Decomposition of β-hydroxypropoxy Radicals in the OH-initiated Oxidation of Propene: A Theoretical and Experimental Study

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SUPPORTING INFORMATION

A. Geometries

The rotamers for the β-hydroxy-propoxy radicals and the transition states for dissociation can be paired (by inverting the sign of all dihedral angles) in enantiomers with the same energy, rotational constants, vibrational wavenumbers, etc. As such, the tabulated material below only distinguishes between the enantiomers when listing the dihedral angles; all other characteristics are only listed once. The names of the structures are derived from the dihedral angles OCCO, and HOCC, and the chiral orientation of the central carbon :

OCCO HOCC chiral

X X X

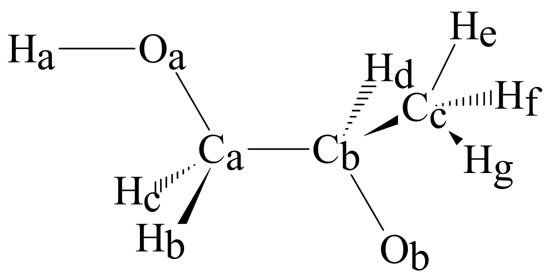
where X can have the following code :

'p' : for angles close to +60° (**p**lus)
'm' : for angles close to -60° (**m**inus)
't' : for angles close to 180° (**t**rans)
'S' : for left-turning orientation of the chiral carbon
'R' : for right-turning orientation of the chiral carbon

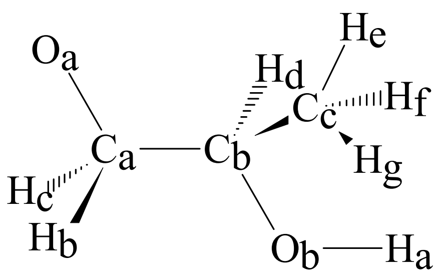
Note that chiral 'left'- and 'right'-turning orientation are based on the relative importance of the substituents, and not on the rotation of the orientation of polarised light.

The geometric parameters are given in Ångstroms for the bond lengths, and degrees for bond angles and dihedral angles.

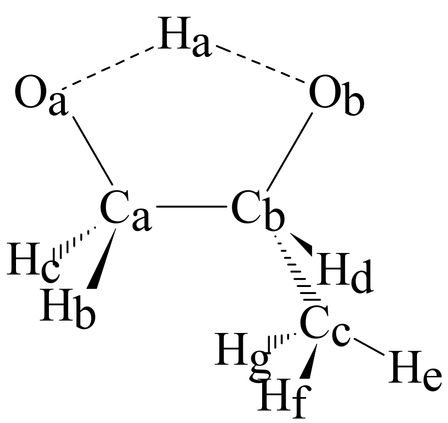
For the oxy radicals formed in the major channel ($HOCH_2CH(O)CH_3$), the following labelling of atoms is used:



For the oxy radicals formed in the minor channel ($OCH_2CH(OH)CH_3$), the following labelling of atoms was used :



The geometric parameters for the transition state of the 1,4-hydrogen shift (isomerisation reaction $HOCH_2CH(O)CH_3 \leftrightarrow HOCH_2CH(O)CH_3$) are given using the following labelling :



The threedimensional representations were created using Rasmol 2.5.1. The structures are sorted by increasing relative energy.

1. β-hydroxypropoxy radicals formed in the major OH-addition channel ($HOCH_2CH(O)CH_3$)

Structure	C_a-C_b	C_a-O_a	C_b-O_b	O_a-H_a	C_a-H_b	C_a-H_c	C_b-H_d	C_b-C_c
mpR / pmS	1.5526	1.4050	1.3722	0.9705	1.1035	1.0948	1.1138	1.5311
pmR / mpS	1.5467	1.4102	1.3729	0.9702	1.1020	1.0954	1.1050	1.5588
ttR / ttS	1.5373	1.4208	1.3708	0.9646	1.0997	1.1019	1.1140	1.5382
tpR / tmS	1.5492	1.4181	1.3650	0.9659	1.0991	1.0940	1.1096	1.5543
tmR / tpS	1.5516	1.4161	1.3678	0.9650	1.0996	1.0938	1.1056	1.5526
ppR / mmS	1.5903	1.3997	1.3563	0.9654	1.1008	1.0916	1.1089	1.5356
mmR / ppS	1.5847	1.3980	1.3555	0.9661	1.1016	1.0927	1.1103	1.5367
ptR / mtS	1.5368	1.4190	1.3754	0.9645	1.1030	1.0997	1.1135	1.5387
mtR / ptS	1.5372	1.4153	1.3719	0.9642	1.1026	1.1008	1.1125	1.5393

Structure	O_a-C_a-C_b	O_b-C_b-C_a	H_a-O_a-C_a	H_b-C_a-C_b	H_c-C_a-C_b	H_d-C_b-C_a	C_c-C_b-C_a
mpR / pmS	110.54	109.77	105.19	107.98	110.15	105.32	114.82
pmR / mpS	110.71	109.94	105.21	108.41	110.28	111.22	110.93
ttR / ttS	107.85	111.78	108.43	108.11	108.78	106.63	113.82
tpR / tmS	111.95	111.64	108.12	109.06	108.95	109.45	110.08
tmR / tpS	112.41	110.76	108.39	108.59	108.50	109.25	110.75
ppR / mmS	114.77	106.29	108.67	105.33	108.00	103.22	111.07
mmR / ppS	114.73	106.21	108.71	105.26	108.13	105.15	109.35
ptR / mtS	107.77	112.57	108.37	109.39	107.84	106.34	113.71
mtR / ptS	107.83	112.55	108.61	109.26	108.16	106.21	113.43

Structure	C_c-H_e	C_c-H_f	C_c-H_g	C_b-C_c-H_e	C_b-C_c-H_f	C_b-C_c-H_g
mpR / pmS	1.0948	1.0946	1.0928	110.99	110.29	110.29
pmR / mpS	1.0938	1.0914	1.0907	108.02	110.66	109.24
ttR / ttS	1.0921	1.0950	1.0925	109.98	109.77	110.24
tpR / tmS	1.0930	1.0930	1.0914	107.17	109.89	110.73
tmR / tpS	1.0944	1.0916	1.0937	108.24	110.52	110.40
ppR / mmS	1.0967	1.0937	1.0931	111.43	110.02	109.97
mmR / ppS	1.0956	1.0931	1.0945	111.27	109.82	110.42
ptR / mtS	1.0946	1.0916	1.0924	110.84	109.51	109.83
mtR / ptS	1.0942	1.0922	1.0951	111.30	109.72	110.31

Structure	O_a-C_a-C_b-O_b	H_a-O_a-C_a-C_b	H_b-C_a-C_b-O_a	H_c-C_a-C_b-O_a	H_d-C_b-C_a-O_b	C_c-C_b-C_a-O_b
mpR	-48.07	43.24	123.14	-119.44	109.73	-129.68
pmS	48.07	-43.24	-123.14	119.44	-109.73	129.68
pmR	51.91	-46.66	-122.93	119.29	123.90	-116.04
mpS	-51.91	46.66	122.93	-119.29	-123.90	116.04
ttR	-170.26	-175.61	121.61	-121.50	112.54	-129.28
ttS	170.26	175.61	-121.61	121.50	-112.54	129.28
tpR	-178.83	72.50	124.31	-118.22	124.60	-117.77
tmS	178.83	-72.50	-124.31	118.22	-124.60	117.77
tmR	-177.26	-78.93	-125.63	117.37	124.56	-117.17
tpS	177.26	78.93	125.63	-117.37	-124.56	117.17
ppR	72.21	70.79	124.25	-119.54	117.63	-123.79
mmS	-72.21	-70.79	-124.25	119.54	-117.63	123.79
mmR	-66.06	-63.47	-124.53	119.43	118.81	-122.56
ppS	66.06	63.47	124.53	-119.43	-118.81	122.56
ptR	74.44	176.54	121.45	-120.95	111.61	-129.53
mtS	-74.44	176.54	-121.45	120.95	-111.61	129.53
mtR	-66.87	161.58	-121.52	121.49	112.22	-128.86
ptS	66.87	-161.58	121.52	-121.49	-112.22	128.86

Structure	H_e-C_c-C_b-O_b	H_f-C_c-C_b-O_b	H_g-C_c-C_b-O_b
mpR	174.49	-65.56	53.90
pmS	-174.49	65.56	-53.90
pmR	173.19	53.58	-67.75
mpS	-173.19	-53.58	67.75
ttR	176.84	-63.80	55.68
ttS	-176.84	63.80	-55.68
tpR	-174.79	-55.90	64.96
tmS	174.79	55.90	-64.96
tmR	178.63	59.79	-60.90
tpS	-178.63	-59.79	60.90
ppR	-178.16	-56.26	62.24
mmS	178.16	56.26	-62.24
mmR	178.42	58.62	-60.36
ppS	-178.42	-58.62	60.36
ptR	172.29	-68.27	51.63
mtS	-172.29	68.27	-51.63
mtR	170.99	50.26	-68.79
ptS	-170.99	-50.26	68.79

2. Transition states for dissociation of ($HOCH_2CH(O)CH_3$) radicals; the products formed

Structure	C_a-C_b	C_a-O_a	C_b-O_b	O_a-H_a	C_a-H_b	C_a-H_c	C_b-H_d	C_b-C_c
TS_mpR / TS_pmS	2.0732	1.3471	1.2565	0.9785	1.0919	1.0886	1.1101	1.5178
TS_pmR / TS_mpS	2.0770	1.3503	1.2558	0.9745	1.0903	1.0880	1.1112	1.5231
TS_tpR / TS_tmS	2.1320	1.3609	1.2446	0.9668	1.0849	1.0883	1.1156	1.5209
TS_tmR / TS_tpS	2.1369	1.3603	1.2452	0.9666	1.0844	1.0887	1.1116	1.5230
TS_ppR / TS_mmS	2.1310	1.3571	1.2446	0.9667	1.0920	1.0841	1.1136	1.5262
TS_mmR / TS_ppS	2.1337	1.3536	1.2423	0.9667	1.0921	1.0854	1.1161	1.5253
$H_2COH\cdots OCHCH_3$	4.1704	1.3643	1.2185	0.9777	1.0884	1.0846	1.1101	1.5007

Structure	O_a-C_a-C_b	O_b-C_b-C_a	H_a-O_a-C_a	H_b-C_a-C_b	H_c-C_a-C_b	H_d-C_b-C_a	C_c-C_b-C_a
TS_mpR / TS_pmS	100.52	97.21	106.11	94.51	110.36	88.98	105.29
TS_pmR / TS_mpS	102.49	96.80	106.70	94.88	108.82	94.35	101.38
TS_tpR / TS_tmS	111.44	100.81	109.61	98.06	97.05	89.26	100.20
TS_tmR / TS_tpS	112.41	100.18	109.51	97.44	96.63	89.81	100.39
TS_ppR / TS_mmS	111.21	103.20	109.70	98.66	97.77	89.16	99.34
TS_mmR / TS_ppS	110.17	103.18	110.00	98.40	99.01	89.07	99.06
$H_2COH\cdots OCHCH_3$	48.46	50.21	87.38	152.53	156.87	78.41	109.13

Structure	C_c-H_e	C_c-H_f	C_c-H_g	C_b-C_c-H_e	C_b-C_c-H_f	C_b-C_c-H_g
TS_mpR / TS_pmS	1.0949	1.0933	1.0974	111.98	110.40	108.87
TS_pmR / TS_mpS	1.0941	1.0969	1.0926	112.09	108.22	110.34
TS_tpR / TS_tmS	1.0939	1.0977	1.0933	111.71	108.60	110.12
TS_tmR / TS_tpS	1.0950	1.0941	1.0972	111.89	110.52	108.57
TS_ppR / TS_mmS	1.0963	1.0932	1.0964	112.52	110.06	108.46
TS_mmR / TS_ppS	1.0950	1.0971	1.0933	112.74	108.31	110.31
$H_2COH\cdots OCHCH_3$	1.0911	1.0972	1.0973	111.10	109.25	109.20

Structure	O_a-C_a-C_b-O_b	H_a-O_a-C_a-C_b	H_b-C_a-C_b-O_a	H_c-C_a-C_b-O_a	H_d-C_b-C_a-O_b	C_c-C_b-C_a-O_b
TS_mpR	-47.82	43.56	119.77	-119.61	119.38	-125.43
TS_pmS	47.82	-43.56	-119.77	119.61	-119.38	125.43
TS_pmR	51.34	-49.64	-119.84	119.45	120.44	-123.61
TS_mpS	-51.34	49.64	119.84	-119.45	-120.44	123.61
TS_tpR	-176.75	80.45	-117.55	123.79	120.16	-126.03
TS_tmS	176.75	-80.45	117.55	-123.79	-120.16	126.03
TS_tmR	174.11	-82.36	117.79	-123.83	120.68	-125.24
TS_tpS	-174.11	82.36	-117.79	123.83	-120.68	125.24
TS_ppR	81.93	78.29	123.65	-117.22	120.42	-125.15
TS_mmS	-81.93	-78.29	-123.65	117.22	-120.42	125.15
TS_mmR	-53.62	-75.03	-123.57	117.18	120.34	-125.67
TS_ppS	53.62	75.03	123.57	-117.18	-120.34	125.67
$H_2COH\cdots OCHCH_3$	-83.63	30.95	132.77	-57.41	-70.17	159.28

Structure	H_e-C_c-C_b-O_b	H_f-C_c-C_b-O_b	H_g-C_c-C_b-O_b
TS_mpR	-159.84	-36.87	81.26
TS_pmS	159.84	36.87	-81.26
TS_pmR	-168.99	71.92	-46.22
TS_mpS	168.99	-71.92	46.22
TS_tpR	-155.13	85.78	-32.35
TS_tmS	155.13	-85.78	32.35
TS_tmR	-160.35	-36.54	81.35
TS_tpS	160.35	36.54	-81.35
TS_ppR	-166.75	-43.17	74.49
TS_mmS	166.75	43.17	-74.49
TS_mmR	-162.10	78.99	-38.67
TS_ppS	162.10	-78.99	38.67
$H_2COH\cdots OCHCH_3$	0.46	-237.57	-121.59

$H_2COH\cdots OCHCH_3 \rightarrow H_a\cdots O_b = 1.8522$ Å

Dissociation fragments at infinite distance :

$CH_2OH \rightarrow$	C_a-O_a = 1.3684	$CH(O)CH_3$ (C_s symm.) $\rightarrow$	C_b-O_b = 1.2106
	C_a-H_b = 1.0834		C_b-H_d = 1.1146
	C_a-H_c = 1.0879		C_b-C_c = 1.5077
	O_a-H_a = 0.9652		C_c-H_e = 1.0914
	H_a-C_a-O_a = 112.97		C_c-$H_{f/g}$ = 1.0970
	H_c-C_a-O_a = 118.82		H_d-C_b-O_b = 120.60
	H_c-C_a-O_a-H_a = 148.45		C_c-C_b-O_b = 124.66
	H_a-O_a-C_a-H_b = -176.00		H_e-C_c-O_b = 110.51
			$H_{f/g}$-C_c-C_b = 109.76
			$H_{f/g}$-C_c-C_b-O_b = ±121.65

3. Rotational constants for the $HOCH_2CH(O)CH_3$ radicals

Structure	A (GHz)	B (GHz)	C (GHz)
mpR / pmS	9.13749	3.65098	2.81615
pmR / mpS	7.15458	4.1867	3.53446
ttR / ttS	8.11397	3.75319	2.80438
tpR / tmS	8.42186	3.66905	2.8317
tmR / tpS	8.40591	3.68401	2.81333
ppR / mmS	8.92385	3.50919	2.78704
mmR / ppS	6.95503	4.1372	3.28692
ptR / mtS	8.85536	3.54344	2.77758
mtR / ptS	6.99873	4.11752	3.30309
TS_mpR / TS_pmS	8.83847	3.34101	2.63714
TS_pmR / TS_mpS	7.00394	3.74933	3.12959
TS_tpR / TS_tmS	7.69807	3.15344	2.46241
TS_tmR / TS_tpS	7.69836	3.20154	2.45847
TS_ppR / TS_mmS	7.03488	3.40952	2.75593
TS_mmR / TS_ppS	8.25550	3.04434	2.42570
$CH_3CHO\cdots HOCH_2$	8.45325	2.17807	1.88641

4. Geometric parameters for the most stable β-hydroxypropoxy radical rotamer formed in the minor OH-addition channel ($OCH_2CH(OH)CH_3$), and its dissociation transition state

Structure	C_a-C_b	C_a-O_a	C_b-O_b	O_a-H_a	C_a-H_b	C_a-H_c	C_b-H_d	C_b-C_c
pmR	1.5479	1.3675	1.4129	0.975	1.1127	1.1046	1.1044	1.5210
TS_pmR	2.1444	1.2473	1.3501	0.9788	1.1078	1.1079	1.0928	1.4918

Structure	O_a-C_a-C_b	O_b-C_b-C_a	H_a-O_a-C_a	H_b-C_a-C_b	H_c-C_a-C_b	H_d-C_b-C_a	C_c-C_b-C_a
pmR	112.23	108.83	105.63	107.20	113.35	106.96	112.34
TS_pmR	98.66	97.64	-40.78	-121.80	123.70	-116.93	121.56

Structure	C_c-H_e	C_c-H_f	C_c-H_g	C_b-C_c-H_e	C_b-C_c-H_f	C_b-C_c-H_g
pmR	1.0951	1.0949	1.0931	111.07	110.35	110.08
TS_pmR	1.0938	1.0939	1.0998	110.69	110.69	110.71

Structure	O_a-C_a-C_b-O_b	H_a-O_a-C_a-C_b	H_b-C_a-C_b-O_a	H_c-C_a-C_b-O_a	H_d-C_b-C_a-O_b	C_c-C_b-C_a-O_b
pmR	47.70	-41.90	-113.83	129.10	-119.52	120.58
TS_pmR	46.15	-40.78	-121.80	123.70	-116.93	121.56

Structure	H_e-C_c-C_b-O_b	H_f-C_c-C_b-O_b	H_g-C_c-C_b-O_b
pmR	179.94	59.08	-60.12
TS_pmR	170.154	48.61	-70.49

Structure	A (GHz)	B (GHz)	C (GHz)
pmR	8.77896	3.80403	2.88411
TS_pmR	8.69651	3.26987	2.58229

5. Geometric parameters for the transition state for 1,4-hydrogen shift in the β-hydroxypropoxy radicals : $HOCH_2CH(O)CH_3 \leftrightarrow OCH_2CH(OH)CH_3$

C_a-C_b	C_a-O_a	C_b-O_b	O_a-H_a	O_b-H_a	C_a-H_b	C_a-H_c	C_b-H_d	C_b-C_c
1.5845	1.3713	1.3757	1.2065	1.2083	1.1085	1.1000	1.1104	1.5246

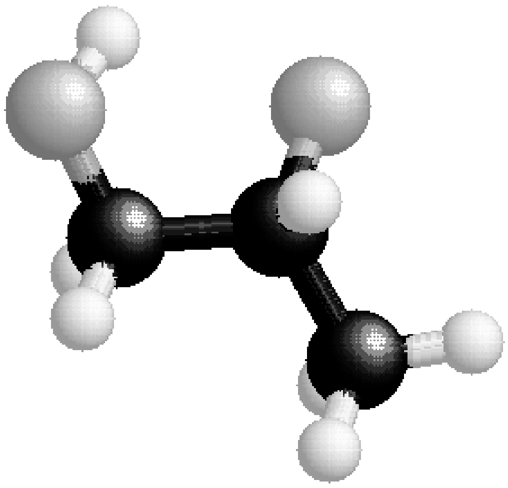
O_a-C_a-C_b	O_b-C_b-C_a	H_a-O_a-C_a	H_a-O_b-C_b	H_b-C_a-C_b	H_c-C_a-C_b	H_d-C_b-C_a	C_c-C_b-C_a
104.48	103.33	93.21	93.83	106.87	114.87	104.92	116.55

C_c-H_e	C_c-H_f	C_c-H_g	C_b-C_c-H_e	C_b-C_c-H_f	C_b-C_c-H_g
1.0956	1.0942	1.0930	110.52	110.25	110.57

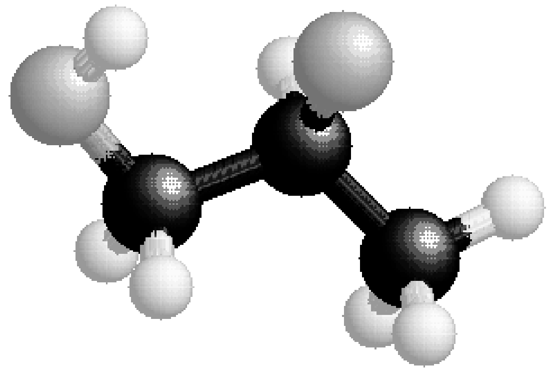
O_a-C_a-C_b-O_b	H_a-O_a-C_a-C_b	H_a-O_b-C_b-C_a	H_b-C_a-C_b-O_a	H_c-C_a-C_b-O_a	H_d-C_b-C_a-O_b	C_c-C_b-C_a-O_b
-18.24	13.28	12.65	117.72	-123.71	114.40	-124.85

H_e-C_c-C_b-O_b	H_f-C_c-C_b-O_b	H_g-C_c-C_b-O_b
-177.92	-57.70	61.98

A (GHz)	B (GHz)	C (GHz)
9.47881	3.98735	3.07830



mpR



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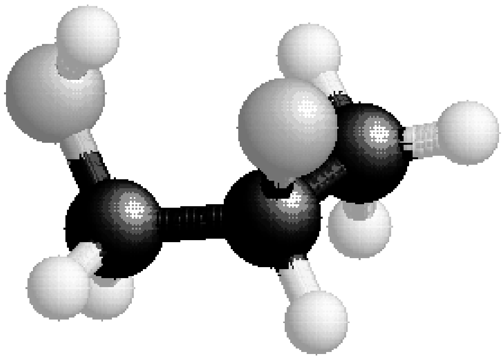

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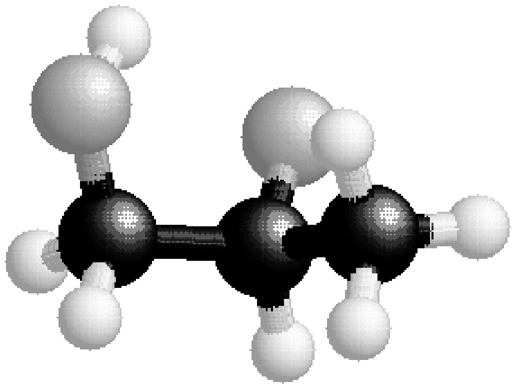

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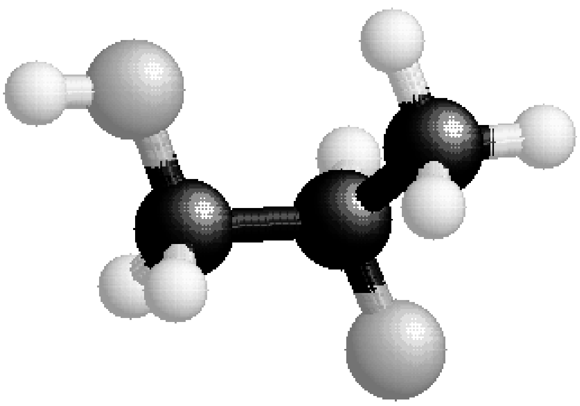
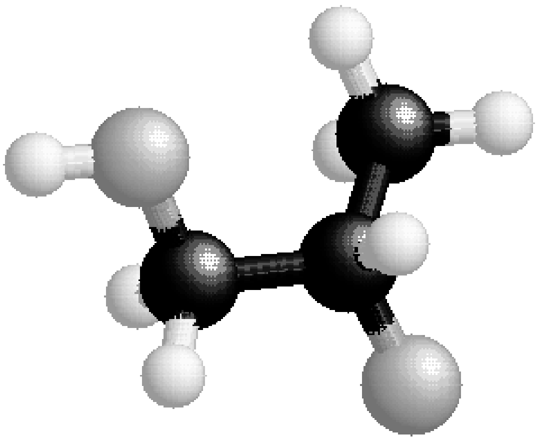
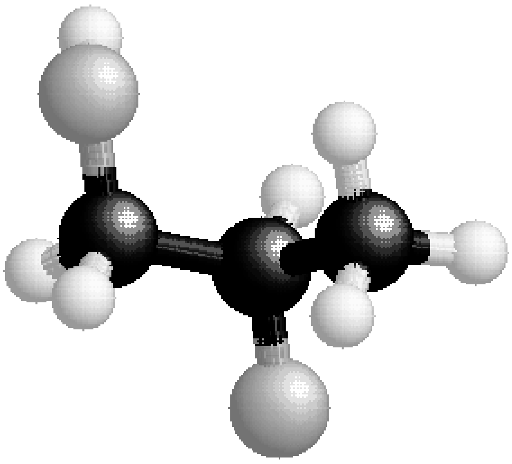


ttR



ttS



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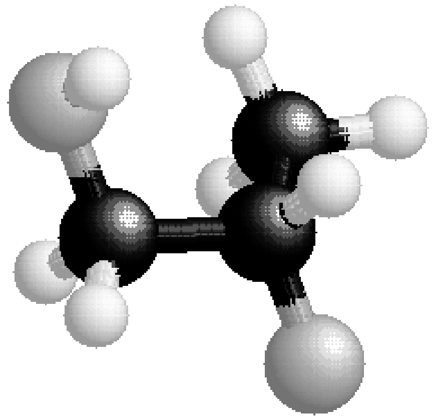

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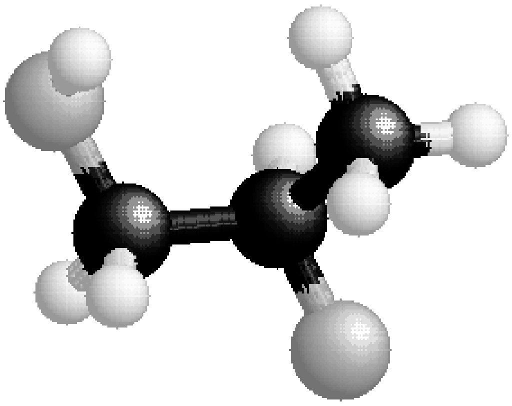

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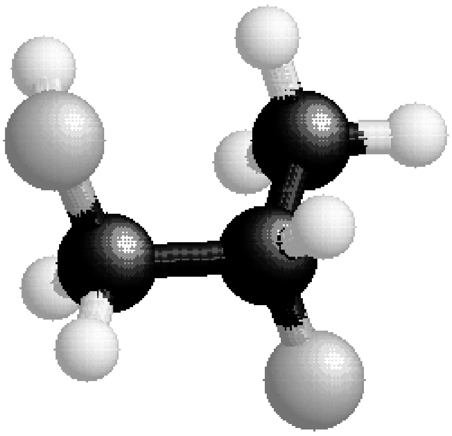

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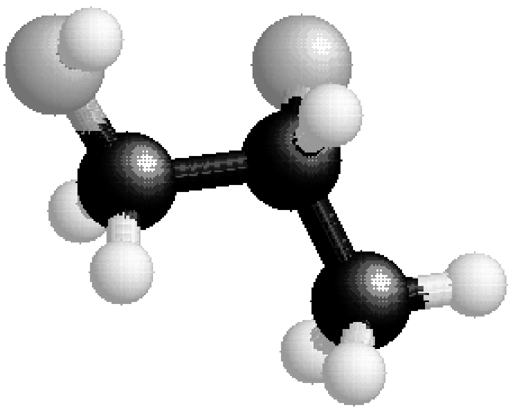

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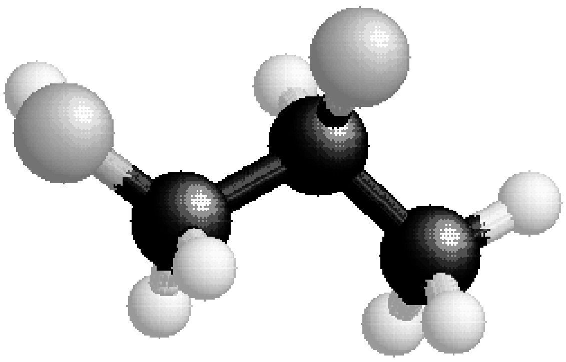

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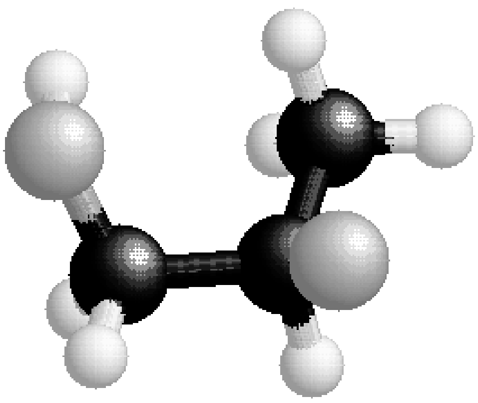

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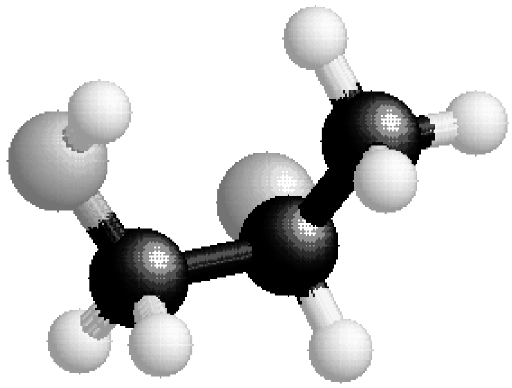

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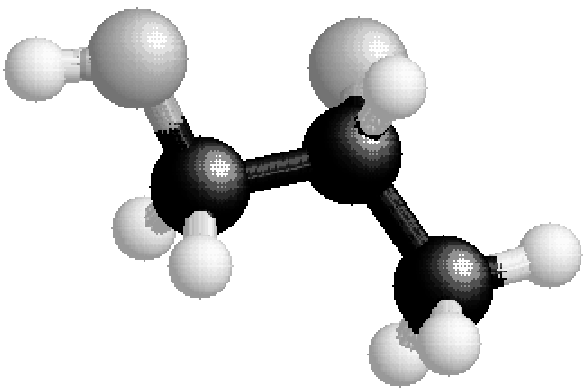

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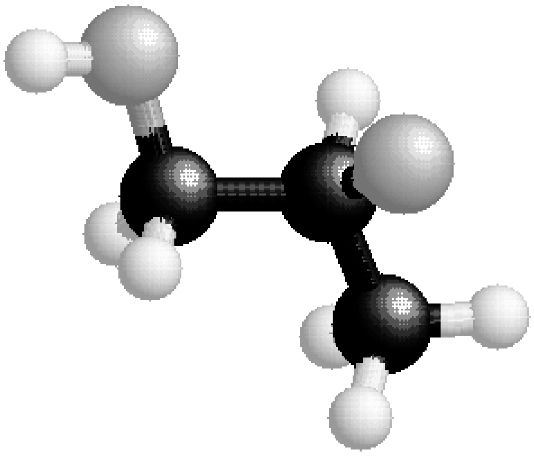

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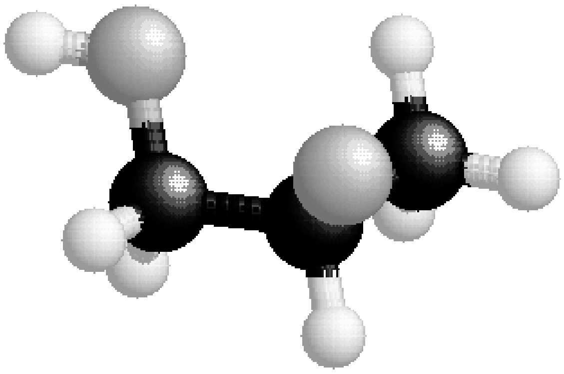

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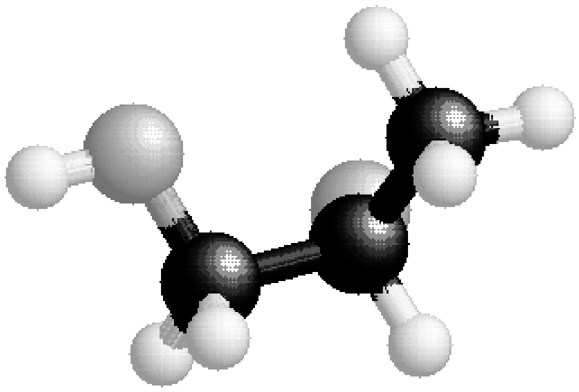
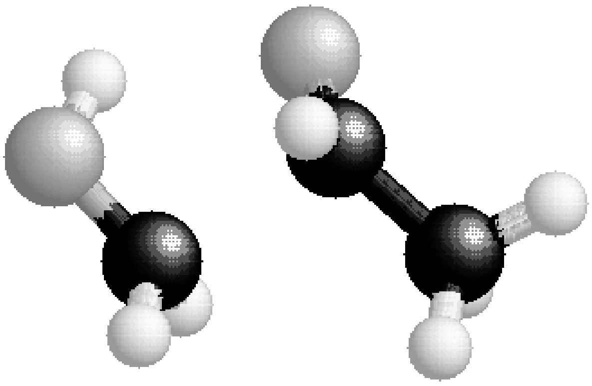
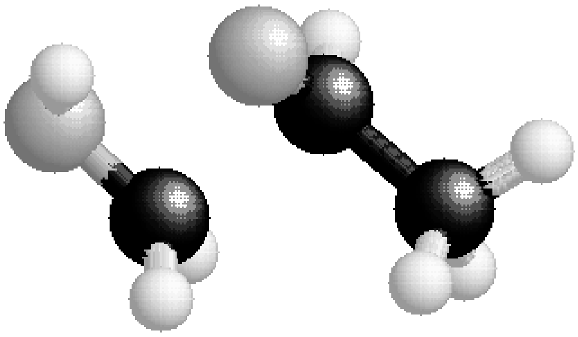


ptS



TS_mpR



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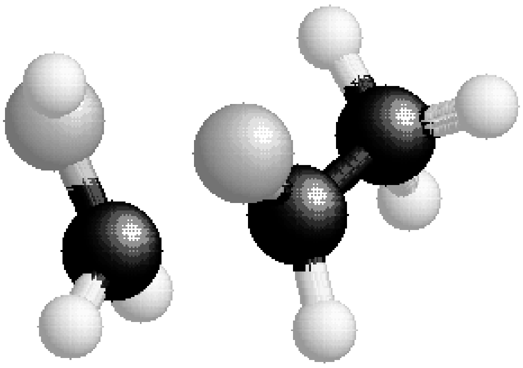

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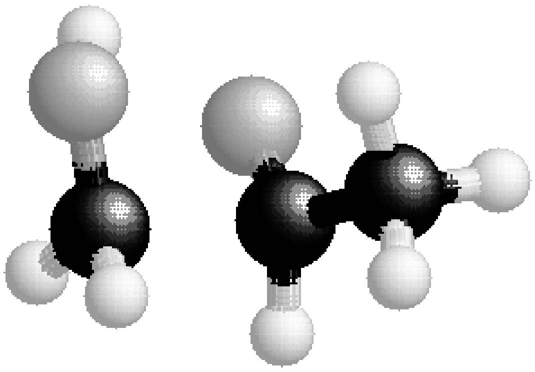

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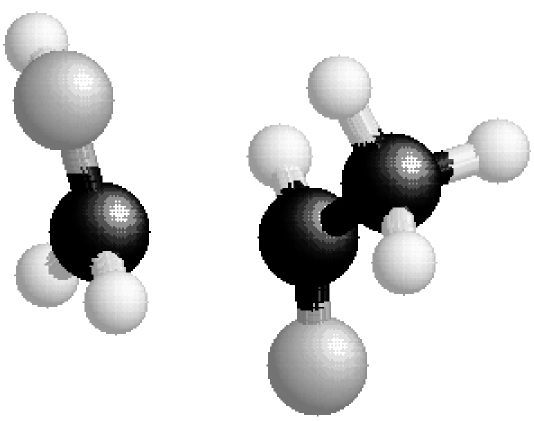

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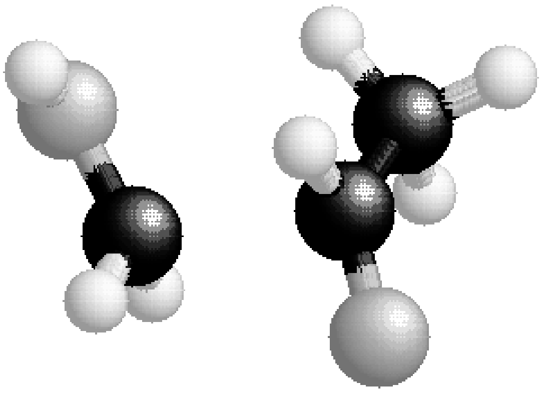
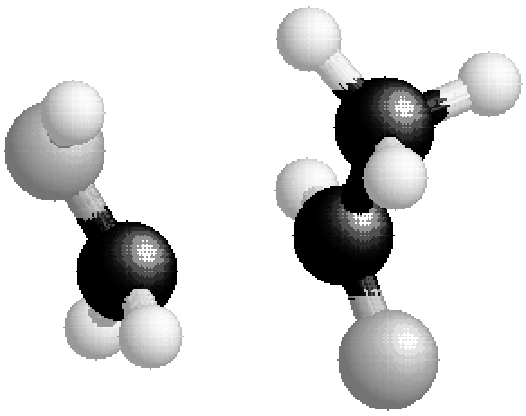


TS_tmS



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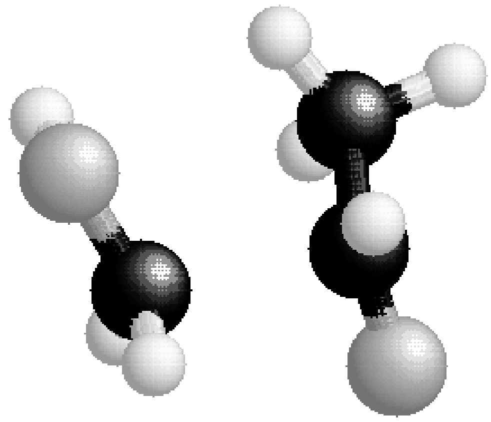

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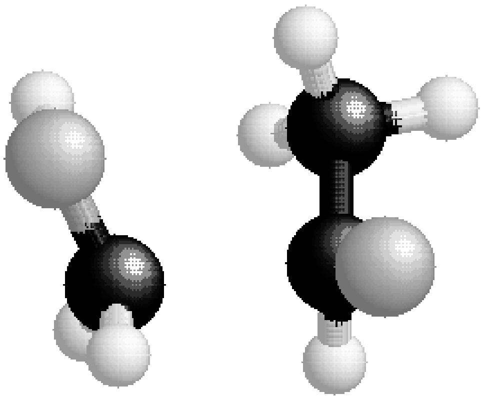
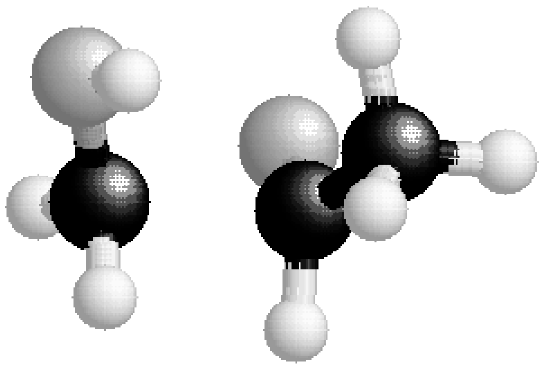
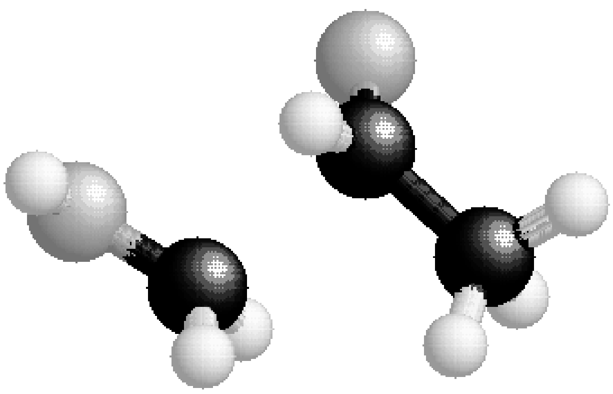


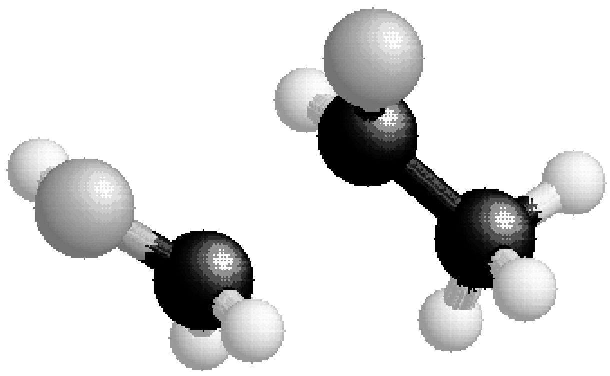
TS_ppR



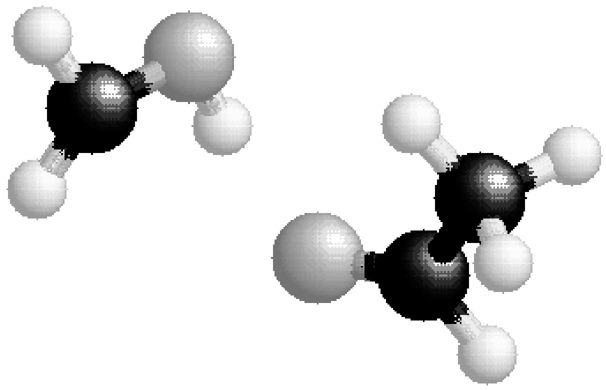
TS_mmS



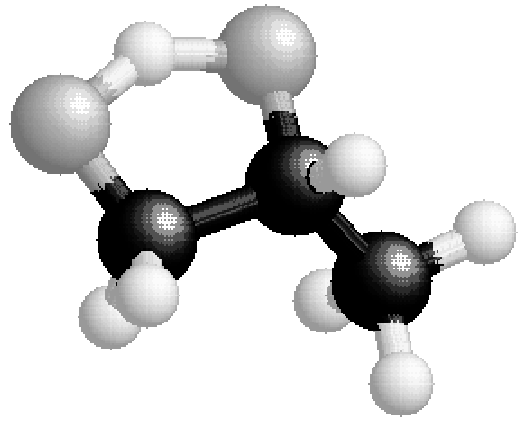
TS_mmR



TS_ppS

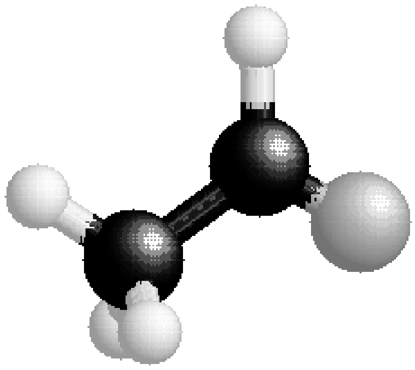


$CH_3CHO{\cdots}HOCH_2$

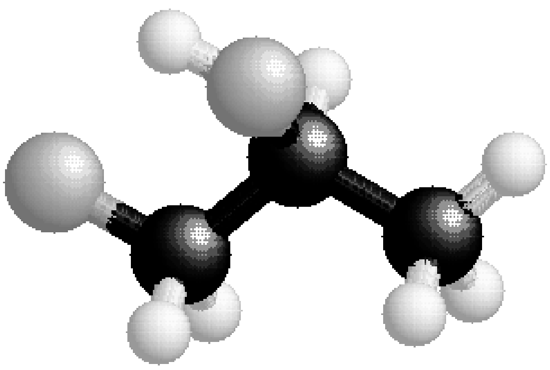


$HOCH_2CH(O)CH_3 \leftrightarrow OCH_2CH(OH)CH_3$

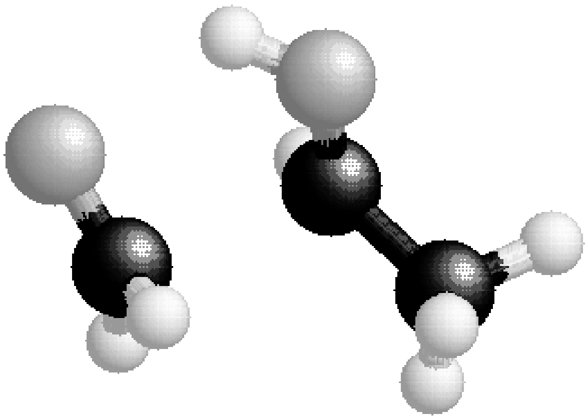
CH_2OH



CH_3CHO (C_s symmetry)



pmR (minor channel)



TS_pmR (minor channel)

B. Vibrational Wavenumbers

The wavenumbers listed below are given in cm^{-1}, and pertain to both enantiomers of each rotamer. All wavenumbers reported here have been scaled by 0.9614, as indicated in the main article.

1. Wavenumbers for the $HOCH_2CH(O)CH_3$ radicals and transition states for dissociation

mpR / pmS	129.42	191.78	239.11	351.26	420.71	475.23	501.28	782.11	864.13	886.77
	1002.68	1040.91	1065.47	1078.65	1124.84	1164.02	1214.52	1307.31	1352.82	1381.95
	1441.35	1447.92	1468.75	2754.91	2861.89	2934.95	2974.68	3004.83	3020.84	3605.35
pmR / mpS	132.98	204.97	260.71	332.42	377.41	477.49	621.51	766.16	864.82	903.59
	949.97	1026.34	1062.35	1089.33	1149.53	1219.52	1256.83	1327.73	1336.47	1380.16
	1429.65	1452.46	1465.95	2844.31	2877.74	2947.77	2968.98	3029.28	3053.23	3611.41
ttR / ttS	113.89	205.94	222.97	244.07	338.84	391.54	476.60	789.05	841.75	897.96
	970.40	1038.64	1048.09	1115.00	1138.64	1180.92	1218.48	1219.93	1338.96	1392.52
	1440.24	1450.94	1474.46	2754.71	2873.87	2919.96	2939.65	3013.68	3036.19	3687.41
tpR / tmS	123.69	221.41	251.70	290.03	317.63	418.86	470.90	791.72	850.54	899.08
	950.42	1023.10	1041.40	1115.45	1118.15	1242.76	1259.35	1328.08	1333.65	1342.90
	1430.70	1447.68	1457.77	2792.82	2904.98	2944.55	2990.32	3029.35	3039.42	3667.76
tmR / tpS	112.12	218.28	247.67	277.43	318.25	411.00	466.19	769.01	838.96	896.61
	930.13	1015.28	1054.48	1109.28	1124.45	1235.82	1264.81	1317.73	1335.94	1352.76
	1434.21	1450.31	1458.41	2839.37	2902.88	2935.55	2990.00	3015.38	3032.8	3682.30
ppR / mmS	116.15	198.80	240.47	309.77	346.58	423.76	451.53	756.31	844.77	873.13
	986.33	998.71	1031.83	1114.83	1159.74	1231.14	1288.26	1333.53	1347.40	1362.57
	1434.12	1446.92	1455.77	2785.17	2877.56	2929.79	3001.03	3005.96	3015.67	3666.83
mmR / ppS	111.08	221.43	252.32	309.34	351.21	397.04	538.05	712.84	839.76	871.90
	944.26	1016.31	1026.59	1100.69	1162.00	1225.38	1300.52	1335.14	1351.38	1354.14
	1440.91	1442.76	1463.14	2797.86	2885.92	2925.74	3000.51	3015.73	3017.84	3678.61
ptR / mtS	113.73	162.32	195.87	246.49	335.30	417.38	469.97	799.76	840.08	913.41
	967.17	1038.58	1045.72	1089.35	1126.76	1186.29	1215.95	1263.57	1347.20	1388.83
	1442.78	1450.67	1465.76	2774.74	2862.72	2906.04	2935.09	3004.10	3026.55	3692.11
mtR / ptS	109.35	205.00	209.90	243.63	350.72	381.27	604.15	764.80	871.20	913.45
	951.53	994.06	1069.56	1109.02	1133.10	1180.99	1219.70	1248.29	1343.43	1397.35
	1437.07	1452.43	1467.06	2761.43	2859.97	2915.11	2942.39	3016.53	3038.96	3688.11
TS_mpR / TS_pmS	133.35	163.38	170.93	266.83	373.12	473.10	559.16	687.80	836.41	876.63
	963.05	1039.44	1078.50	1101.95	1195.80	1311.38	1344.58	1354.18	1423.67	1432.23
	1464.94	1513.15	2793.14	2921.04	2963.16	2984.80	3019.60	3083.15	3477.25	*338.07i*
TS_pmR / TS_mpS	119.58	164.28	203.82	233.36	411.92	496.26	527.72	680.86	821.16	864.38
	970.10	1044.21	1081.79	1093.73	1188.01	1319.01	1344.16	1356.17	1426.79	1435.53
	1461.10	1509.94	2780.15	2925.76	2976.59	2992.44	3028.22	3095.28	3548.19	*356.93i*
TS_tpR / TS_tmS	82.72	164.04	187.43	274.75	350.31	412.85	477.36	662.56	833.27	859.09
	955.80	1043.93	1050.76	1081.72	1162.97	1320.43	1326.33	1346.19	1425.98	1433.58
	1449.01	1544.12	2727.40	2920.56	2989.10	3003.48	3024.72	3131.26	3667.62	*274.93i*
TS_tmR / TS_tpS	67.83	167.75	199.68	291.97	352.70	396.56	478.14	669.10	831.17	857.88
	955.49	1039.85	1049.09	1078.32	1164.75	1320.84	1326.38	1346.09	1432.56	1433.19
	1449.52	1540.09	2776.49	2919.53	2982.53	3001.25	3013.38	3132.73	3671.05	*268.60i*
TS_ppR / TS_mmS	60.63	172.35	189.57	215.76	345.83	384.64	478.24	626.65	814.63	866.09
	931.77	1024.81	1054.74	1075.99	1178.19	1325.34	1329.33	1352.59	1432.11	1435.48
	1453.39	1578.51	2753.48	2919.58	2975.02	2981.70	3021.08	3134.07	3669.52	*304.54i*
TS_mmR / TS_ppS	58.00	155.64	181.46	262.96	304.10	398.71	475.86	669.50	829.31	871.46
	960.26	1033.37	1062.88	1075.26	1189.34	1322.61	1330.10	1348.69	1426.04	1434.88
	1452.81	1542.17	2720.57	2921.54	2965.25	2984.82	3019.17	3113.65	3666.52	*305.18i*

2. Wavenumbers for the $OCH_2CH(OH)CH_3$ radical and transition state for dissociation

pmR	135.57	216.93	245.60	341.16	449.97	471.42	511.64	770.22	826.20	894.56
	1005.23	1024.40	1072.67	1075.97	1138.78	1210.02	1253.41	1320.47	1336.49	1356.26
	1395.94	1439.52	1455.16	2769.50	2847.37	2867.17	2932.61	3002.83	3015.00	3605.25
TS_mpR	130.80	158.32	168.54	293.41	352.92	432.57	583.83	608.60	843.49	896.91
	991.08	1053.58	1087.11	1193.03	1201.84	1286.96	1352.03	1396.86	1420.29	1435.40
	1449.12	1572.37	2794.37	2846.84	2903.32	2976.56	2983.82	3019.80	3466.80	*182.11i*

3. Wavenumbers for the products

$CH_3CHO\cdots HOCH_2$	36.60	81.54	106.73	140.03	165.32	208.00	219.65	513.25	616.14	748.24
	764.03	864.81	1075.62	1101.56	1112.28	1188.71	1340.93	1382.75	1386.34	1417.96
	1432.83	1444.53	1741.71	2826.98	2922.22	2978.67	2995.12	3046.87	3126.77	3461.39
CH_2OH	424.51	620.48	1023.60	1175.38	1313.97	1443.08	3002.98	3142.26	3684.96	
$OCHCH_3$	150.59	485.45	745.53	855.51	1086.49	1094.55	1333.88	1381.43	1416.00	1426.61
	1772.11	2773.70	2922.66	2979.68	3041.48					

4. Wavenumbers for the 1,4-hydrogen shift transition state

$HOCH_2CH(O)CH_3 \leftrightarrow OCH_2CH(OH)CH_3$

1,4-H-shift	91.15	227.46	303.80	433.67	594.87	683.94	735.54	859.36	887.24	975.94
	989.37	1069.68	1092.73	1135.41	1145.19	1163.95	1220.92	1247.19	1357.87	1399.09
	1437.80	1451.57	1920.43	2773.57	2802.21	2912.35	2932.08	3003.60	3018.25	*-1987.75i*