High Accuracy Ab Initio Calculations on Reactions of OH with 1-Alkenes. The Case of Propene Supplementary Material

Róbert Izsák,[*,†] Milán Szőri,[‡,¶] Peter J. Knowles,[†] and Béla Viskolcz[‡]

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom, Department of Chemical Informatics, Faculty of Education, University of Szeged, Boldogasszony sgt. 6. 6725 Szeged, Hungary, and Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo náměstí 2, 16610 Prague 6, Czech Republic

E-mail: izsakr@cf.ac.uk

[†]School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

[‡]Department of Chemical Informatics, Faculty of Education, University of Szeged, Boldogasszony sgt. 6. 6725 Szeged, Hungary

[¶]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo náměstí 2, 16610 Prague 6, Czech Republic

Table 1: Cartesian coordinates of direct ($\mathbf{A_{dir}}$) and consecutive ($\mathbf{A_{con}}$) allylic H-abstraction transition states in Å units at the [5,5]-CASPT2/cc-pVTZ level of theory.

species	atom	X	Y	Z
$\mathbf{A_{dir}}$	C	0.000000	0.000000	0.000000
	C	0.000000	0.000000	1.339786
	H	0.921504	0.000000	-0.561946
	H	-0.925798	0.002005	-0.558230
	H	0.945032	-0.008992	1.868036
	C	-1.231435	-0.017968	2.167978
	H	-2.136291	0.087293	1.575405
	H	-1.213540	0.721840	2.965344
	H	-1.297689	-1.043792	2.690504
	O	-1.489035	-2.231243	3.549423
	H	-2.010559	-1.765867	4.221649
$\mathbf{A_{con}}$	C	0.000000	0.000000	0.000000
	C	0.000000	0.000000	1.340398
	H	0.921005	0.000000	-0.562935
	H	-0.926334	-0.010257	-0.557713
	H	0.946157	0.009198	1.867201
	C	-1.229729	0.024126	2.170413
	H	-1.200049	-0.680810	2.998271
	H	-2.135964	-0.109444	1.586375
	H	-1.321463	1.054900	2.688663
	O	-1.255390	2.488923	2.969937
	H	-0.873475	2.693654	2.101744

Table 2: Cartesian coordinates of central (**C**) and terminal (**T**) OH-addition transition states in Å units at the [5,5]-CASPT2/cc-pVTZ level of theory.

species	atom	X	Y	Z
C	C	0.000000	0.000000	0.000000
	H	0.000000	0.000000	1.081429
	C	1.184456	0.000000	-0.646875
	H	2.117482	-0.064215	-0.108097
	H	1.226882	0.050541	-1.726531
	C	-1.240395	-0.041119	-0.833230
	H	-1.004891	-0.257270	-1.873253
	H	-1.924121	-0.801239	-0.464812
	H	-1.757943	0.923958	-0.791981
	O	0.185220	-2.226050	0.582902
	H	0.798192	-2.464609	-0.128190
T	C	0.000000	0.000000	0.000000
	H	0.000000	0.000000	1.083983
	C	1.179838	0.000000	-0.649534
	H	2.115620	0.045134	-0.114575
	H	1.220105	0.049464	-1.727131
	C	-1.328476	-0.032628	-0.683708
	H	-1.207449	-0.046603	-1.764055
	H	-1.897879	-0.915303	-0.393481
	H	-1.930128	0.841342	-0.410336
	O	1.207245	-2.305627	-1.018281
	H	0.844502	-2.486421	-0.138893

Table 3: Cartesian coordinates of the π-complex (**R**), and the initial propene and OH geometries in Å units at the [5,5]-CASPT2/cc-pVTZ level of theory. Although the supermolecular approach was used, here the reactant structures are given separately.

species	atom	X	Y	Z
R	C	0.000000	0.000000	0.000000
	C	0.000000	0.000000	1.339986
	H	0.921173	0.000000	-0.563366
	H	-0.926226	-0.014377	-0.558680
	H	0.950679	0.006784	1.860438
	C	-1.232008	-0.002973	2.187891
	H	-1.246356	-0.872446	2.844049
	H	-2.130195	-0.019191	1.574509
	H	-1.264076	0.886422	2.825628
	O	-0.397375	3.244879	1.020974
	H	-0.213382	2.326495	0.756719
Propene	C	0.000000	0.000000	0.000000
	C	0.000000	0.000000	1.337450
	H	0.920829	0.000000	-0.563337
	H	-0.925964	0.001876	-0.558392
	H	0.949030	-0.000778	1.860099
	C	-1.234686	0.001518	2.181955
	H	-1.263598	-0.871498	2.833575
	H	-2.130209	-0.001506	1.564441
	H	-1.265101	0.884856	2.828867
OH	O	0.000000	0.000000	0.000000
	H	0.000000	0.000000	0.968441

Table 4: Cartesian coordinates of direct ($\mathbf{A_{dir}}$) and consecutive ($\mathbf{A_{con}}$) allylic H-abstraction transition states in Å units at the UCCSD(T)/cc-pVTZ level of theory.

species	atom	X	Y	Z
$\mathbf{A_{dir}}$	C	0.000000	0.000000	0.000000
	C	0.000000	0.000000	1.341394
	H	0.924097	0.000000	-0.563968
	H	-0.928366	0.004675	-0.560600
	H	0.946779	-0.013112	1.872627
	C	-1.233614	-0.014517	2.168414
	H	-2.142878	0.128413	1.584459
	H	-1.197723	0.679826	3.009093
	H	-1.326647	-1.082104	2.650589
	O	-1.523695	-2.254435	3.405062
	H	-1.949722	-1.816939	4.159556
$\mathbf{A_{con}}$	C	0.000000	0.000000	0.000000
	C	0.000000	0.000000	1.341818
	H	0.923548	0.000000	-0.564949
	H	-0.928815	-0.011762	-0.560167
	H	0.947536	0.011887	1.872006
	C	-1.232167	0.019071	2.170687
	H	-1.193408	-0.656117	3.026578
	H	-2.143159	-0.130208	1.591719
	H	-1.337540	1.078761	2.676763
	O	-1.340228	2.437768	2.996473
	H	-1.007105	2.713772	2.127046

Table 5: Cartesian coordinates of central (**C**) and terminal (**T**) OH-addition transition states in Å units at the UCCSD(T)/cc-pVTZ level of theory.

species	atom	X	Y	Z
C	C	0.000000	0.000000	0.000000
	H	0.000000	0.000000	1.083757
	C	1.190464	0.000000	-0.648690
	H	2.123302	-0.098434	-0.109845
	H	1.233998	0.065080	-1.731077
	C	-1.246367	-0.034201	-0.834975
	H	-1.019387	-0.314968	-1.865393
	H	-1.959599	-0.749275	-0.425286
	H	-1.721935	0.950674	-0.845805
	O	0.238751	-2.102407	0.554128
	H	0.561400	-2.409131	-0.307976
T	C	0.000000	0.000000	0.000000
	H	0.000000	0.000000	1.087152
	C	1.185405	0.000000	-0.651886
	H	2.122605	0.071828	-0.116281
	H	1.226351	0.063763	-1.731335
	C	-1.331305	-0.056909	-0.685201
	H	-1.209129	-0.064167	-1.768901
	H	-1.876693	-0.959637	-0.398018
	H	-1.951159	0.799890	-0.406395
	O	1.158212	-2.189266	-0.910212
	H	1.059361	-2.374064	0.036695

Table 6: Cartesian coordinates of the π-complex (**R**), and the initial propene and OH geometries in Å units at the UCCSD(T)/cc-pVTZ level of theory. Although the supermolecular approach was used, here the reactant structures are given separately.

species	atom	X	Y	Z
R	C	0.000000	0.000000	0.000000
	C	0.000000	0.000000	1.340520
	H	0.923618	0.000000	-0.565407
	H	-0.928692	-0.015533	-0.561143
	H	0.952982	0.007407	1.863247
	C	-1.235980	-0.002945	2.193698
	H	-1.244748	-0.869988	2.858779
	H	-2.136892	-0.030024	1.578246
	H	-1.272976	0.890771	2.821664
	O	-0.439546	3.256058	1.028234
	H	-0.243768	2.342278	0.750565
Propene	C	0.000000	0.000000	0.000000
	C	0.000000	0.000000	1.338046
	H	0.923527	0.000000	-0.565162
	H	-0.928282	0.001427	-0.561212
	H	0.951542	-0.002100	1.862874
	C	-1.238315	0.003137	2.188068
	H	-1.267906	-0.874284	2.839733
	H	-2.137098	0.002112	1.568848
	H	-1.266698	0.884124	2.835031
OH	O	0.000000	0.000000	0.000000
	H	0.000000	0.000000	0.971116

Table 7: RHF reference and UCCSD(T) energies used for extrapolation on [5,5]-CASPT2/cc-pVTZ optimized geometries. A*n* is a shorthand notation for aug-cc-pV*n*Z bases.

level	$\mathbf{A_{dir}}$	$\mathbf{A_{con}}$	**C**	**T**	**R**	*Propene* + *OH*
RHF/A2	-192.458085	-192.457718	-192.473409	-192.474049	-192.488437	-192.485824
RHF/A3	-192.505602	-192.505138	-192.520514	-192.521316	-192.536033	-192.533928
RHF/A4	-192.517379	-192.516906	-192.532233	-192.533072	-192.547795	-192.545825
RHF/CBS	-192.521260	-192.520790	-192.536114	-192.536965	-192.551655	-192.549735
UCCSD(T)/A2	-193.157166	-193.157683	-193.167071	-193.166496	-193.167771	-193.161120
UCCSD(T)/A3	-193.331503	-193.332125	-193.340747	-193.340461	-193.341834	-193.335777
UCCSD(T)/CBS	-193.400559	-193.401261	-193.409639	-193.409457	-193.410706	-193.404869

Table 8: RHF reference and UCCSD(T) energies used for extrapolation on UCCSD(T)/cc-pVTZ optimized geometries. An is a shorthand notation for aug-cc-pVnZ bases.

level	$\mathbf{A_{dir}}$	$\mathbf{A_{con}}$	**C**	**T**	**R**	$Propene + OH$
RHF/A2	-192.451343	-192.451174	-192.466494	-192.467221	-192.488514	-192.485757
RHF/A3	-192.498578	-192.498321	-192.513193	-192.514136	-192.535914	-192.533645
RHF/A4	-192.510323	-192.510056	-192.524863	-192.525842	-192.547663	-192.545547
RHF/CBS	-192.514210	-192.513946	-192.528751	-192.529734	-192.551535	-192.549484
UCCSD(T)/A2	-193.157523	-193.158027	-193.167696	-193.167320	-193.168349	-193.161626
UCCSD(T)/A3	-193.331533	-193.332138	-193.341019	-193.340980	-193.341985	-193.335874
UCCSD(T)/CBS	-193.400544	-193.401222	-193.409893	-193.409943	-193.410757	-193.404918

Table 9: Thermochemical data for all species calculated from [5,5]-CASPT2/cc-pVTZ geometries and frequencies scaled by a factor of 0.958. The UCCSD(T)/CBS total energies (E_{tot}), zero point vibrational energies ($ZPVE$) and thermal corrections at $T = 298.15K$ for energies ($E_{therm}(T)$), enthalpies ($H_{therm}(T)$) and free energies ($G_{therm}(T)$) are in Hartree units. Energies relative to the separate Propene+OH (E_{rel}) are in kJ/mol, and entropies ($S(T)$) are in J/molK units.

species	E_{tot}	E_{rel}	$ZPVE$	$E_{therm}(T)$	$H_{therm}(T)$	$G_{therm}(T)$	S(T)
$\mathbf{A_{dir}}$	-193.400559	11.32	0.083565	0.090089	0.091033	0.052406	340.15
$\mathbf{A_{con}}$	-193.401261	9.47	0.083831	0.090174	0.091119	0.053491	331.34
C	-193.409639	-12.52	0.087122	0.093486	0.094430	0.057408	326.02
T	-193.409447	-12.02	0.087089	0.093553	0.094498	0.056911	330.98
R	-193.410706	-15.32	0.087042	0.094302	0.095246	0.055330	351.50
$Propene + OH$	-193.404869	0.00	0.085023	0.091589	0.093478	0.042364	450.11

Table 10: Thermochemical data for all species calculated from UCCSD(T)/cc-pVTZ geometries and frequencies scaled by a factor of 0.975. The UCCSD(T)/CBS total energies (E_{tot}), zero point vibrational energies ($ZPVE$) and thermal corrections at $T = 298.15K$ for energies ($E_{therm}(T)$), enthalpies ($H_{therm}(T)$) and free energies ($G_{therm}(T)$) are in Hartree units. Energies relative to the separate Propene+OH (E_{rel}) are in kJ/mol, and entropies ($S(T)$) are in J/molK units.

species	E_{tot}	E_{rel}	$ZPVE$	$E_{therm}(T)$	$H_{therm}(T)$	$G_{therm}(T)$	S(T)
$\mathbf{A_{dir}}$	-193.400544	11.48	0.083787	0.090136	0.091080	0.053391	331.89
$\mathbf{A_{con}}$	-193.401222	9.70	0.083953	0.090228	0.091172	0.053761	329.44
C	-193.409893	-13.06	0.088374	0.094477	0.095421	0.059176	319.18
T	-193.409943	-13.19	0.088305	0.094559	0.095503	0.058586	325.09
R	-193.410757	-15.33	0.087857	0.095100	0.096045	0.056152	351.30
$Propene + OH$	-193.404918	0.00	0.085815	0.092344	0.094232	0.043166	449.68

Table 11: Unscaled vibrational frequencies and rotational constants for the various species at the [5,5]-CASPT2/cc-pVTZ level of theory.

species	B (cm^{-1})	vibrational frequencies (cm^{-1})
$\mathbf{A_{dir}}$	0.598, 0.090, 0.085	663i, 44, 81, 111, 324, 418, 577, 722, 910, 945, 968, 1011, 1106, 1177, 1204, 1328, 1363, 1448, 1483, 1600, 1692, 3115, 3186, 3191, 3210, 3287, 3785
$\mathbf{A_{con}}$	0.448, 0.109, 0.097	870i, 63, 116, 166, 305, 423, 565, 773, 913, 941, 955, 990, 1018, 1197, 1321, 1338, 1383, 1456, 1492, 1535, 1691, 3119, 3185, 3194, 3209, 3286, 3776
C	0.283, 0.193, 0.131	217i, 105, 155, 167, 230, 421, 574, 582, 885, 938, 950, 1006, 1055, 1203, 1314, 1403, 1457, 1488, 1507, 1644, 3031, 3134, 3182, 3184, 3222, 3287, 3794
T	0.371, 0.146, 0.119	199i, 72, 135, 164, 219, 423, 559, 612, 922, 941, 947, 1004, 1060, 1199, 1316, 1408, 1460, 1488, 1503, 1655, 3030, 3119, 3172, 3192, 3202, 3300, 3800
R	0.273, 0.124, 0.094	61, 70, 123, 206, 312, 387, 422, 597, 923, 941, 950, 1025, 1069, 1201, 1327, 1410, 1463, 1491, 1505, 1688, 3039, 3125, 3170, 3182, 3198, 3282, 3717
Propene	1.552, 0.312, 0.273	199, 422, 581, 908, 942, 948, 1013, 1064, 1199, 1327, 1408, 1463, 1492, 1505, 1696, 3033, 3118, 3167, 3184, 3200, 3283
OH	18.956, 18.956, 0.000	3805

Table 12: Unscaled vibrational frequencies and rotational constants for the various species at the UCCSD(T)/cc-pVTZ level of theory.

species	B (cm^{-1})	vibrational frequencies (cm^{-1})
$\mathbf{A_{dir}}$	0.577, 0.093, 0.088	860i, 81, 96, 117, 355, 413, 582, 723, 928, 937, 960, 988, 1011, 1125, 1195, 1318, 1321, 1436, 1464, 1492, 1680, 3071, 3138, 3143, 3163, 3234, 3751
$\mathbf{A_{con}}$	0.462, 0.108, 0.097	1020i, 69, 120, 154, 329, 420, 568, 788, 926, 933, 948, 961, 1015, 1169, 1218, 1318, 1320, 1429, 1449, 1482, 1679, 3074, 3139, 3145, 3163, 3233, 3745
C	0.288, 0.205, 0.138	244i, 135, 160, 208, 253, 418, 580, 674, 886, 927, 944, 1005, 1055, 1196, 1303, 1402, 1451, 1486, 1501, 1628, 3035, 3102, 3130, 3139, 3182, 3241, 3746
T	0.379, 0.156, 0.127	222i, 93, 137, 173, 242, 419, 630, 667, 930, 940, 941, 994, 1057, 1193, 1308, 1406, 1452, 1483, 1497, 1641, 3030, 3090, 3121, 3145, 3162, 3251, 3752
R	0.271, 0.123, 0.094	59, 72, 120, 208, 297, 368, 419, 598, 929, 938, 945, 1025, 1074, 1194, 1320, 1411, 1456, 1487, 1501, 1688, 3033, 3099, 3116, 3136, 3150, 3230, 3681
Propene	1.547, 0.310, 0.271	200, 418, 583, 925, 931, 942, 1014, 1068, 1192, 1320, 1408, 1456, 1488, 1502, 1696, 3029, 3089, 3112, 3138, 3151, 3230
OH	18.852, 18.852, 0.000	3744