 1383.000 31
1.57357802E+01 2.09915055E-02-7.04989002E-06 1.08100591E-09-6.21720177E-14 2
-4.52024140E+04-5.19729695E+01 6.34778181E+00 3.72690547E-02-1.52263779E-05 3
1.39275560E-09 3.99982971E-13-4.13289245E+04 5.31251022E-01 4
CQCDOCCJ requence is frC 4H 7O 3 OG 300.000 5000.000 1394.000 31
1.85623542E+01 1.64667406E-02-5.57992215E-06 8.60790466E-10-4.97164109E-14 2
-2.14030226E+04-6.63089763E+01 5.67686728E+00 4.92097235E-02-3.85586612E-05 3
1.63706776E-08-2.87991804E-12-1.71382976E+04 2.04716544E+00 4
CQCDOCCJC requence is frC 4H 7O 3 OG 300.000 5000.000 1393.000 31
1.82520138E+01 1.66998514E-02-5.65447534E-06 8.71886593E-10-5.03427538E-14 2
-2.67450821E+04-6.40217394E+01 5.86672337E+00 4.66135446E-02-3.39522738E-05 3
1.33361134E-08-2.19240384E-12-2.25045712E+04 2.20942461E+00 4
CYCOCCDO requences fromC 4H 6O 2 OG 300.000 5000.000 1391.000 11
1.24647122E+01 1.75600268E-02-5.99433285E-06 9.29493473E-10-5.38835322E-14 2
-3.18724030E+04-4.17143734E+01-4.95360752E-01 4.56109410E-02-2.84142506E-05 3
7.74867344E-09-1.04849993E-12-2.71511149E+04 2.86748793E+01 4
COJCDOCC his molecule iC 4H 7O 2 OG 300.000 5000.000 1386.000 21
1.34174753E+01 1.86774129E-02-6.33500430E-06 9.77906046E-10-5.65064458E-14 2
-2.70720890E+04-4.30231775E+01 3.40330904E+00 3.81136292E-02-1.93961406E-05 3
4.32154965E-09-2.56062700E-13-2.31497085E+04 1.22442931E+01 4
CQJCOHDCC requence from C 4H 7O 3 OG 300.000 5000.000 1381.000 31
1.57953295E+01 1.84246571E-02-6.18922564E-06 9.50600612E-10-5.47798791E-14 2
-2.26350575E+04-6.16450028E+01-1.62679740E+00 5.57017409E-02-3.43464520E-05 3
9.43954695E-09-8.01312637E-13-1.63708899E+04 3.29234504E+01 4
ODCCDOCC his molecule iC 4H 6O 2 OG 300.000 5000.000 1387.000 21
1.44584985E+01 1.56223729E-02-5.36408858E-06 8.34949925E-10-4.85292649E-14 2
-4.23369229E+04-4.83294337E+01 3.56887758E+00 3.91121949E-02-2.44211275E-05 3
7.79656698E-09-1.02258591E-12-3.83188023E+04 1.09155543E+01 4
ODCCOHDCC requence is frC 4H 6O 2 OG 300.000 5000.000 1397.000 21
1.51576999E+01 1.48189328E-02-5.04123543E-06 7.79845948E-10-4.51317913E-14 2
-4.01616649E+04-5.36454966E+01 2.30590437E+00 4.65974927E-02-3.56646556E-05 3
1.44110193E-08-2.39287225E-12-3.58679531E+04 1.47635932E+01 4
ODYCCOCC requence is frC 4H 6O 2 OG 300.000 5000.000 1389.000 01
1.21064682E+01 1.83208734E-02-6.26580941E-06 9.72964109E-10-5.64638730E-14 2
-4.12683388E+04-4.30539959E+01-2.24916041E+00 4.86881046E-02-2.93854484E-05 3
8.30054174E-09-8.23702064E-13-3.59956903E+04 3.51191444E+01 4
CCCOJDO requence B3LYPC 3H 5O 2 OG 300.000 5000.000 1684.000 21
7.24711962E+00 1.65108183E-02-5.69609396E-06 8.93904195E-10-5.23705089E-14 2
-3.07878495E+04-1.48360898E+01-4.43361259E-01 3.18119408E-02-1.54631918E-05 3
2.88327205E-09-3.73345773E-14-2.80255019E+04 2.71808577E+01 4

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CQCJDO	requence is frC	2H	30	3	OG	300.000	5000.000	1401.000	01
1.17461503E+01	8.53492583E-03	-2.90833679E-06	4.50464284E-10	-2.60942269E-14					2
-1.45783992E+04	-3.39954301E+01	2.14041055E+00	3.41861878E-02	-2.96632387E-05					3
1.32539112E-08	-2.36871675E-12	-1.15733763E+04	1.64377401E+01						4
CQCJOHDCD	rom therm RMG C	4H	70	3	OG	300.000	5000.000	1393.000	01
1.85016339E+01	1.70108910E-02	-6.29331989E-06	1.08414762E-09	-6.82817410E-14					2
-2.23921548E+04	-6.53423991E+01	2.06788554E+00	5.90792817E-02	-4.83016173E-05					3
2.04128677E-08	-3.49400600E-12	-1.70667579E+04	2.15905357E+01						4
cojcdocdc	his molecule iC	4H	50	2	OG	300.000	5000.000	1395.000	21
1.36263521E+01	1.31931158E-02	-4.40368908E-06	6.72870272E-10	-3.86172485E-14					2
-9.05538793E+03	-4.92582234E+01	1.60834865E+00	4.31305181E-02	-3.32505241E-05					3
1.34164292E-08	-2.20474427E-12	-5.09251936E+03	1.45847052E+01						4
TS02a	his molecule iC	4H	70	1	OG	300.000	5000.000	1396.000	11
1.34386715E+01	1.63600720E-02	-5.50325213E-06	8.45208817E-10	-4.86795310E-14					2
1.77601431E+04	-4.67557397E+01	-5.36228496E-01	4.90119082E-02	-3.43734864E-05					3
1.23268922E-08	-1.78138639E-12	2.25696215E+04	2.82240548E+01						4
TS02	his molecule iC	4H	70	1	OG	300.000	5000.000	1400.000	11
1.32881544E+01	1.59295388E-02	-5.23000227E-06	7.89457542E-10	-4.48996145E-14					2
1.78562506E+04	-4.30769221E+01	2.47337138E+00	4.43177674E-02	-3.45780228E-05					3
1.48171836E-08	-2.62166250E-12	2.13196007E+04	1.39293963E+01						4
TS03new	his molecule iC	4H	70	1	OG	300.000	5000.000	1403.000	11
1.39014414E+01	1.54862086E-02	-5.09293834E-06	7.69617979E-10	-4.38044369E-14					2
2.86647399E+04	-4.74038171E+01	6.96198337E-01	5.31316851E-02	-4.71628936E-05					3
2.22179357E-08	-4.18197330E-12	3.25917503E+04	2.11390952E+01						4
TS04	his molecule iC	4H	70	1	OG	300.000	5000.000	1399.000	11
1.32068190E+01	1.62320173E-02	-5.38398467E-06	8.18515682E-10	-4.67904128E-14					2
3.39058069E+03	-4.22971109E+01	1.96678729E+00	4.46811328E-02	-3.36652292E-05					3
1.38518837E-08	-2.36888679E-12	7.09491555E+03	1.73240486E+01						4
TS1	his molecule iC	4H	70	3	OG	300.000	5000.000	1399.000	11
1.80243524E+01	1.76636084E-02	-5.97742101E-06	9.21928571E-10	-5.32610001E-14					2
-1.72598463E+04	-7.09469457E+01	-1.26304818E+00	6.58405199E-02	-5.22113751E-05					3
2.11239309E-08	-3.43093820E-12	-1.09510132E+04	3.14027947E+01						4
TS2	his molecule iC	4H	70	3	OG	300.000	5000.000	1400.000	11
1.81477295E+01	1.75528715E-02	-5.93832038E-06	9.15763386E-10	-5.29005097E-14					2
-1.39151703E+04	-7.20766742E+01	-2.14124101E+00	6.93660895E-02	-5.69601347E-05					3
2.38297713E-08	-3.98953067E-12	-7.39179723E+03	3.51861776E+01						4
TS3	his molecule iC	4H	70	3	OG	300.000	5000.000	1398.000	11
1.63734068E+01	1.88566872E-02	-6.34091318E-06	9.73519221E-10	-5.60521645E-14					2
-6.89294326E+03	-5.98198760E+01	1.36218381E+00	5.26803657E-02	-3.46214149E-05					3
1.13386805E-08	-1.44960792E-12	-1.61292846E+03	2.11442844E+01						4
TS4	his molecule iC	4H	70	3	OG	300.000	5000.000	1396.000	11
1.74342970E+01	1.80673198E-02	-6.09242138E-06	9.37140462E-10	-5.40292894E-14					2
-5.37105250E+03	-6.37640570E+01	1.62998410E+00	5.60582239E-02	-4.11217534E-05					3
1.56644037E-08	-2.43208486E-12	-2.20481092E+01	2.06808111E+01						4
TS5	his molecule iC	4H	70	3	OG	300.000	5000.000	1401.000	11
1.69368437E+01	1.84043626E-02	-6.19090152E-06	9.50747830E-10	-5.47529003E-14					2
-1.13810021E+04	-6.55979089E+01	-1.19534355E+00	6.42648603E-02	-5.10239875E-05					3
2.09955752E-08	-3.49160255E-12	-5.48611003E+03	3.04539233E+01						4
TS11	his molecule iC	4H	70	3	OG	300.000	5000.000	1402.000	11
1.75829992E+01	1.76201800E-02	-5.86873015E-06	8.95102365E-10	-5.12966677E-14					2
-1.12764685E+04	-6.44759322E+01	1.65358227E+00	5.83720929E-02	-4.62796741E-05					3
1.92465907E-08	-3.24662070E-12	-6.13734074E+03	1.97537302E+01						4
TS12	his molecule iC	4H	60	2	OG	300.000	5000.000	1390.000	11
1.30762258E+01	1.63056265E-02	-5.40491309E-06	8.21607123E-10	-4.69721623E-14					2
-7.64071188E+03	-4.10692095E+01	3.85520633E+00	3.51432074E-02	-1.89163960E-05					3
4.63248155E-09	-3.39533398E-13	-4.17887003E+03	9.39389765E+00						4
TS1*2*OH	his molecule iC	4H	70	3	OG	300.000	5000.000	1402.000	11
1.31656336E+01	1.63657404E-02	-5.82136199E-06	1.08289797E-09	-7.45207290E-14					2
-3.19021183E+03	-4.16338803E+01	2.73155895E+00	4.08878345E-02	-2.84753054E-05					3
1.08842448E-08	-1.73812129E-12	4.82883207E+02	1.44556203E+01						4
TS13	his molecule iC	4H	70	3	OG	300.000	5000.000	1399.000	11
1.79174949E+01	1.72302136E-02	-5.71473122E-06	8.69333065E-10	-4.97351660E-14					2
1.09827634E+03	-6.25207472E+01	3.28736846E+00	5.25299008E-02	-3.81671203E-05					3
1.43661968E-08	-2.18893582E-12	6.00851745E+03	1.55563535E+01						4
TS13bis	his molecule iC	4H	70	3	OG	300.000	5000.000	1404.000	11
2.00326140E+01	1.56690210E-02	-5.22559958E-06	7.97931256E-10	-4.57720032E-14					2
-9.28861771E+02	-7.62453961E+01	1.31480579E+00	6.70200331E-02	-5.98958283E-05					3
2.73070925E-08	-4.92996349E-12	4.75138995E+03	2.14798068E+01						4
TS13B	his molecule iC	4H	70	3	OG	300.000	5000.000	1403.000	11
1.90572856E+01	1.65172476E-02	-5.52362803E-06	8.45099406E-10	-4.85472460E-14					2
-1.50974188E+04	-7.62707985E+01	-1.43100107E+00	7.27767831E-02	-6.54859189E-05					3
2.99556602E-08	-5.41872805E-12	-8.88400935E+03	3.06817704E+01						4
TS14	his molecule iC	4H	60	2	OG	300.000	5000.000	1515.000	11
2.56325752E+01	1.03723825E-02	-4.53600171E-06	8.34219267E-10	-5.49371470E-14					2
-1.71082998E+04	-1.12939569E+02	1.69720825E+01	-1.46343219E-02	7.02572321E-05					3
-5.49077906E-08	1.29874251E-11	-9.38710025E+03	-5.00328461E+01						4
TS15	his molecule iC	4H	70	3	OG	300.000	5000.000	1399.000	11
1.79991931E+01	1.77378224E-02	-6.01472419E-06	9.28972571E-10	-5.37206740E-14					2
-1.50969129E+04	-7.08452226E+01	-1.56122609E+00	6.62029478E-02	-5.20293435E-05					3
2.07809744E-08	-3.32725138E-12	-8.66480610E+03	3.30839902E+01						4
TS16	his molecule iC	4H	70	3	OG	300.000	5000.000	1408.000	11
1.68730951E+01	1.75526804E-02	-5.70449294E-06	8.55332901E-10	-4.84254474E-14					2
-1.70000552E+03	-5.91932354E+01	3.09707134E+00	5.26459120E-02	-4.00873129E-05					3
1.61750583E-08	-2.65258504E-12	2.73198605E+03	1.36566552E+01						4
TS17	his molecule iC	4H	70	3	OG	300.000	5000.000	1408.000	11

1.68730951E+01	1.75526804E-02	-5.70449294E-06	8.55332901E-10	-4.84254474E-14	2
-2.16345804E+04	-5.91932354E+01	3.09707134E+00	5.26459120E-02	-4.00873129E-05	3
1.61750583E-08	-2.65258504E-12	-1.72025888E+04	1.36566552E+01		4
TS18	his molecule iC	4H 70 3 OG	300.000 5000.000 1404.000		11
1.85075838E+01	1.70460366E-02	-5.72062301E-06	8.77440309E-10	-5.04970320E-14	2
-1.16807024E+04	-7.51882885E+01	-2.65108495E+00	7.34307290E-02	-6.38127495E-05	3
2.81353408E-08	-4.92269112E-12	-5.11835096E+03	3.58290018E+01		4
TS21	his molecule iC	4H 70 3 OG	300.000 5000.000 1403.000		11
1.63273535E+01	1.82665028E-02	-6.00218414E-06	9.06867537E-10	-5.16224243E-14	2
-1.21152179E+04	-5.49943292E+01	3.72784403E+00	4.79843409E-02	-3.25755814E-05	3
1.16035620E-08	-1.68481791E-12	-7.80994620E+03	1.25009518E+01		4
TS22	his molecule iC	4H 70 3 OG	300.000 5000.000 1403.000		11
1.78223903E+01	1.73500632E-02	-5.76043137E-06	8.76594439E-10	-5.01532250E-14	2
-8.49806111E+03	-6.42014448E+01	1.51645157E+00	6.08333735E-02	-5.09422759E-05	3
2.23773780E-08	-3.95839965E-12	-3.40251672E+03	2.14114897E+01		4
TS31	his molecule iC	4H 70 3 OG	300.000 5000.000 1400.000		11
1.59445667E+01	1.86738860E-02	-6.16174121E-06	9.33821459E-10	-5.32768332E-14	2
-2.55243870E+04	-5.54002545E+01	2.39098803E+00	5.02262123E-02	-3.38316464E-05	3
1.17806922E-08	-1.65431918E-12	-2.08570934E+04	1.73445733E+01		4
TS41	his molecule iC	4H 70 2 OG	300.000 5000.000 1390.000		11
1.46192560E+01	1.78818662E-02	-6.02106767E-06	9.25145391E-10	-5.32933689E-14	2
-2.48405780E+04	-4.86004806E+01	2.31872112E+00	4.43771643E-02	-2.69358344E-05	3
8.03513070E-09	-9.14092685E-13	-2.03576802E+04	1.82339021E+01		4
TS4*1*O	his molecule iC	4H 70 3 OG	300.000 5000.000 1399.000		11
1.79174949E+01	1.72302136E-02	-5.71473122E-06	8.69333065E-10	-4.97351660E-14	2
4.13300207E+03	-6.25207472E+01	3.28736846E+00	5.25299008E-02	-3.81671203E-05	3
1.43661968E-08	-2.18893582E-12	9.04324319E+03	1.55563535E+01		4
TS51	his molecule iC	4H 70 3 OG	300.000 5000.000 1396.000		11
1.55442143E+01	1.93004283E-02	-6.43869320E-06	9.83198358E-10	-5.63950285E-14	2
-1.10368144E+04	-5.63164479E+01	1.40972728E+00	5.09953799E-02	-3.28262796E-05	3
1.06247773E-08	-1.35116898E-12	-6.04078826E+03	1.99885660E+01		4
CCJOOH	his molecule iC	2H 50 2 OG	300.000 5000.000 1401.000		31
1.04826523E+01	1.00266666E-02	-3.24129180E-06	4.84087230E-10	-2.73264336E-14	2
-8.94588369E+02	-2.61504095E+01	3.00927879E+00	3.05981820E-02	-2.54441379E-05	3
1.14669317E-08	-2.09584294E-12	1.39332458E+03	1.28880374E+01		4
CCOJDO	his molecule iC	2H 30 2 OG	300.000 5000.000 1385.000		11
7.77537625E+00	8.90849590E-03	-3.03075109E-06	4.68848716E-10	-2.71337434E-14	2
-2.52942745E+04	-1.44114012E+01	2.54251011E+00	1.91245246E-02	-9.89005622E-06	3
2.18521183E-09	-1.13706169E-13	-2.32612469E+04	1.44296082E+01		4
O2	J 9/65 O 2H 0 0 OG	300.000 5000.000 1375.000			01
3.52299790E+00	1.06762110E-03	-4.24843320E-07	7.28399482E-11	-4.54846876E-15	2
-1.20661302E+03	4.07242932E+00	3.10345411E+00	1.43699061E-03	-1.28484674E-07	3
-3.18221668E-10	9.83941334E-14	-9.87446941E+02	6.56298379E+00		4
H	J 6/74 C OH 10 0 OG	300.000 5000.000 1000.000			01
2.50104422E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	2
2.54747466E+04	-4.65341317E-01	2.50104422E+00	0.00000000E+00	0.00000000E+00	3
0.00000000E+00	0.00000000E+00	2.54747466E+04	-4.65341317E-01		4
H2	J 3/61 C OH 20 0 OG	300.000 5000.000 1381.000			01
2.80415949E+00	9.74369356E-04	-1.86434220E-07	1.10486646E-11	1.23189540E-16	2
-7.38374105E+02	-2.71788588E-01	3.55406298E+00	-3.86047762E-04	6.47844699E-07	3
-1.73787376E-10	6.87310472E-15	-1.04786862E+03	-4.45469397E+00		4
CO2	J 9/65 C 10 20 0 OG	300.000 5000.000 1400.000			11
1.24315133E+01	-9.44186185E-03	5.70345608E-06	-1.38968608E-09	1.12558244E-13	2
-5.23801905E+04	-4.61422929E+01	-4.26082321E+00	3.94498101E-02	-5.13291894E-05	3
2.90665590E-08	-6.01606925E-12	-4.74168300E+04	4.02530643E+01		4
CO	J 9/65 C 10 10 0 OG	300.000 5000.000 1418.000			01
2.94419059E+00	1.49099067E-03	-5.36750490E-07	8.51785238E-11	-5.01038236E-15	2
-1.42176971E+04	6.61233481E+00	3.32195735E+00	3.10440464E-04	7.76786589E-07	3
-5.42856731E-10	1.05242721E-13	-1.43065062E+04	4.70976778E+00		4
C2H2	STULL C 2H 20 0 OG	300.000 5000.000 1375.000			11
6.17654299E+00	2.96591258E-03	-1.05671308E-06	1.68603011E-10	-9.97014442E-15	2
2.48121342E+04	-1.28995806E+01	2.79381682E+00	1.04498077E-02	-7.32160939E-06	3
2.54774387E-09	-3.59079365E-13	2.60346529E+04	5.42699191E+00		4
C2H3	3 C 2H 30 0 OG	300.000 5000.000 1407.000			01
4.88346287E+00	6.51212107E-03	-2.16248862E-06	3.28858576E-10	-1.87981118E-14	2
3.35397878E+04	-3.31750380E+00	1.29156374E+00	1.54065219E-02	-1.08336948E-05	3
4.26240701E-09	-7.11046605E-13	3.47500361E+04	1.58156037E+01		4
O	J 6/74 C OH 00 1 OG	300.000 5000.000 1000.000			01
2.55136704E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	2
2.92091138E+04	4.82418517E+00	2.55136704E+00	0.00000000E+00	0.00000000E+00	3
0.00000000E+00	0.00000000E+00	2.92091138E+04	4.82418517E+00		4

END