

Table 1. Absolute Energies (Hartrees) and Zero Point Energies (kcal/mole, at B3LYP/6-31G(d,p)) of Radicals, Transition States [in brackets], and Reaction Products. For the alkoxy radicals, III, V, and VI, 6-31G(d,p) refers to 6-31G(d); for all other species 6-31G(d,p) refers to the 6-31G(d,p) basis set. 1 Hartree=627.51 kcal/mole.

Species	6-31G(d,p)	6-311G(2df,2p)	ZPE
(Z) 1	-271.11890	-271.20271	80.5
(E) 1	-271.12027	-271.20413	80.5
[(E) 1 -> (Z) 1]	-271.09414	-271.17826	79.8
(E) 4	-271.11594	-271.19953	80.4
(Z) 4	-271.11529	-271.19905	80.2
[(E) 4 -> (Z) 4]	-271.09264	-271.17656	79.7
1-butoxy	-233.01131	-233.07783	77.0
[H-shift of 1-butoxy]	-232.99201	-233.06064	74.8
III	-346.29278	-346.41807	83.4
[H-shift of III]	-346.27307	-346.40104	81.2
product of H-shift of III	-346.30758	-346.44040	83.9
(Z)V	-346.29137	-346.41542	83.7
[H-shift of (Z)V]	-346.27746	-346.40565	80.8
product of H-shift of (Z)V	-346.31639	-346.44961	83.9
(E) V	-346.28361	-346.41027	82.0
[H-shift of (E) V]	-346.26456	-346.39394	80.2
product of H-shift of (E)V	-346.30169	-346.43476	83.8
(Z)VI	-346.29115	-346.41524	84.7
[H-shift of (Z) VI]	-346.27662	-346.40507	80.7
product of H-shift of (Z) VI	-346.31847	-346.45103	83.8
(E)VI	-346.28361	-346.41027	82.0
[1, 4 H-shift of (E) VI]	-346.24657	-346.37514	80.9
product of H-shift of (E) VI	-346.30177	-346.43473	83.8

Table 2. Absolute Energies (Hartrees) and Zero Point Energies (ZPE, kcal/mole, at MPW1K/6-31G(d,p)) of Alkoxy Radicals and Transition States for 1,5 H-shift reactions [in brackets]. 1 Hartree=627.51 kcal/mole.

Species	6-31G(d,p)	6-311(2df,2p)	ZPE
1-butoxy	-232.94760	-233.00910	79.5
[H-shift of 1-butoxy]	-232.92285	-232.98517	77.1
III	-346.20363	-346.30294	86.2
[H-shift of III]	-346.18057	-346.28063	83.6
(E) V	-346.20014	-346.29887	87.3
[H-shift of (E) V]	-346.18350	-346.28419	83.5
(Z)V	-346.19701	-346.29663	85.3
[H-shift of (Z)V]	-346.17339	-346.27437	82.9
(E)VI	-346.19701	-346.29663	85.3
[H-shift of (E) VI]	-346.17339	-346.27437	82.9

Table 3. Absolute Energies (Hartrees) of isoprene-OH adducts and transition states to their E/Z isomerization [in brackets] at the CBS-QB3 level of theory, 0 K, including zero point energies. 1 Hartree=627.51 kcal/mole.

Species	CBS-QB3 Energy
(E) 1	-270.60987
(Z) 1	-270.60856
[(E) 1 -> (Z) 1]	-270.58581
(E) 4	-270.60777
(Z) 4	-270.60871
[(E) 4 -> (Z) 4]	-270.58398

Table 4. Cartesian coordinates (Angstroms) at B3LYP/6-311G(2df,2p) of all reactant radicals, transition states, and products.

(E) 1	(HOCH2C(CH3)=CHCH2.)		
1	-1.951439	-0.529601	-1.331085
6	0.068830	0.076355	0.175394
6	0.091812	1.570163	0.070280
6	-1.257150	-0.550613	0.491148
6	1.198884	-0.722888	0.031773
8	-2.268218	-0.234424	-0.471780
1	-1.650659	-0.162587	1.435273
1	-1.148457	-1.634458	0.601893
1	0.222665	2.030463	1.056390
1	-0.854812	1.932117	-0.330223
1	0.896474	1.933497	-0.566733
6	2.489146	-0.308161	-0.204902
1	1.039381	-1.793758	0.127400
1	2.751821	0.735395	-0.302167
1	3.291639	-1.024806	-0.298670

(Z) 1	(HOCH2C(CH3)=CHCH2.)		
1	-1.356364	-1.251025	-1.248705
6	0.031803	0.448868	0.131596
6	-0.727564	1.731687	-0.007843
6	-0.777132	-0.745742	0.544861
6	1.398851	0.388842	-0.127433
8	-1.794680	-1.070396	-0.411619
1	-1.323581	-0.527614	1.465838
1	-0.144684	-1.613344	0.741822
1	-0.118361	2.523854	-0.440754
1	-1.092219	2.080055	0.965379
1	-1.613017	1.589380	-0.631140
6	2.235318	-0.702711	-0.054260
1	3.285685	-0.603227	-0.284384
1	1.860822	1.326700	-0.424350
1	1.891501	-1.687282	0.227721

Transition State for E-Z isomerization of 1

1	2.332714	-0.353239	1.014755
6	-0.051412	0.214982	0.116434
6	0.231580	1.663815	-0.111548
6	0.958071	-0.816778	-0.285136
6	-1.395297	-0.215633	0.539284
8	2.301379	-0.478328	0.061334
1	0.981473	-0.934425	-1.376703

1	0.676204	-1.792459	0.125874
1	-0.269600	2.030783	-1.018048
1	1.300255	1.839488	-0.225110
1	-0.140939	2.282584	0.709062
6	-2.414568	-0.471833	-0.274259
1	-1.559368	-0.332599	1.612503
1	-2.325183	-0.373372	-1.349318
1	-3.376832	-0.787452	0.107662
(E) 4 (.CH2C(CH3)=CHCH2OH with CH3 group trans to CH2OH)			
1	0.524699	2.161530	-0.081544
6	1.296005	1.408336	-0.137859
1	-2.332354	-0.416119	-1.239584
6	1.028149	0.062720	0.008585
1	2.303005	1.755558	-0.319523
6	-0.245914	-0.454557	0.237219
6	2.182250	-0.919477	-0.054469
1	-1.840253	0.330942	1.421836
1	2.512316	-1.194534	0.949295
1	3.037426	-0.495108	-0.578278
1	1.892792	-1.838230	-0.564419
1	-1.405723	1.348234	0.056621
1	-0.355213	-1.528932	0.341127
6	-1.519703	0.308510	0.375864
8	-2.597677	-0.319568	-0.320196
(Z) 4 (.CH2C(CH3)=CHCH2OH with CH3 group cis to CH2OH)			
1	3.105708	-0.733056	-0.262584
6	2.086087	-1.041899	-0.082624
1	-2.279447	-0.326509	-1.256566
6	1.059824	-0.125243	0.019605
1	1.897802	-2.102352	0.015136
6	-0.246076	-0.553284	0.252215
6	1.377856	1.350351	-0.114554
1	-1.803114	0.309763	1.434221
1	0.790951	1.817081	-0.907162
1	2.430175	1.499425	-0.348431
1	1.161584	1.892877	0.806945
1	-1.250524	1.340762	0.122508
1	-0.425041	-1.618937	0.349790
6	-1.457827	0.301586	0.395368
8	-2.568410	-0.208514	-0.346740
Transition state for E-Z isomerization of 4			
1	-2.687791	1.416305	-0.477216
6	-1.654867	1.340821	-0.160447
1	2.645435	1.034102	0.174224
6	-1.095413	0.163261	0.108438
1	-1.100959	2.265583	-0.069372
6	0.312404	0.048660	0.538046
6	-1.867082	-1.132307	-0.010924
1	1.487695	-1.438870	-0.474258
1	-1.398325	-1.802532	-0.735535
1	-2.895986	-0.956136	-0.322737
1	-1.880295	-1.664180	0.943406
1	1.177803	0.017948	-1.407878
1	0.546275	0.021089	1.597793

6	1.404004	-0.346636	-0.397035
8	2.688984	0.082987	0.037888
1-butoxy	(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O.)		
8	2.023269	-0.763288	-0.257224
6	-2.351221	-0.121084	-0.139236
6	-0.917773	-0.342668	0.338549
6	0.063475	0.703019	-0.189732
6	1.511857	0.413206	0.201780
1	-2.413239	-0.159252	-1.228370
1	-2.730163	0.852755	0.177341
1	-3.024282	-0.882146	0.256751
1	-0.569956	-1.329821	0.027168
1	-0.891623	-0.339763	1.432863
1	0.006321	0.746043	-1.281044
1	-0.206762	1.698491	0.176642
1	1.615138	0.366394	1.305615
1	2.190384	1.238763	-0.077340

## Transition State for 1,5 H-shift of 1-butoxy

8	-1.117639	-1.102329	-0.090248
6	-1.299362	0.247283	0.230851
6	-0.162945	1.117329	-0.322711
6	1.173088	0.600087	0.231050
6	1.332448	-0.872557	-0.066845
1	0.105277	-1.272219	-0.020524
1	-1.383396	0.399727	1.317021
1	-2.249005	0.557137	-0.222120
1	-0.322818	2.162875	-0.052399
1	-0.165224	1.050904	-1.413237
1	1.205077	0.769907	1.309517
1	1.998935	1.173784	-0.203451
1	1.879865	-1.463013	0.662719
1	1.613018	-1.113315	-1.089614

III (CH<sub>2</sub>=C(CH<sub>3</sub>)CH(OH)CH<sub>2</sub>O.)

1	2.975936	-1.237650	-0.022249
6	1.954346	-1.176189	-0.373283
6	1.168824	-0.149764	-0.059166
1	1.604162	-1.988295	-0.997639
6	1.632509	1.011717	0.772406
6	-0.266001	-0.130368	-0.515165
6	-1.232136	-0.583111	0.632019
1	-0.394852	-0.854301	-1.328549
8	-0.640077	1.161847	-0.931543
1	-1.009513	0.073575	1.495863
1	-1.044700	-1.618503	0.948773
8	-2.522576	-0.331475	0.316607
1	-1.605217	1.190879	-0.882935
1	1.031488	1.124997	1.679123
1	1.526514	1.942586	0.215857
1	2.672159	0.890024	1.070381

## TS for 1,5 H-shift of III

1	-3.055511	.373484	-.445840
6	-2.208671	-.295162	-.526074
6	-1.037297	-.020806	.065018
1	-2.357624	-1.211552	-1.082258

6	-.736313	1.213000	.787159
6	.184467	-.888721	-.137889
6	1.146322	-.026399	-1.006218
1	-.070884	-1.815427	-.651437
8	.829117	-1.230794	1.075473
1	.689447	.193543	-1.978491
1	2.058475	-.613417	-1.166338
8	1.502759	1.116616	-.297920
1	1.434624	-.506673	1.279858
1	.386376	1.503094	.235247
1	-.380814	1.073772	1.805628
1	-1.450156	2.025129	.691225

Product of 1,5 H-shift of III (CH<sub>2</sub>=C(CH<sub>2</sub>.)CH(OH)CH<sub>2</sub>OH)

6	-0.961503	-0.333342	-0.090359
6	-1.009608	-1.623279	-0.590614
1	-0.284381	-1.979597	-1.307813
1	1.173527	0.499163	1.443606
1	-1.797902	-2.301920	-0.295568
6	0.214504	0.544046	-0.485517
6	-1.916289	0.159428	0.780886
1	0.576764	2.457100	-0.626800
1	-2.744347	-0.461791	1.092709
1	-1.872663	1.174453	1.141290
1	0.487824	0.312517	-1.520839
6	1.439937	0.266573	0.406480
8	-0.165582	1.908904	-0.358859
1	2.247176	0.940798	0.110532
8	1.956079	-1.041602	0.266112
1	1.287786	-1.659690	0.579604

(Z) V (HOCH<sub>2</sub>C(CH<sub>3</sub>)=CHCH<sub>2</sub>O.)

8	-2.082827	.426523	-.007668
6	2.185235	-.891377	-.120510
6	.774620	-.439215	.121073
6	-.269257	-1.237805	-.114652
6	-1.720060	-.880891	.042886
6	.614634	.993091	.594149
8	.398635	1.896509	-.479501
1	2.664422	-.227150	-.844511
1	2.777638	-.833872	.796481
1	2.236089	-1.910509	-.500800
1	-.091046	-2.252504	-.457983
1	-.196535	1.060392	1.328179
1	1.530350	1.321328	1.087053
1	-2.168448	-1.376148	.925715
1	-2.289639	-1.347275	-.792493
1	-.500328	1.718665	-.781971

TS for 1,5 H-shift of (Z) V

6	-1.877974	-1.277243	.090759
6	-.543947	-.575539	.103749
6	1.955979	-.488118	-.178582
6	.610007	-1.175689	-.171829
6	-.551509	.886399	.442077
1	-1.787548	-2.305652	-.254824
1	-2.585500	-.753380	-.554056

1	-2.318085	-1.288398	1.091290
1	-.847221	1.112286	1.467900
8	-1.323110	1.692564	-.394818
1	.622623	1.157853	.373207
1	-1.125409	1.459259	-1.308731
1	.637001	-2.232879	-.413038
1	2.378488	-.590966	-1.191345
1	2.612946	-1.059065	.497892
8	1.930281	.842697	.216651

Product of 1,5 H-shift of (Z) V (HOCH.C(CH3)=CHCH2OH)

6	2.421139	-0.602182	0.181157
6	0.982087	-0.165053	-0.022007
6	-1.430370	-0.972479	-0.435044
6	0.011765	-1.161971	-0.107777
6	0.766900	1.205276	-0.096535
1	2.715181	-1.347901	-0.558570
1	2.561867	-1.048944	1.167414
1	3.110635	0.237109	0.101852
1	1.610779	1.882195	-0.121645
8	-0.402634	1.855619	-0.146931
1	-1.910347	-0.365684	1.376064
1	-1.145357	1.261816	0.107939
1	0.345361	-2.186435	0.000209
1	-1.944266	-1.934400	-0.459774
1	-1.574926	-0.496055	-1.407929
8	-2.132123	-0.083526	0.481391

(E) V (HOCH2C(CH3)=CHCH2O.)

6	-0.379411	0.387212	0.038902
6	0.160113	1.789211	-0.018213
1	-0.103436	2.260877	-0.969575
1	1.237963	1.819462	0.085289
1	-0.293792	2.402290	0.765628
6	0.335192	-0.736952	0.072181
6	-1.893387	0.329915	0.072378
1	2.124477	-1.499228	0.979890
1	-2.242262	0.740144	1.024193
8	-2.467809	-0.959068	-0.025032
1	-2.286448	0.996044	-0.707822
8	2.682762	0.083376	-0.110627
1	-0.218316	-1.668418	0.144814
6	1.823120	-0.944580	0.065444
1	2.080414	-1.696300	-0.713942
1	-2.291990	-1.298175	-0.907364

TS for 1,5 H-shift of (E) V

6	.025914	1.361984	-.232841
6	-.350220	-.077374	-.256006
6	2.035364	-.708886	.132386
6	.573944	-1.017502	-.083239
6	-1.810645	-.415395	-.458230
1	1.276373	1.259856	.003997
1	-.402656	1.944844	.579611
1	-.060393	1.883277	-1.186214
1	-2.177203	.034886	-1.382427
8	-2.637617	.121932	.569152

1	-1.931323	-1.500180	-.543725
1	-2.352843	-.260680	1.404527
1	.310606	-2.069331	-.101549
1	2.606407	-1.171065	-.687509
1	2.352425	-1.203302	1.062811
8	2.329176	.656159	.210606

Product of 1,5 H-shift of	(E) V	(HOCH <sub>2</sub> C(CH <sub>2</sub> )=CHCH <sub>2</sub> OH)	
6	0.317958	1.346135	-0.174869
6	0.409384	-0.016834	-0.004231
6	-2.091487	-0.526239	-0.391829
6	-0.668303	-0.897327	-0.103789
6	1.767815	-0.629385	0.328050
1	-2.348815	0.415854	1.295468
1	-0.630412	1.823130	-0.364337
1	1.202593	1.960152	-0.095776
1	1.855603	-0.753467	1.408983
8	2.878701	0.164746	-0.046963
1	1.831316	-1.630116	-0.113968
1	2.853581	0.283636	-1.001121
1	-0.462902	-1.957961	-0.005989
1	-2.725148	-1.411005	-0.268359
1	-2.199972	-0.204764	-1.432970
8	-2.602207	0.562310	0.379224

(Z) VI	(.OCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH)		
8	-2.111188	0.374736	0.180298
6	2.275696	-0.732276	-0.061541
6	0.845176	-0.335395	0.158301
6	-0.178466	-1.169222	-0.068784
6	-1.660583	-0.934136	-0.051936
6	0.630724	1.138223	0.541574
8	0.205404	1.619827	-0.675058
1	2.730055	-0.089703	-0.818909
1	2.861573	-0.611805	0.852889
1	2.361824	-1.764939	-0.395951
1	0.076622	-2.195057	-0.324976
1	-0.107833	1.249343	1.337954
1	1.591919	1.569934	0.841990
1	-2.099682	-1.561837	0.731738
1	-2.055680	-1.333455	-0.999777
1	-1.587794	0.977842	-0.372559

TS for 1,5 H-shift of (Z) VI			
8	-2.458553	-0.618076	0.476782
6	2.252498	-1.097203	0.067444
6	0.964544	-0.335888	-0.033146
6	-0.214636	-0.909876	-0.260809
6	-1.471012	-0.130900	-0.379641
6	1.073643	1.162001	0.196793
8	-0.065161	1.891129	-0.100253
1	2.932193	-0.825221	-0.744080
1	2.770964	-0.866769	1.001554
1	2.087586	-2.172170	0.024737
1	-0.295883	-1.990663	-0.331339
1	1.400147	1.305998	1.240555
1	1.893452	1.530919	-0.441929

1	-1.832399	-0.013833	-1.407717
1	-1.086416	0.981268	-0.104999
1	-3.310153	-0.262757	0.207135

Product of 1,5 H-shift of (Z) VI (HOCH<sub>2</sub>C(CH<sub>3</sub>)=CHCH.OH)

6	2.371168	-0.615928	-0.074871
6	0.918249	-0.254133	0.044532
8	-2.213832	-0.084264	0.147997
6	-0.063618	-1.236399	-0.093519
6	0.615547	1.158468	0.445885
8	-0.393463	1.807356	-0.369450
1	1.526595	1.760577	0.429352
1	0.205701	1.214580	1.458170
1	2.905418	-0.484649	0.873620
1	2.889615	0.015391	-0.804224
1	2.502692	-1.653057	-0.380094
6	-1.441469	-1.170105	-0.009610
1	-1.687476	0.728463	-0.018419
1	0.296872	-2.239330	-0.295897
1	-2.023009	-2.079960	-0.072866
1	-0.157309	1.661825	-1.292519

(E) VI (.OCH<sub>2</sub>C(CH<sub>3</sub>)=CHCH<sub>2</sub>OH)

8	2.454925	0.481985	0.611957
6	-0.335455	1.427861	-0.465575
6	-0.450210	-0.054506	-0.262312
6	0.569387	-0.909538	-0.175156
6	2.040067	-0.573896	-0.253582
6	-1.865696	-0.590424	-0.168475
8	-2.688069	0.051585	0.705954
1	-0.956752	1.950440	0.262911
1	0.688110	1.774303	-0.368451
1	-0.715454	1.704575	-1.454059
1	0.338062	-1.961797	-0.036186
1	-2.372936	-0.440150	-1.148788
1	-1.884454	-1.681386	-0.018337
1	2.307692	-0.239636	-1.258371
1	2.623983	-1.478506	-0.055170
1	2.088351	0.306621	1.483773

TS for 1,4 H-shift of (E) VI

8	2.355272	-0.753284	-0.462960
6	-0.551021	-1.169332	0.536425
6	-0.418468	0.283227	0.226087
6	0.696928	0.992960	0.071188
6	2.105228	0.471603	0.226187
6	-1.831701	0.764306	-0.025650
8	-2.523682	-0.392925	-0.478711
1	-1.647958	-1.262838	-0.127959
1	0.236102	-1.833654	0.202741
1	-0.914660	-1.397101	1.538248
1	0.600905	2.041683	-0.193113
1	-2.288265	1.147310	0.897495
1	-1.876199	1.548925	-0.785118
1	2.329526	0.258334	1.273202
1	2.812510	1.241703	-0.098029
1	2.089521	-0.631272	-1.379518



Product of 1,4 H-shift of (E) VI ( HOCH<sub>2</sub>C(CH<sub>2</sub>.)=CHCH<sub>2</sub>OH)

8	2.535335	0.029625	0.547075
6	0.075029	1.732947	-0.046706
6	-0.436278	0.457856	-0.164916
6	0.335302	-0.691468	-0.323734
6	1.829630	-0.747616	-0.422512
6	-1.954240	0.296622	-0.169742
8	-2.417896	-0.943065	0.342247
1	-2.135832	-1.011998	1.259098
1	1.137471	1.917587	-0.052730
1	-0.585965	2.581846	0.068319
1	-0.196106	-1.628610	-0.428230
1	-2.408692	1.138296	0.363035
1	-2.318272	0.332994	-1.198038
1	2.162251	-0.354609	-1.388933
1	2.153338	-1.792953	-0.380444
1	2.155642	-0.165080	1.409015