Electronic Supplementary Material for PCCP

Quantum Chemistry and TST Study of the Mechanisms and Branching Ratios for the Reactions of OH with Unsaturated Aldehydes

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Supplementary information

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Table S1. Gibbs Free Energies of activation (kcal/mol) at 298 *K* at M05-2X level using different basis sets and calculated from experimental data.

Basis set	$\Delta G^{\neq}$ abstraction ("error")	$\Delta G^{\neq}$ addition β ("error")	$\Delta G^{\neq}$addition-$\Delta G^{\neq}$abstract.
6-311++G(d,p)	5.83 (0.02)	5.84 (-0.47)	0.01
aug-cc-pVTZ	5.60(-0.21)	5.65(-0.66)	0.05
Aug-cc-pVQZ	5.61(-0.2)	5.96(-0.35)	0.35
[b] From Experiment	5.81	6.31	0.5

Table S2. Gibbs Free Energies of activation (kcal/mol) at 298 *K* and calculated rate constants at M05-2X/6-311++G(d,p) level compared with experimental data (or calculated from it) for two model reactions Acetaldehyde +OH and propene + OH.

Basis set	Acetaldehyde	Propene
$\Delta G^{\neq}_{\text{calc (error)}}$	5.44 (0.32)	4.78 (0.58)
$\Delta G^{\neq}_{\text{from exp}}$	5.76	5.35
k_{calc} (cm^3 $molec^{-1}$ s^{-1}) x 10^{11}	2.6	7.9
k_{exp} (cm^3 $molec^{-1}$ s^{-1}) x 10^{11}	1.5	3.0

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Cartesian coordinates and absolute energies of stationary points used for kinetic calculation (M05-2X//6-311++G(d,p))

OH radical

8	0.000000	0.000000	0.107744
1	0.000000	0.000000	-0.861953

Sum of electronic and zero-point Energies=	-75.737320
Sum of electronic and thermal Energies=	-75.734959
Sum of electronic and thermal Enthalpies=	-75.734015
Sum of electronic and thermal Free Energies=	-75.754236

Acrolein

6	-1.748223	0.145840	-0.000170
1	-2.675179	-0.409959	-0.000383
1	-1.818189	1.227594	-0.000331
6	-0.562719	-0.455774	0.000245
1	-0.446929	-1.531819	0.000401
6	0.672842	0.348486	0.000186
1	0.516465	1.442985	0.000731
8	1.781554	-0.120015	-0.000248

Sum of electronic and zero-point Energies=	-191.872968
Sum of electronic and thermal Energies=	-191.868628
Sum of electronic and thermal Enthalpies=	-191.867684
Sum of electronic and thermal Free Energies=	-191.899252

PRC abstraction channel acrolein

6	-2.681570	0.439570	0.000018
1	-3.705564	0.093889	0.000056
1	-2.518992	1.511031	-0.000015
6	-1.653019	-0.403998	0.000016
1	-1.769667	-1.479583	0.000046
6	-0.281400	0.119412	-0.000035
1	-0.192364	1.219099	-0.000083
8	0.703439	-0.581909	-0.000029
8	3.461374	0.307490	0.000028
1	2.564027	-0.078988	0.000010

Sum of electronic and zero-point Energies=	-267.618203
Sum of electronic and thermal Energies=	-267.611078
Sum of electronic and thermal Enthalpies=	-267.610134
Sum of electronic and thermal Free Energies=	-267.650961

TS abstraction channel acrolein

6	-0.869628	-1.626674	-0.003209
1	-1.581830	-2.437715	0.056110
1	0.181657	-1.876057	-0.082262
6	-1.257236	-0.354442	0.026483
1	-2.289693	-0.041406	0.112117
6	-0.240530	0.706600	-0.050528
1	0.817831	0.289958	-0.176510
8	-0.438911	1.883720	0.005787
8	2.237165	-0.457376	-0.021019
1	2.690361	0.301567	0.375928

Sum of electronic and zero-point Energies=	-267.613098
Sum of electronic and thermal Energies=	-267.606600
Sum of electronic and thermal Enthalpies=	-267.605656
Sum of electronic and thermal Free Energies=	-267.644190

TS beta addition acrolein

6	1.051049	0.992094	0.197847
1	1.828715	1.526975	-0.325682
1	1.174612	0.860411	1.263973
6	-0.104009	0.640923	-0.405834
1	-0.292125	0.819518	-1.456848
6	-1.152717	-0.052801	0.356336
1	-0.917798	-0.233739	1.419389
8	-2.197773	-0.412024	-0.125126
1	1.609827	-1.264059	-0.863319
8	1.926627	-0.986777	0.009175

Sum of electronic and zero-point Energies=	-267.613135
Sum of electronic and thermal Energies=	-267.606948
Sum of electronic and thermal Enthalpies=	-267.606004
Sum of electronic and thermal Free Energies=	-267.643532

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Methacrolein

6	1.501862	-0.936139	-0.000106
1	2.531866	-0.604949	-0.000557
1	1.321046	-2.004236	-0.000256
6	0.485950	-0.073830	0.000207
6	-0.884796	-0.635550	0.000219
1	-0.943907	-1.738561	0.000553
8	-1.881643	0.040727	-0.000242
6	0.608953	1.417339	0.000047
1	0.109648	1.834109	-0.874618
1	0.109649	1.834266	0.874622
1	1.653029	1.722635	-0.000017

Sum of electronic and zero-point Energies=	-231.169145
Sum of electronic and thermal Energies=	-231.163488
Sum of electronic and thermal Enthalpies=	-231.162544
Sum of electronic and thermal Free Energies=	-231.197710

PRC abstraction channel methacrolein

6	-2.164036	-1.182127	0.006086
1	-1.781542	-2.195446	0.001396
6	-1.334493	-0.138110	0.000722
6	0.110424	-0.432255	-0.011668
8	0.962019	0.427065	-0.016554
8	3.792421	-0.141338	0.014590
1	2.861513	0.155318	-0.018892
1	-3.238316	-1.055626	0.015308
6	-1.740666	1.301925	0.006542
1	-1.325249	1.805424	0.879340
1	-1.339891	1.808471	-0.871322
1	-2.823751	1.399435	0.015682
1	0.384350	-1.499995	-0.015899

Sum of electronic and zero-point Energies=	-306.914428
Sum of electronic and thermal Energies=	-306.905966
Sum of electronic and thermal Enthalpies=	-306.905022
Sum of electronic and thermal Free Energies=	-306.949511

TS abstraction channel acrolein

6	-0.328553	-1.664140	-0.036104
1	-1.003899	-2.508435	0.007407
1	0.734582	-1.862368	-0.089321
6	-0.782549	-0.411134	-0.016742
6	0.231346	0.663870	-0.072350
1	1.299518	0.267565	-0.171456
8	0.007520	1.837667	-0.024050
8	2.758629	-0.376017	0.016313
1	3.151371	0.411593	0.421630
6	-2.216950	0.012149	0.064871
1	-2.377400	0.629780	0.948566
1	-2.481202	0.619457	-0.800963
1	-2.871922	-0.855261	0.107980

Sum of electronic and zero-point Energies=	-306.908965
Sum of electronic and thermal Energies=	-306.901061
Sum of electronic and thermal Enthalpies=	-306.900117
Sum of electronic and thermal Free Energies=	-306.942169

TS beta addition methacrolein

6	1.103807	0.234945	0.994438
1	1.792860	1.061284	1.093726
1	1.339458	-0.674083	1.529627
6	-0.074033	0.366375	0.347785
6	-0.957143	-0.818431	0.292744
1	-0.574852	-1.719345	0.800926
8	-2.022251	-0.817851	-0.271634
1	1.729356	-0.206279	-1.453799
8	2.084922	-0.743807	-0.731470
6	-0.535075	1.601240	-0.356829
1	-0.743264	1.386472	-1.405965
1	-1.475376	1.945207	0.075813
1	0.205114	2.395236	-0.284327

Sum of electronic and zero-point Energies=	-306.910381
Sum of electronic and thermal Energies=	-306.902645
Sum of electronic and thermal Enthalpies=	-306.901701
Sum of electronic and thermal Free Energies=	-306.943016

Crotonaldehyde

6	1.032223	0.392224	0.000035
1	0.939714	1.475648	-0.000013
6	-0.087244	-0.332087	-0.000039
1	-0.080909	-1.415375	-0.000100
6	-1.397180	0.331667	-0.000036
1	-1.359766	1.437121	-0.000075
8	-2.453377	-0.249381	0.000043
6	2.417135	-0.162496	0.000004
1	2.965025	0.185957	0.877348
1	2.408205	-1.250312	-0.000108
1	2.965140	0.186161	-0.877178

Sum of electronic and zero-point Energies=	-231.168438
Sum of electronic and thermal Energies=	-231.162663
Sum of electronic and thermal Enthalpies=	-231.161719
Sum of electronic and thermal Free Energies=	-231.197074

PRC abstraction channel crotonaldehyde

6	-1.940709	-0.440438	-0.000137
1	-1.724125	-1.505786	-0.000713
6	-0.912161	0.410329	0.000015
1	-1.042584	1.485340	0.000573
6	0.456268	-0.101010	-0.000580
1	0.552828	-1.200368	-0.001171
8	1.442066	0.603176	-0.000447
8	4.164692	-0.335471	0.000634
1	3.272464	0.065186	-0.000330
6	-3.378861	-0.050470	0.000436
1	-3.880808	-0.463128	-0.876487
1	-3.880301	-0.463864	0.877303
1	-3.498754	1.030517	0.000925

Sum of electronic and zero-point Energies=	-306.914498
Sum of electronic and thermal Energies=	-306.905956
Sum of electronic and thermal Enthalpies=	-306.905011
Sum of electronic and thermal Free Energies=	-306.949461

TS abstraction channel crotonaldehyde

6	1.227589	0.237596	-0.038778
1	0.753064	1.210676	-0.128766
6	0.438720	-0.838107	0.012466
1	0.817897	-1.848229	0.109756
6	-1.014024	-0.667461	-0.054955
1	-1.322271	0.422981	-0.192731
8	-1.839222	-1.532114	0.018269
8	-1.578012	2.034138	-0.021912
1	-2.418871	1.928018	0.447639
6	2.715980	0.205520	0.026149
1	3.066425	0.796221	0.874481
1	3.092665	-0.810533	0.121116
1	3.139373	0.659390	-0.871649

Sum of electronic and zero-point Energies=	-306.909059
Sum of electronic and thermal Energies=	-306.901072
Sum of electronic and thermal Enthalpies=	-306.900128
Sum of electronic and thermal Free Energies=	-306.942409

TS beta addition channel crotonaldehyde

6	-0.858644	-0.366443	0.401949
1	-0.807620	-0.046149	1.436412
6	0.308273	-0.507536	-0.274617
1	0.343342	-0.887710	-1.288797
6	1.576255	-0.105833	0.341696
1	1.492909	0.299403	1.364822
8	2.645703	-0.195254	-0.210783
1	-0.523748	1.793959	-0.951934
8	-0.889724	1.748948	-0.056231
6	-2.187621	-0.817405	-0.099582
1	-2.935151	-0.049783	0.090703
1	-2.156919	-1.034695	-1.165472
1	-2.490215	-1.721274	0.433696

Sum of electronic and zero-point Energies=	-306.909910
Sum of electronic and thermal Energies=	-306.902357
Sum of electronic and thermal Enthalpies=	-306.901413
Sum of electronic and thermal Free Energies=	-306.942052

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TS alpha addition channel (3C´) crotonaldehyde

6	0.907178	-0.558191	-0.189906
1	0.540251	-1.106815	-1.051476
6	-0.014903	-0.053932	0.660412
1	0.280106	0.438975	1.576329
6	-1.460949	-0.325220	0.455368
1	-2.130334	0.054678	1.241561
8	-1.900037	-0.904326	-0.506850
1	-0.498532	1.577223	-1.115692
8	-0.261390	1.890457	-0.230453
6	2.374232	-0.373120	-0.041436
1	2.771344	0.160666	-0.907430
1	2.617086	0.190352	0.856492
1	2.878147	-1.341349	-0.007996

Sum of electronic and zero-point Energies= -306.907969
Sum of electronic and thermal Energies= -306.900196
Sum of electronic and thermal Enthalpies= -306.899252
Sum of electronic and thermal Free Energies= -306.940669