Main Groups Comparison

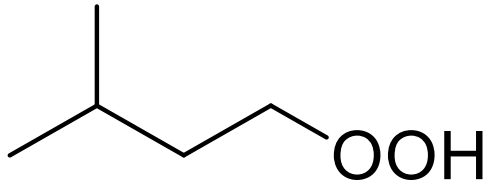
Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
C/C/H3	This work	–10.16	30.34	6.01	7.68	9.24	10.51	12.69	14.45	17.28	18.78	19.59	20.09	21.36
	Benson	–10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58				
C/C2/H2	This work	–4.91	9.74	5.63	7.05	8.38	9.56	11.35	12.60	14.47	15.38	15.90	16.18	16.89
	Benson	–4.93	9.42	5.50	6.95	8.25	9.35	11.07	12.34	14.25				
C/C3/H	This work	–1.58	–13.84	5.28	7.03	8.41	9.59	10.95	11.52	12.03	12.10	12.29	12.32	12.42
	Benson	–1.90	–12.07	4.54	6.00	7.17	8.05	9.31	10.05	11.17				
C/C4	This work	0.45	–34.05	4.38	6.16	7.53	8.71	9.76	9.85	9.37	8.84	8.69	8.47	7.95
	Benson	0.50	–35.10	4.37	6.13	7.36	8.12	8.77	8.76	8.12				

Main Groups Comparison

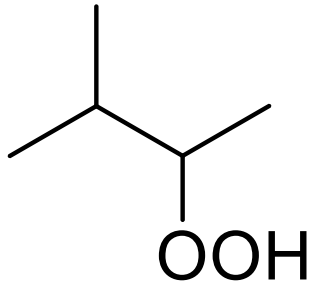
Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
C/H3/OO	This work	–9.01	29.65	7.31	8.53	9.67	10.65	12.22	13.39	15.24	16.21	16.74	17.05	17.88
	Burke et al.	–8.30	30.30	6.19	7.84	9.40	10.79	13.02	14.77	17.58				
C/C/H2/OO	This work	–8.20	6.65	7.34	8.40	9.41	10.23	11.56	12.49	13.84	14.51	14.88	15.14	15.68
	Burke et al.	–8.20	6.62	3.85	4.84	6.52	7.45	9.28	10.60	12.24				
C/C2/H/OO	This work	–6.97	–15.20	7.11	8.38	9.23	9.98	10.96	11.64	12.44	12.84	13.05	13.19	13.45
	Burke et al.	–7.03	–15.46	4.43	5.32	6.63	7.23	7.94	8.74					
C/C3/OO	This work	–6.91	–34.20	7.13	8.40	9.40	10.16	10.82	11.02	11.13	11.12	11.19	11.20	11.18
	Burke et al.	–5.80	–34.64	3.53	4.61	5.83	5.96	6.70	6.53					

OO/C/H

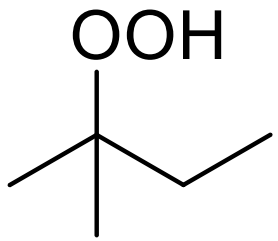
OO/ME/H



OO/CP/H



OO/CS/H

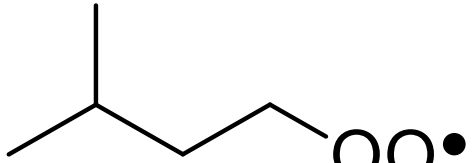


OO/CT/H

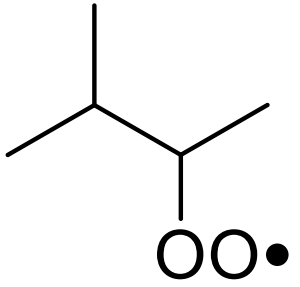
Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
OO/ME/H	This work	–21.37	37.49	7.31	8.53	9.67	10.65	12.22	13.39	15.24	16.21	16.74	17.05	17.88
	Burke et al.	–20.60	38.54	9.52	11.05	11.56	12.53	13.40	14.05					
OO/CP/H	This work	–20.24	39.71	7.34	8.40	9.41	10.23	11.56	12.49	13.84	14.51	14.88	15.14	15.68
	Burke et al.	–20.60	38.54	9.52	11.05	11.56	12.53	13.40	14.05					
OO/CS/H	This work	–19.75	40.15	7.11	8.38	9.23	9.98	10.96	11.64	12.44	12.84	13.05	13.19	13.45
	Burke et al.	–20.60	38.54	9.52	11.05	11.56	12.53	13.40						
OO/CT/H	This work	–18.99	35.73	7.13	8.40	9.40	10.16	10.82	11.02	11.13	11.12	11.19	11.20	11.18
	Burke et al.	–20.60	38.54	9.52	11.05	11.56	12.53	13.40						

ALPEROX

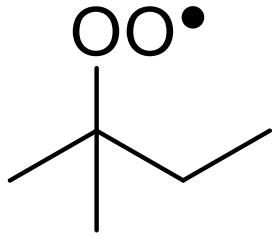
MEPEROX



ALPEROX/P



ALPEROX/S



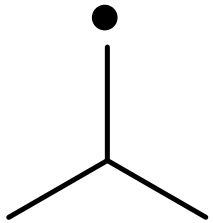
ALPEROX/T

Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
MEPEROX	This work	85.45	–1.84	–2.59	–2.93	–3.13	–3.26	–3.48	–3.69	–4.12	–4.43	–4.57	–4.65	–4.97
	Burke et al.	85.40	–1.15	–2.05	–2.84	–3.55	–4.09	–4.72	–4.97	–5.08				
ALPEROX/P	This work	85.22	–1.39	–2.98	–3.14	–3.43	–3.21	–3.74	–4.18	–4.72	–4.80	–5.02	–5.25	–5.49
	Burke et al.	85.40	–1.15	–2.05	–2.84	–3.55	–4.09	–4.72	–4.97	–5.08				
ALPEROX/S	This work	84.47	–1.34	–2.41	–2.99	–3.43	–3.46	–3.64	–4.11	–4.59	–4.92	–5.11	–5.26	–5.49
	Burke et al.	85.40	–1.15	–2.05	–2.84	–3.55	–4.09	–4.72	–4.97	–5.08				
ALPEROX/T	This work	84.14	–0.80	–1.89	–2.50	–3.27	–3.50	–4.10	–4.45	–4.93	–5.17	–5.38	–5.58	–5.97
	Burke et al.	85.40	–1.15	–2.05	–2.84	–3.55	–4.09	–4.72	–4.97	–5.08				

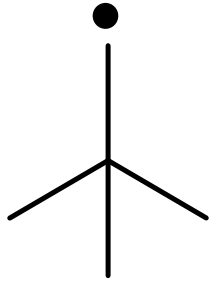
Old Special Groups

C2H5

CC.C



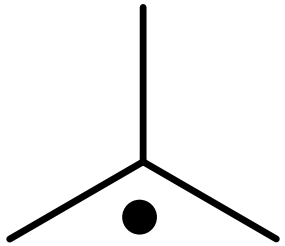
IC4H9



NEO-C5

Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
C2H5	This work	101.09	2.04	–0.17	–0.57	–1.27	–1.66	–2.42	–3.14	–4.29	–4.92	–5.21	–5.42	–5.96
	Burke et al.	100.77	2.27	–0.21	–0.77	–1.33	–1.89	–2.80	–3.48	–4.60				
IC4H9	This work	101.71	4.68	–0.20	–1.08	–1.94	–2.52	–3.44	–4.06	–4.86	–5.19	–5.46	–5.59	–5.96
	Burke et al.	101.60	1.64	–0.23	–0.90	–1.54	–2.09	–3.01	–3.60	–4.66				
NEO-C5	This work	102.38	4.81	–0.18	–0.31	–1.16	–1.79	–2.83	–3.64	–4.69	–5.14	–5.44	–5.57	–5.96
	Burke et al.	101.50	3.03	–0.59	–1.32	–2.05	–2.65	–3.50	–4.06	–4.87				
CC.C	This work	98.18	5.70	–1.22	–2.09	–2.71	–2.99	–3.47	–3.90	–4.71	–5.17	–5.43	–5.56	–5.96
	Burke et al.	98.45	4.51	–1.30	–2.36	–3.02	–3.44	–3.98	–4.36	–4.99				

New Special Groups

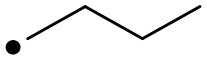


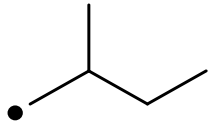
TC4H9

Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
TC4H9	This work	96.59	8.98	–1.35	–3.18	–4.27	–4.73	–5.13	–5.26	–5.42	–5.49	–5.65	–5.72	–5.96
T	Burke et al.	96.14	5.14	–2.81	–4.19	–4.84	–5.10	–5.33	–5.36	–5.39				

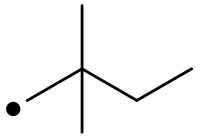
P, S and T for Alkyl Radicals

Primary, P



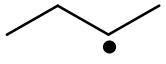


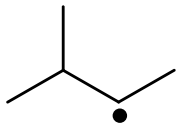
NOT
IC4H9

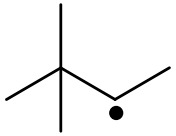


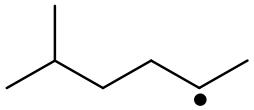
NOT
NEO-C5

Secondary, S

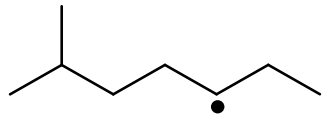






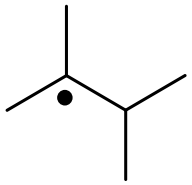


NOT
RCCJC

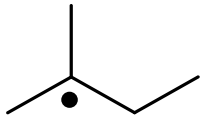


NOT
RCCJCC

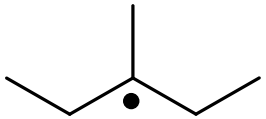
Tertiary, T



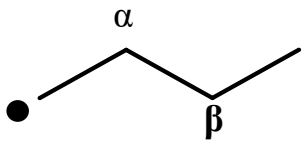
NOT
TC4H9



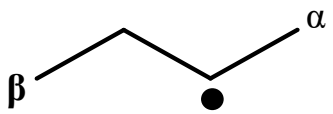
NOT
TC4H9



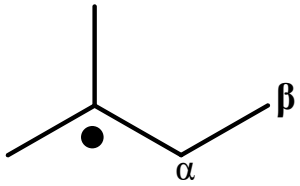
β-corrections for P, S and T of Alkyl Radicals



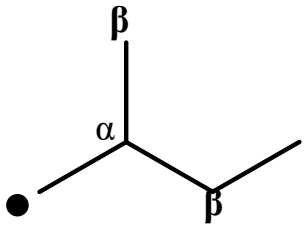
P/BETA × 1



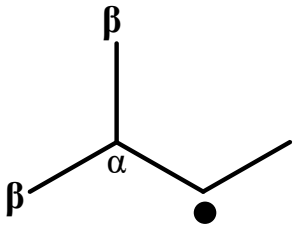
S/BETA × 1



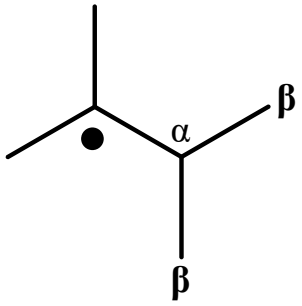
T/BETA × 1



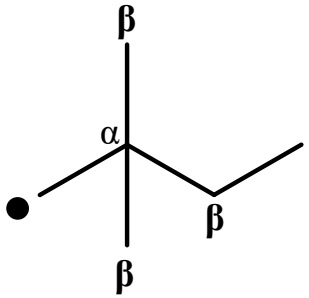
P/BETA × 2



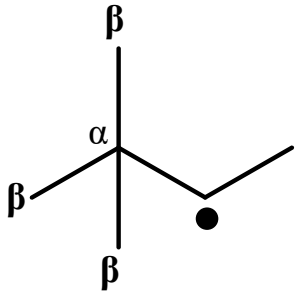
S/BETA × 2



T/BETA × 2

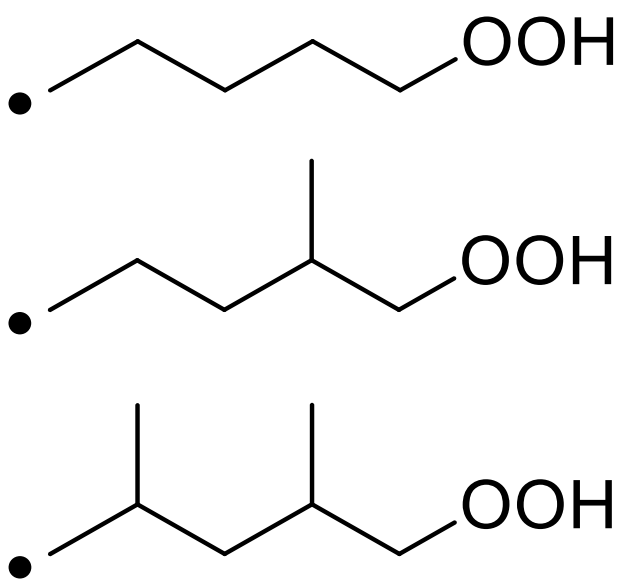


P/BETA × 3

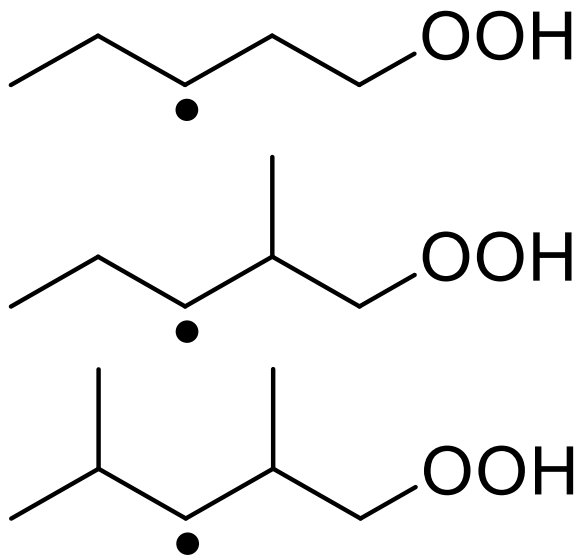


S/BETA × 3

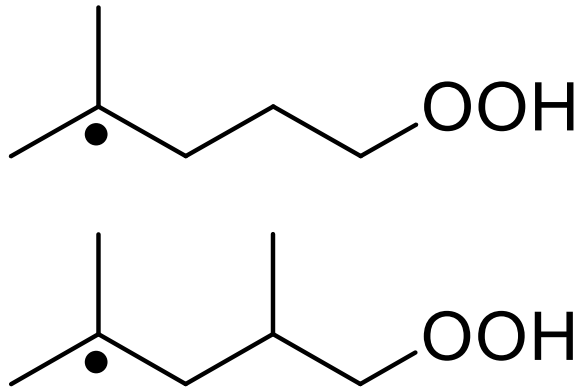
P, S and T for QOOH



P/QOOH

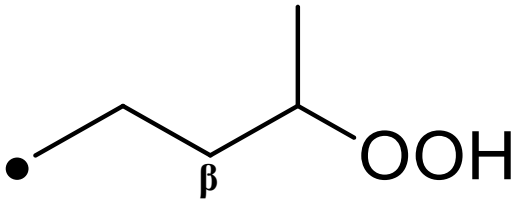


S/QOOH

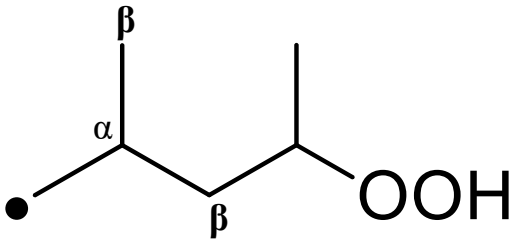


T/QOOH

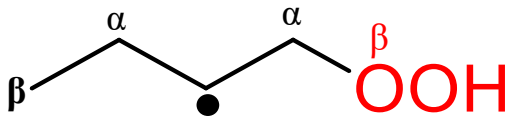
β-corrections for P, S and T of QOOH



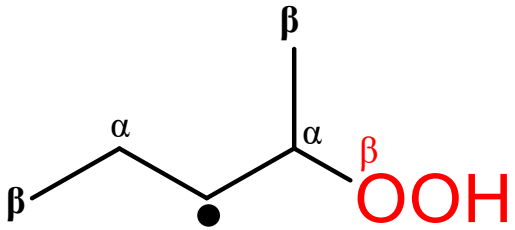
P/QOOH/C-BETA × 1



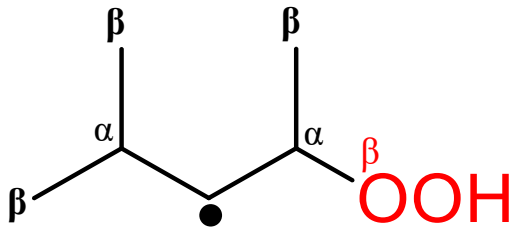
P/QOOH/C-BETA × 2



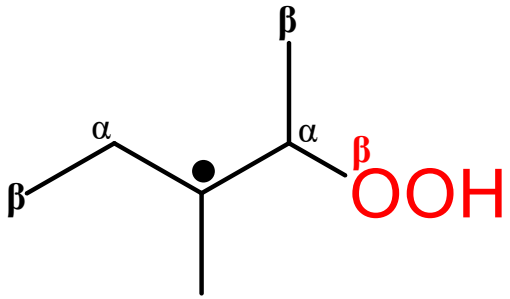
S/QOOH/C-BETA × 1
S/QOOH/O-BETA × 1



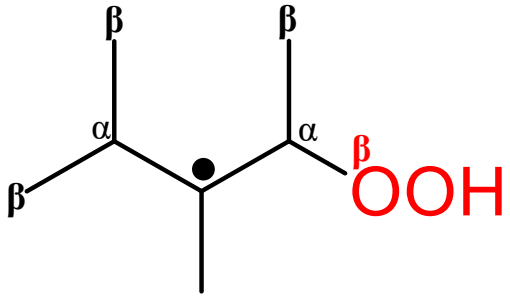
S/QOOH/C-BETA × 2
S/QOOH/O-BETA × 1



S/QOOH/C-BETA × 3
S/QOOH/O-BETA × 1



T/QOOH/C-BETA × 2
T/QOOH/O-BETA × 1

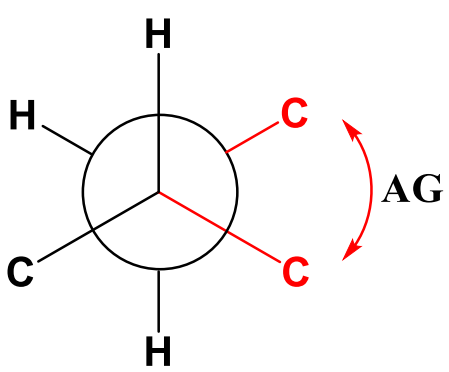


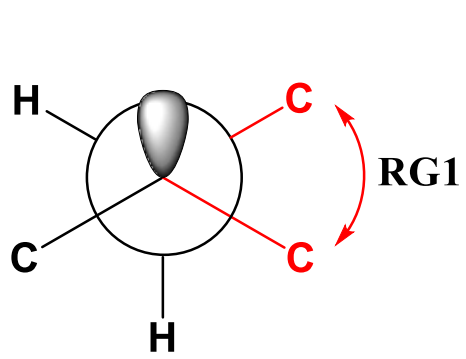
T/QOOH/C-BETA × 3
T/QOOH/O-BETA × 1

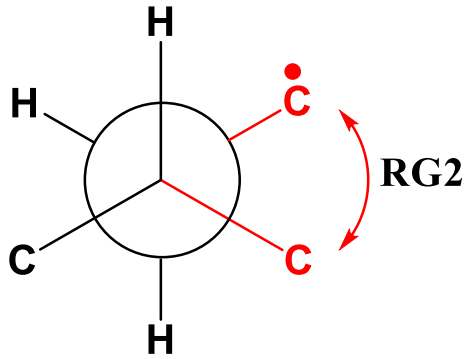
Comparison

Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
P	This work	101.16	2.82	–0.54	–0.83	–1.40	–1.90	–2.70	–3.36	–4.57	–5.08	–5.33	–5.54	–5.96
	Burke et al.	101.15	2.51	–1.14	–1.64	–2.14	–2.60	–3.32	–3.89	–4.66				
S	This work	98.14	2.50	–1.30	–1.80	–2.33	–2.76	–3.43	–3.96	–4.82	–5.22	–5.57	–5.65	–5.94
	Burke et al.	98.07	4.26	–1.78	–2.98	–3.49	–3.81	–4.40	–4.78	–5.20				
T	This work	96.77	**12.24**	–0.92	–3.23	–4.77	–5.24	–5.91	–6.52	–6.67	–6.54	–6.51	–6.46	–5.96
	Burke et al.	96.14	**5.14**	–2.81	–4.19	–4.84	–5.10	–5.33	–5.36	–5.39				
P/QOOH	This work	100.87	2.92	0.67	0.01	–0.46	–0.89	–2.00	–2.96	–4.40	–4.92	–5.29	–5.43	–5.92
S/QOOH	This work	97.66	3.51	0.34	–0.99	–1.32	–1.70	–2.64	–4.08	–5.23	–5.69	–5.76	–5.98	–6.05
T/QOOH	This work	95.74	**6.88**	–0.03	–2.32	–2.62	–3.56	–4.18	–5.80	–5.91	–5.92	–5.89	–6.02	–5.89

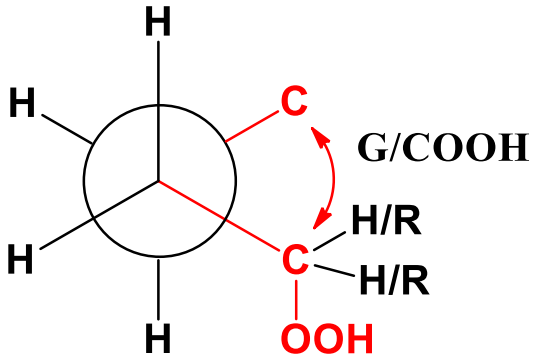
Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
P/BETA	This work	0.37	–0.76	0.34	0.23	0.19	0.16	0.10	0.02	0.01	0.01	0.00	–0.02	0.00
S/BETA	This work	0.45	1.11	–0.10	–0.08	–0.06	–0.04	–0.02	–0.02	–0.02	–0.02	–0.02	–0.02	–0.02
T/BETA	This work	0.53	–2.22	–0.44	–0.15	0.11	0.10	0.21	0.25	0.31	0.20	0.10	0.12	–0.02
P/QOOH/C–BETA	This work	0.44	–1.13	–0.07	–0.06	0.03	–0.05	–0.10	–0.16	–0.08	–0.05	–0.01	–0.02	–0.03
S/QOOH/C–BETA	This work	0.60	0.26	–0.46	–0.09	0.00	0.00	0.05	0.20	0.25	0.26	0.21	0.16	0.06
S/QOOH/O–BETA	This work	0.73	–1.32	1.50	0.55	0.24	0.10	0.09	0.19	0.21	0.10	0.10	0.10	0.14
T/QOOH/C–BETA	This work	0.84	0.10	0.04	0.00	–0.03	–0.01	0.11	0.20	0.17	0.10	0.08	0.05	–0.03
T/QOOH/O–BETA	This work	0.04	–0.42	0.23	0.06	0.08	0.10	0.12	0.17	0.22	0.21	0.23	0.26	0.30

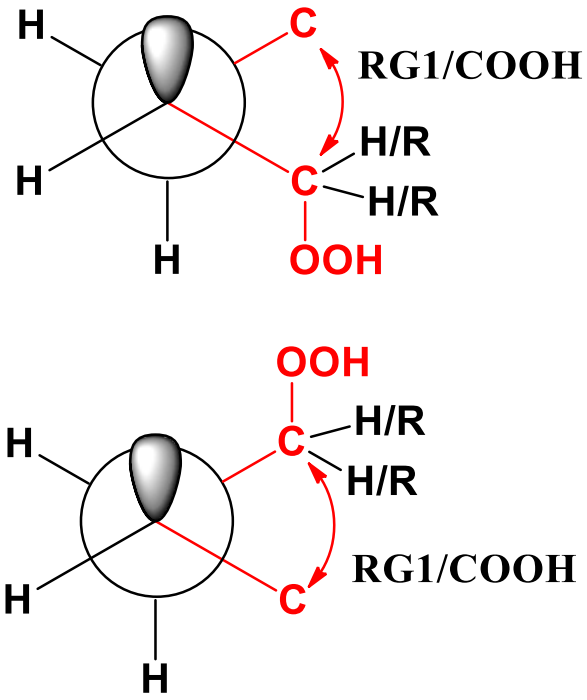


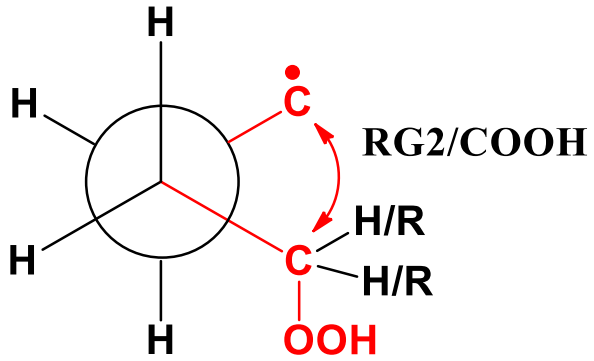




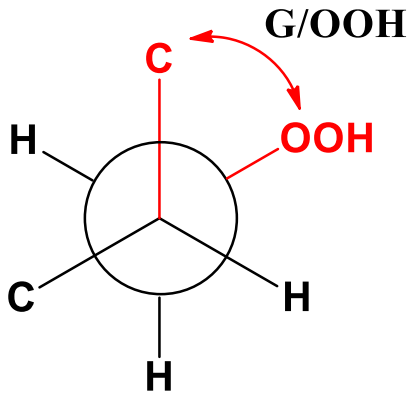
Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
AG	This work	0.70	0.30	0.15	0.10	0.03	–0.02	–0.10	–0.13	–0.05	0.05	0.03	0.02	0.00
RG1	This work	0.09	0.93	–0.11	–0.16	–0.21	–0.24	–0.28	–0.20	–0.03	0.13	0.13	0.10	0.02
RG2	This work	0.21	1.81	0.08	–0.02	–0.20	–0.51	–0.72	–0.57	–0.26	–0.15	–0.06	–0.06	0.00

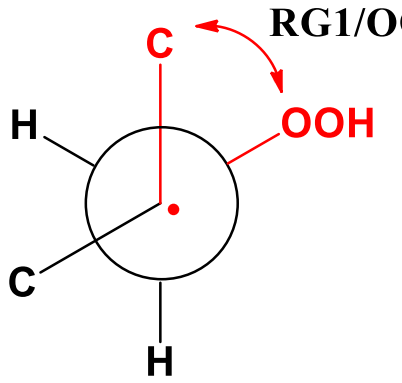


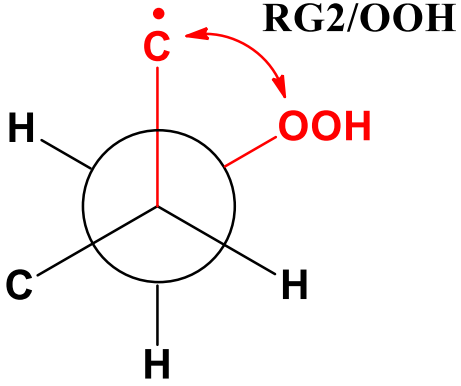


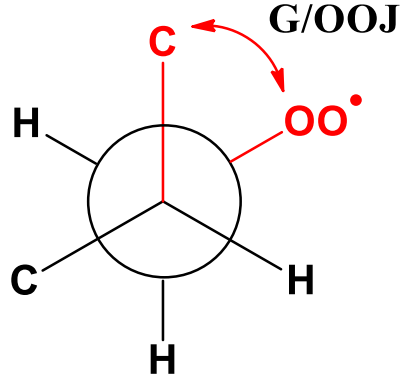


Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
G/COOH	This work	0.91	–0.64	0.72	0.67	0.65	0.64	0.63	0.61	0.57	0.50	0.37	0.20	0.10
RG1/COOH	This work	0.59	0.77	0.88	0.52	0.24	0.18	0.13	0.06	0.01	0.03	0.02	0.01	–0.04
RG2/COOH	This work	0.24	–0.62	0.41	0.05	–0.31	–0.26	–0.22	–0.20	–0.12	0.04	0.01	–0.05	–0.07

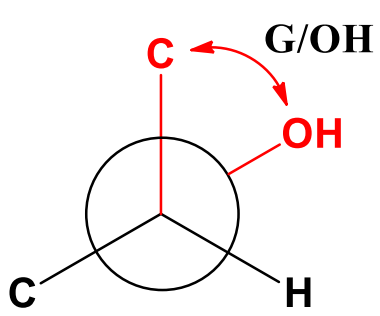


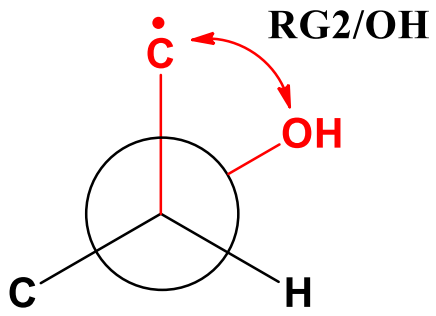


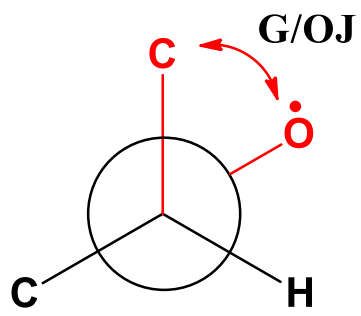




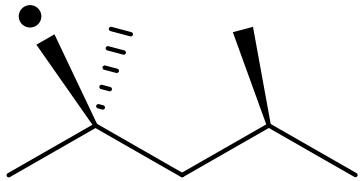
Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
G/OOH	This work	0.60	–0.36	0.74	0.55	0.38	0.25	0.07	–0.03	–0.07	–0.07	–0.07	–0.07	–0.07
RG1/OOH	This work	0.30	–0.29	–0.38	–0.25	–0.16	–0.09	–0.06	–0.04	–0.08	–0.16	–0.20	–0.23	–0.25
RG2/OOH	This work	0.45	–1.43	0.70	0.50	0.04	–0.16	0.00	0.11	0.12	0.09	–0.04	–0.04	–0.05
G/OOJ	This work	0.30	–0.60	0.42	0.45	0.52	0.21	0.14	0.16	0.10	0.05	0.02	0.02	0.00



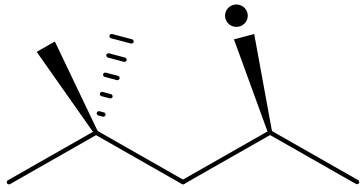




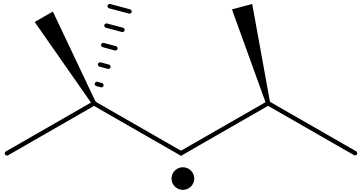
Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
G/OH	This work	–0.12	0.00	0.03	0.03	0.02	0.02	0.02	0.01	0.01	0.01	0.00	0.00	0.00
RG2/OH	This work	–0.01	–0.55	0.25	0.61	0.23	0.07	0.09	0.03	0.02	0.02	0.01	0.00	0.00
G/OJ	This work	–0.09	–0.19	0.08	0.06	0.04	0.05	0.07	0.11	0.19	0.24	0.29	0.37	0.45

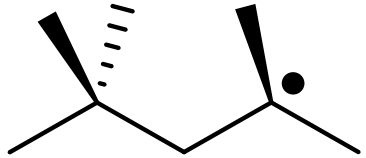


(a)



(b)



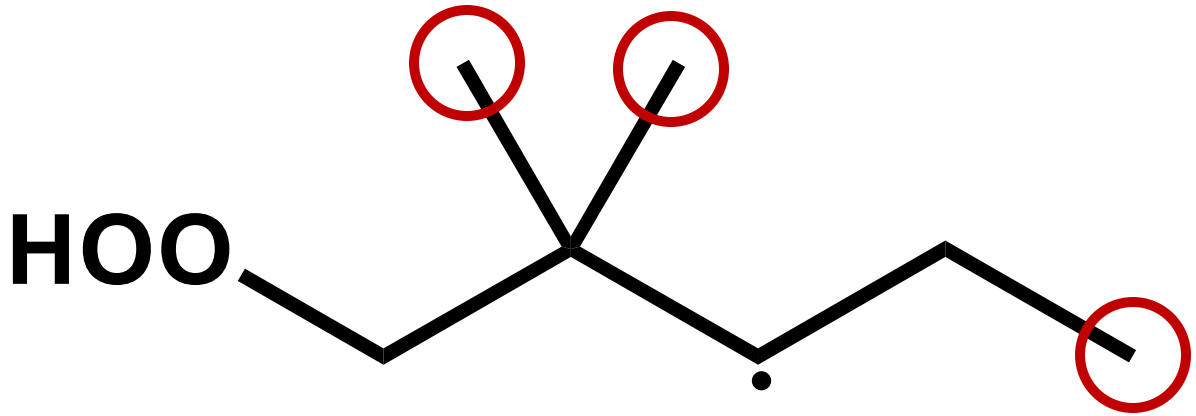


H/15/1J **H/15/2J** **H/15/3J**

Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
H/15/1J	This work	1.10	–1.00	0.74	0.87	1.03	1.19	1.44	1.45	0.90	0.48	0.18	–0.02	0.00
H/15/2J	This work	–0.23	–1.62	–0.28	0.22	0.42	0.75	1.02	1.09	0.76	0.68	0.49	0.38	0.00
H/15/3J	This work	0.02	–3.38	2.66	2.42	1.95	1.40	0.65	0.15	–0.27	–0.59	–0.49	–0.41	–0.21

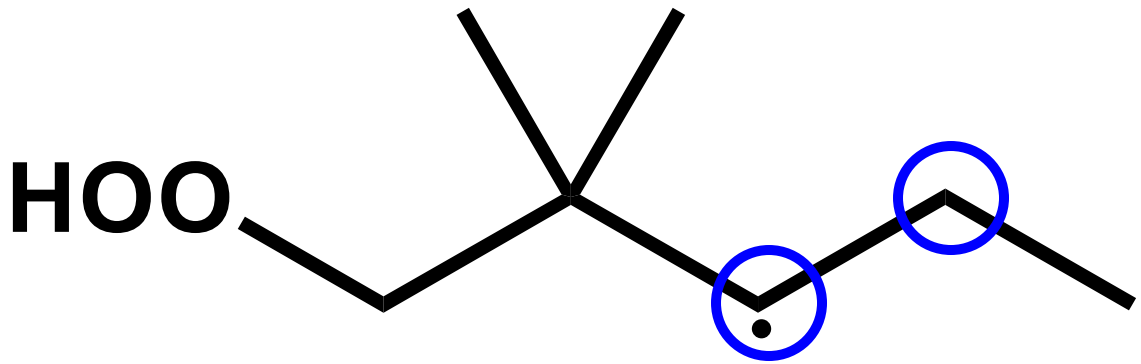
Group		H_f (kcal/mol)	S (cal/mol/K)	C_p (cal/mol/K)										
				300	400	500	600	800	1000	1500	2000	2500	3000	INF
CJCOOH	This work	103.27	3.23	–0.78	–1.20	–1.75	–2.13	–3.09	–3.83	–4.85	–5.32	–5.53	–5.70	–6.03
	Burke et al.	101.10	2.73	–0.66	–1.28	–1.86	–2.35	–3.14	–3.72	–4.65				
C2JCOOH	This work	102.73	0.68	1.39	0.17	–0.52	–1.00	–2.16	–3.21	–4.48	–5.11	–5.40	–5.67	–5.97
	Burke et al.	101.10	2.76	–0.65	–1.28	–1.88	–2.38	–3.16	–3.75	–4.67				
C3JCOOH	This work	**103.24**	**–0.65**	1.43	0.56	–0.17	–0.85	–1.04	–1.98	–3.90	–4.65	–5.24	–5.41	–5.96
	Burke et al.	**101.10**	**3.15**	–0.48	–1.24	–2.00	–2.60	–3.47	–4.04	–4.87				
CCJCOOH	This work	99.52	4.43	–0.71	–1.31	–1.91	–2.35	–3.23	–3.86	–4.69	–5.01	–5.22	–5.40	–5.78
	Burke et al.	98.45	3.07	–0.61	–1.55	–2.28	–2.81	–3.54	–4.05	–4.84				
CCCJCOOH	This work	99.83	**–2.10**	2.68	1.03	–0.07	–0.71	–1.36	–1.86	–4.21	–4.58	–4.85	–5.20	–5.78
	Burke et al.	98.45	**4.19**	0.40	–0.83	–1.79	–2.47	–3.35	–3.93	–4.79				
C2CJCOOH	This work	97.13	6.19	–0.88	–2.34	–3.37	–4.29	–5.36	–5.85	–5.96	–5.76	–5.78	–5.81	–5.49
	Burke et al.	96.30	4.59	–0.49	–2.12	–3.22	–3.88	–4.53	–4.87	–5.31				

Main Group



C/C/H3 × 3

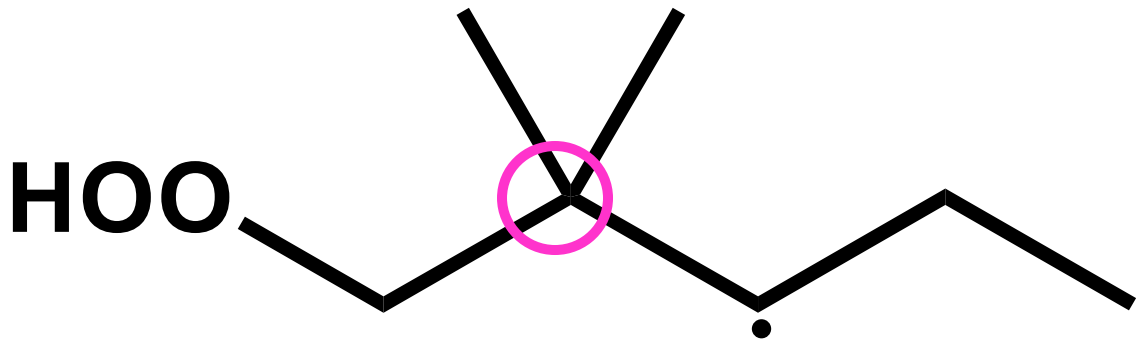
Main Group



C/C/H3 × 3

C/C2/H2 × 2

Main Group

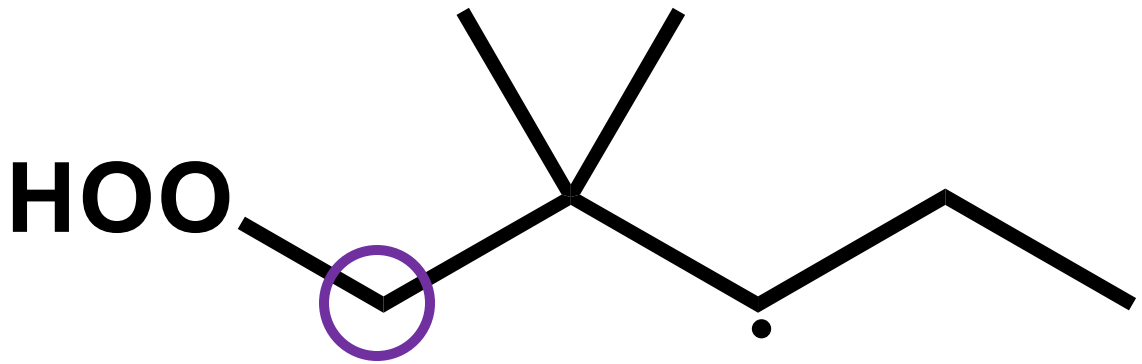


C/C/H3 × 3

C/C2/H2 × 2

C/C4 × 1

Main Group



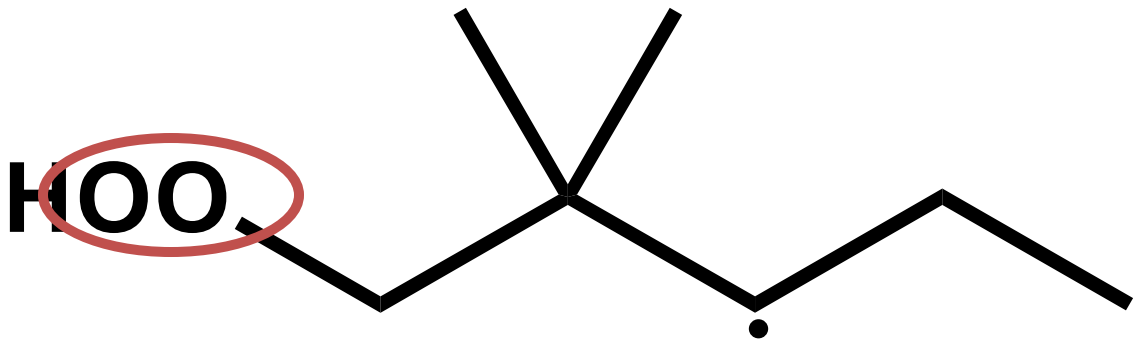
C/C/H3 × 3

C/C2/H2 × 2

C/C4 × 1

C/C/H2/OO × 1

Main Group



C/C/H3 × 3

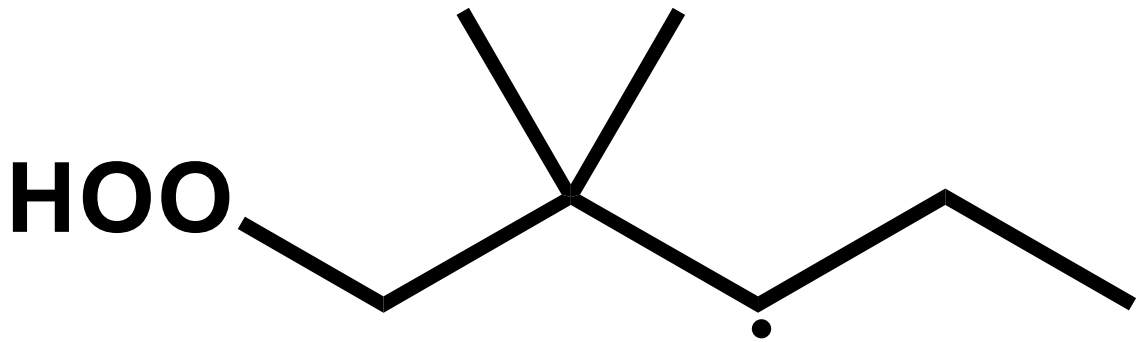
C/C2/H2 × 2

C/C4 × 1

C/C/H2/OO × 1

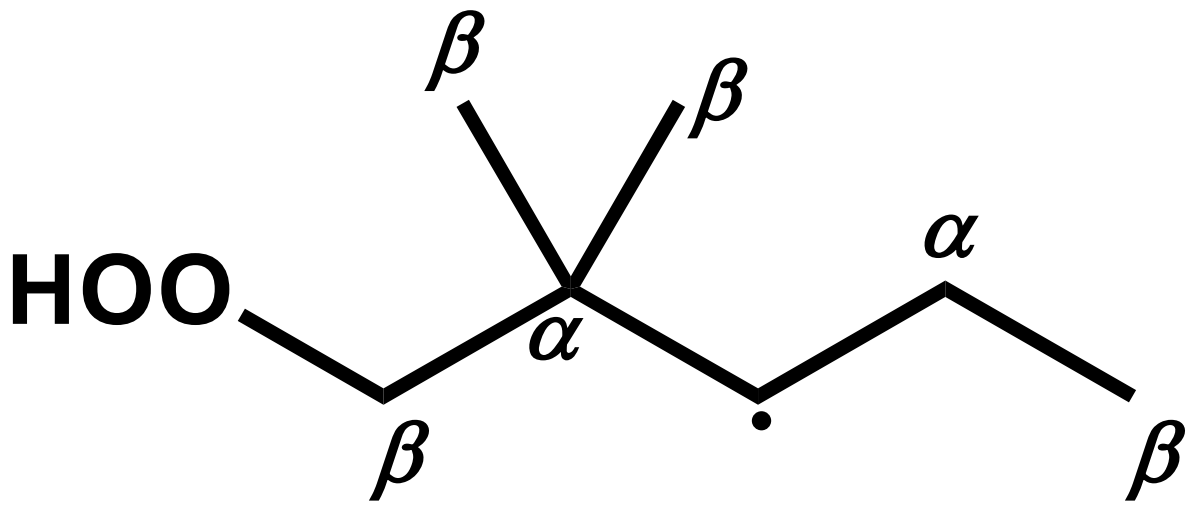
OO/CP/H × 1

BDE



S/QOOH

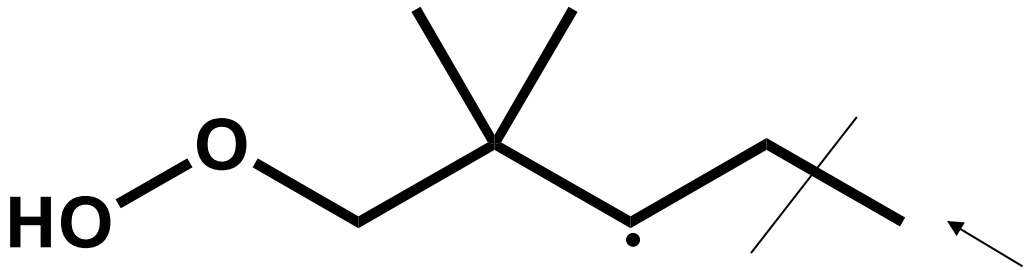
BDE

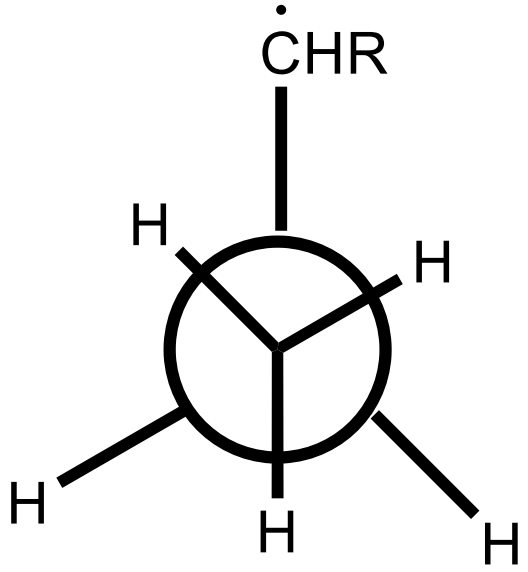


S/QOOH

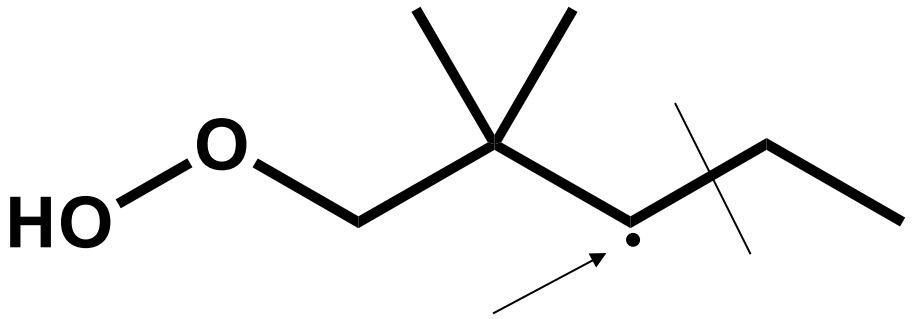
S/QOOH/C-BETA × 4

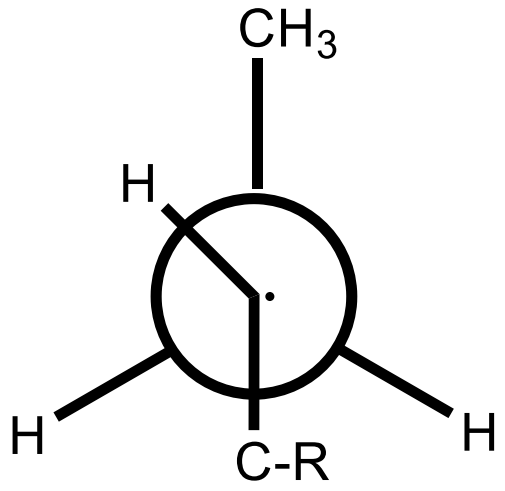
Gauche

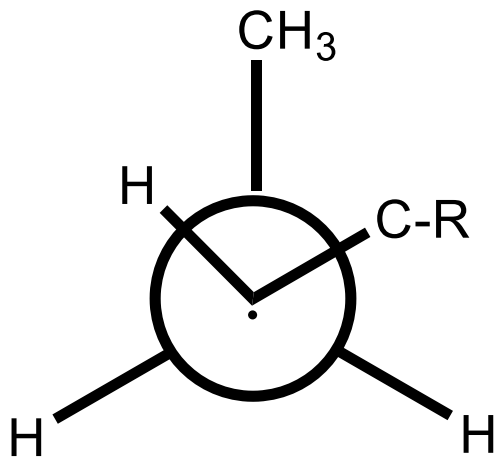




Gauche



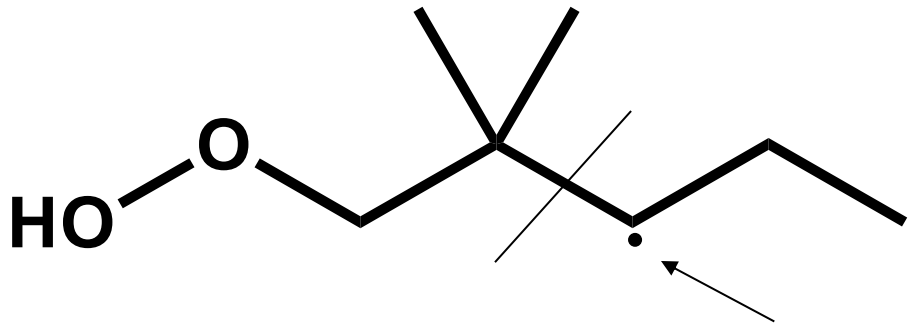


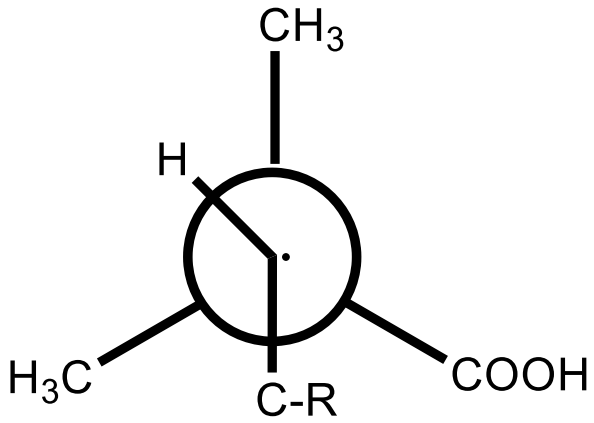


RG1 × 1

This can be avoided

Gauche

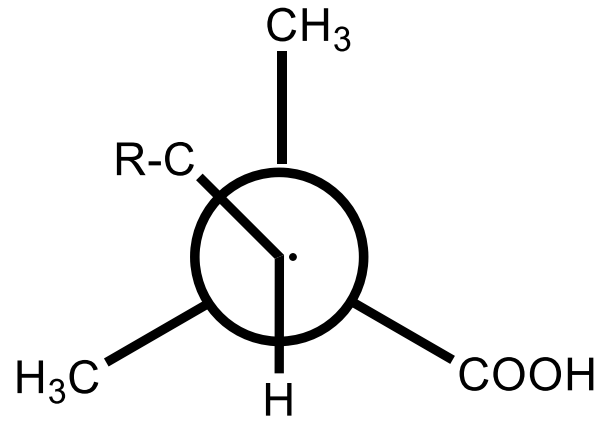




RG1 × 1 + RG1/COOH × 1

= 0.82 × 1 + 1.21 × 1

= 1.93



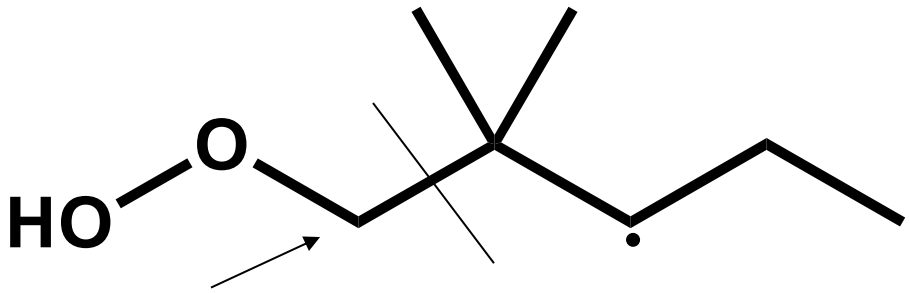
RG1 × 2

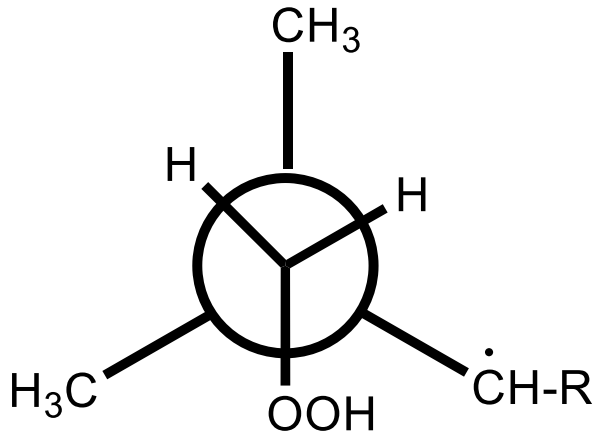
= 0.82 × 2

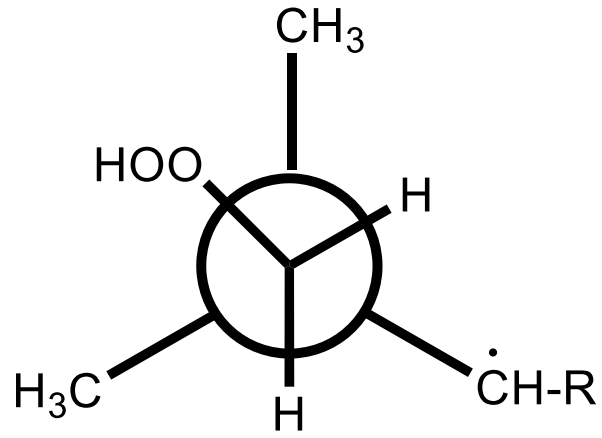
=1.64

Select the lower energy structure

Gauche







RG2/OOH × 1+ G/OOH × 1

= 0.8 × 1 + 0.65 × 1

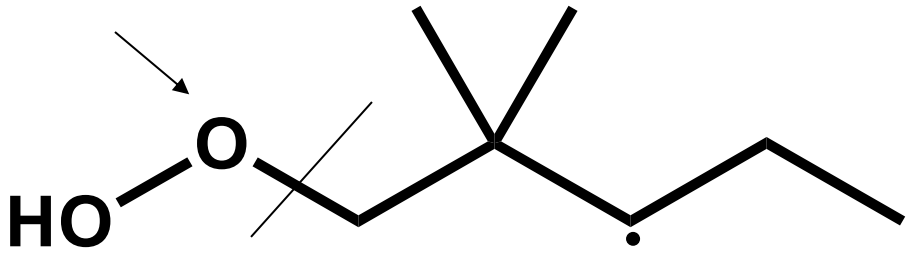
= 1.45

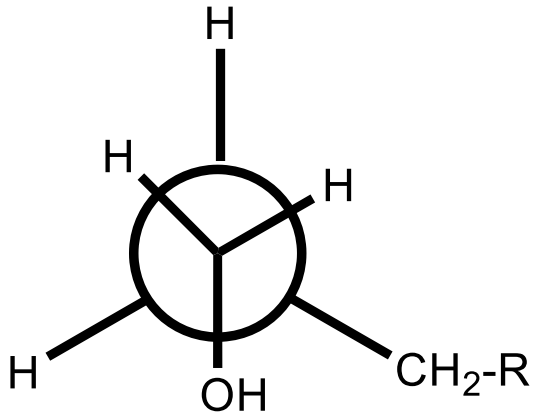
G/OOH × 2

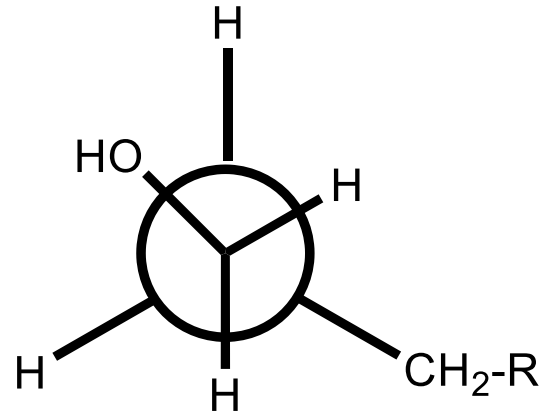
= 0.65 × 2

= 1.3

Gauche

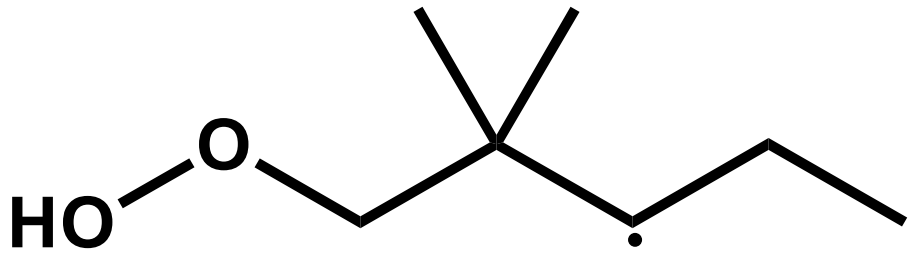






G/OH × 1 = -0.21

ALL



C/C/H3 × 3

C/C2/H2 × 2

C/C4 × 1

C/C/H2/OO × 1

OO/CP/H × 1

S/QOOH

S/QOOH/C-BETA × 4

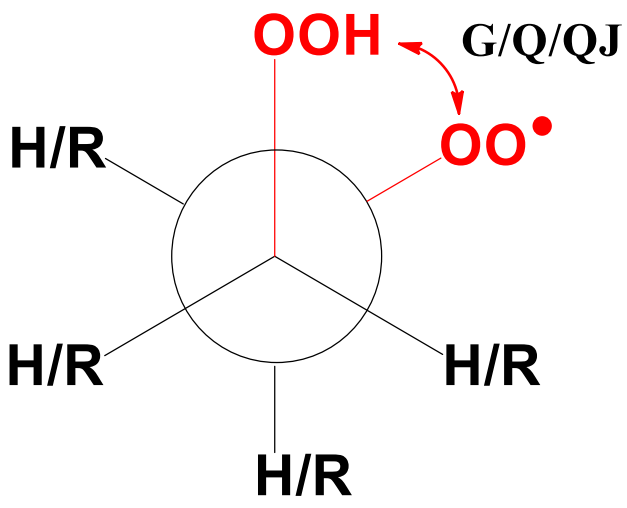
G/OOH × 2

AG × 2

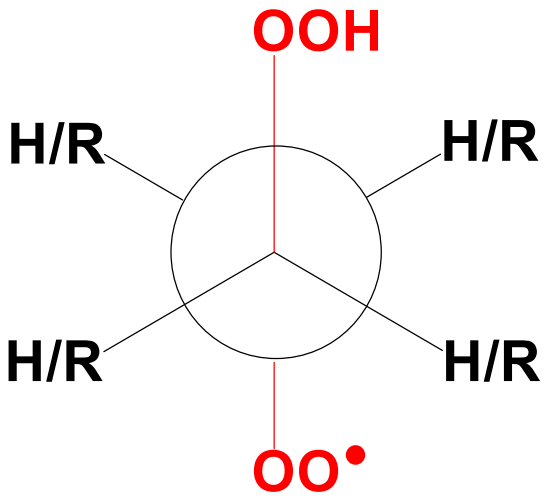
G/OH × 1

OI × 1

New groups only for O2QOOH

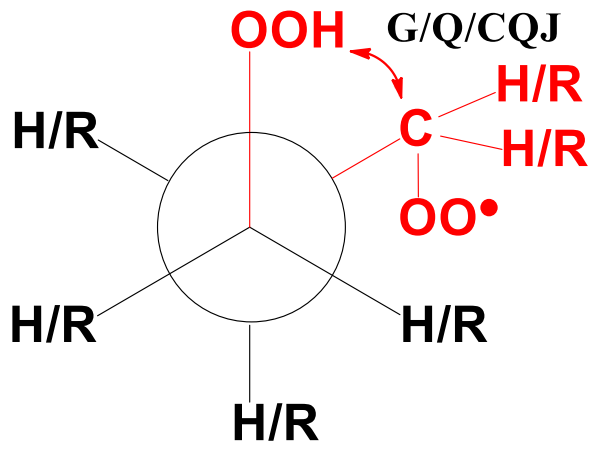


G/Q/QJ

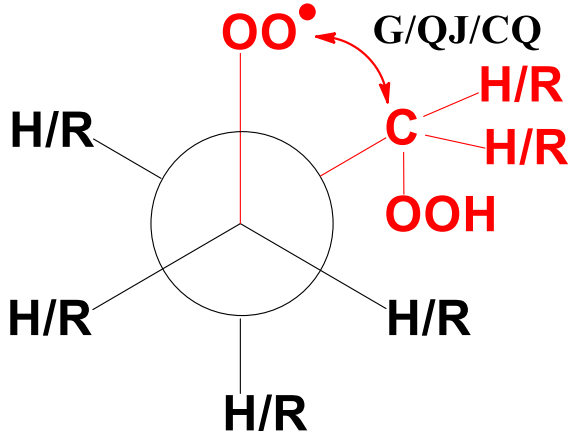


TRANS/Q/QJ

New groups only for O2QOOH

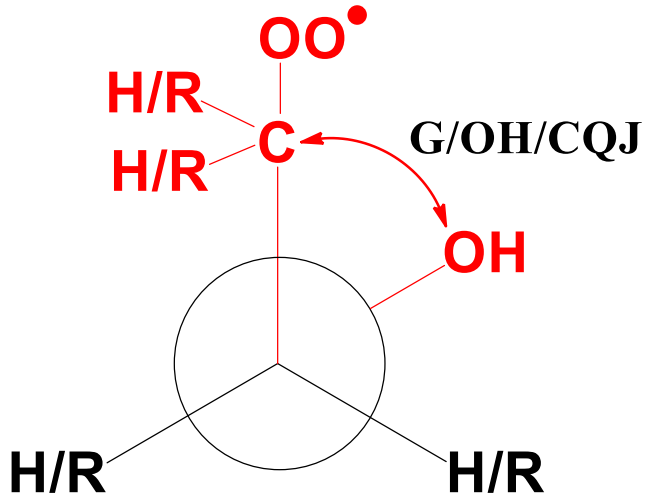


G/Q/CQJ

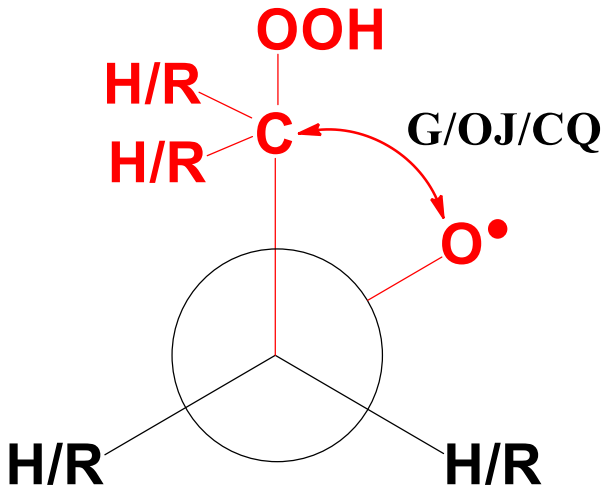


G/CQ/QJ

New groups only for O2QOOH

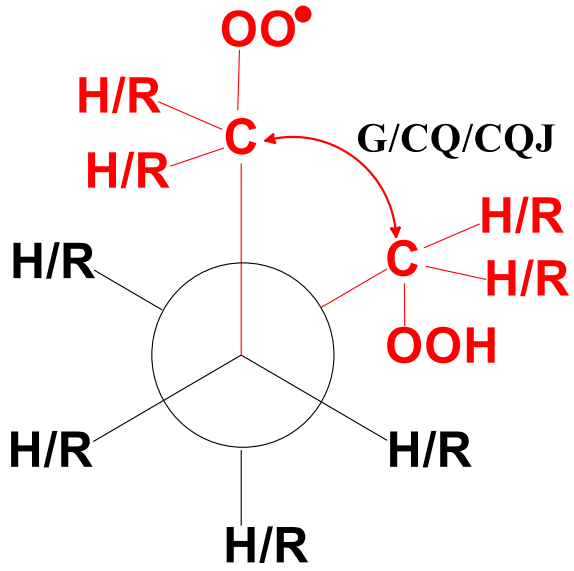


GO/OH/CQJ



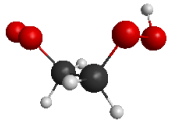
GO/OJ/CQ

New groups only for O2QOOH

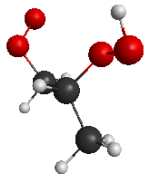


C2 – C5
Rules:
OOJ – 1° (gauche)
OOJ – 2° and 3° (trans)

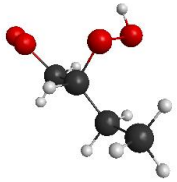
Gauche orientation (OOJ at 1° position)



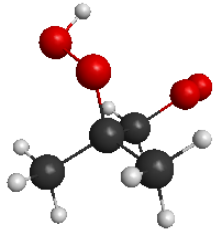
C2H4O2H-2O2



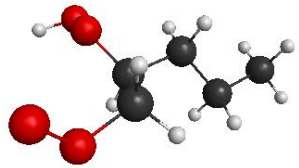
IC3H6O2H-1O2



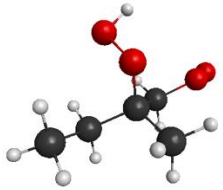
NBT2O2H-1O2



IBT2O2H-1O1

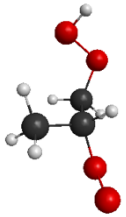


NPT2O2H-1O2

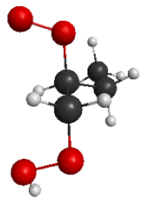


IPT2O2H-1O2

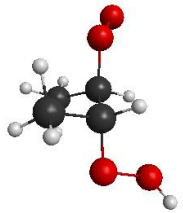
Trans orientation (OOJ at 2°/3° position)



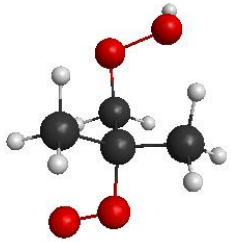
NC3H6O2H-2O2



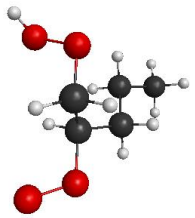
NBT1O2H-2O2



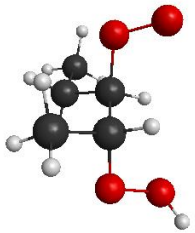
NBT2O2H-3O2



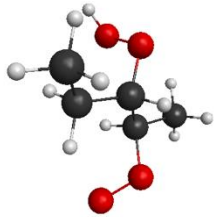
IBT1O2H-2O2



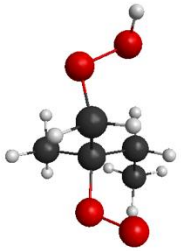
NPT1O2H-2O2



NPT2O2H-3O2



NPR3O2H-2O2



IPT1O2H-2O2