Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Computational Methods

The electronic structure calculations were performed using Gaussian 09. The cc-pVTZ basis set was used with either MP2 (for the methylhydroxycarbene calculations) or M06-2X (for the Phenyl Pyruvic Acid Derivative calculations) methods, and no normal mode scaling was used.

For the methylhydroxycarbene calculations, the barrier heights were corrected using single point energy calculations at the CCSD(T) level of theory.

1D-SCTST calculations were performed using the in-house *pySCTST* code, available at bitbucket.org/timothyburd/pysctst, along with tutorials on running 1D and FD SCTST calculations.

8 single point energies were calculated along the reaction mode away from the TS with a step size of $\delta Q = 0.02 a_0 $Da^{0.5}$ in order to determine the anharmonicity of the reaction path, calculated using Richardson extrapolation. Full details of the 1D-SCTST method can be found in reference 12. Reaction coordinates are given in atomic units, and refer to mass-weighted coordinates (in contrast to the reaction coordinates used in ref. 7) . The atomic unit is thus $m_e^{0.5}$ a_0.

For the methylhydroxycarbene calculations, the methane group was treated as a hindered rotor, via the `tanh' approximation, discussed in ref. 10, but its anharmonic treatment had a negligible effect on the rates.

Optimised Geometries

Phenyl Pyruvic Acid Derivative structures have been optimised at M06-2X/cc-pVTZ level of theory

Methylhydroxycarbene decay structures have been optimised at MP2/cc-pVTZ level of theory.

Coordinates are in Angstroms

Phenyl Pyruvic Acid Derivative Carbene reactant

C	-3.114536302914145	0.44561854408777096	-0.4401657767215406
C	-3.8673730678063194	-0.6588707257334379	0.25608440029427987
O	-5.063375021819029	-0.20866259702840492	0.49346192378487996
H	-5.591410313030114	-0.9039806395050547	0.9078812629147156
H	-3.471244578001133	1.4418952193888728	-0.166726143098634
H	-3.381972420053937	0.2958888235951704	-1.4964333019668572
C	-1.6245585183760336	0.31852631598512887	-0.2949062574097229
C	-1.008643043404537	-0.9307585196766696	-0.3791445605438571
C	-0.8285444017559481	1.4319729297762174	-0.07538151923826782
C	0.3611366670349208	-1.0562096131500274	-0.2558546220253765
H	-1.6192921891361942	-1.8105894958231343	-0.5248618467161641
C	0.5520863847311405	1.3240849738313198	0.051692930256470204
H	-1.2833753024268428	2.410409088202565	0.0027785015631488007
C	1.138261687854815	0.07578589106011543	-0.040483756340862986
H	0.8014546986227471	-2.0411503596076175	-0.32626733502969935
H	1.1236505442140943	2.2220144031698577	0.22251325110749606
C	2.9172554360749587	-1.0015649384070355	1.2597690246842876
H	2.4603241834395635	-1.969879550834827	1.0902857201623553
H	3.995851134286019	-1.1058053869844027	1.3464505003578218
H	2.5008054725446116	-0.545270942132602	2.1531249659178764
C	3.170595854633483	-0.7163884040823311	-1.1626914076671948
H	2.936524101161259	-0.05619320441923054	-1.9928137153137293
H	4.246097681255566	-0.8256633864071175	-1.0482018337581953
H	2.710957389611452	-1.6857700282652455	-1.3181207815648863
C	3.3370672518241857	1.1878074015253137	0.3198339726631214
H	3.1603774692058635	1.8469045039765617	-0.5244321669943438
H	2.9801790776535664	1.6368956764267644	1.2413969657085904
H	4.397150151089309	0.9666850641334763	0.40188125090569565
N	2.620633629549431	-0.10387316255261064	0.09304781774671875

Phenyl Pyruvic Acid Derivative Decay - Aldehyde-pathway TS

C	-3.1196411008112426	0.403843173816824	-0.5809649819995297
C	-3.885283615463604	-0.5794154082566595	0.261848282582992
O	-4.9988187680100715	-0.1715175453194831	0.7481849956028459
H	-4.656879236119891	-1.2920348852610848	0.9337983569809373
H	-3.4971823946468197	1.4093893769482475	-0.3784230956846089
H	-3.3836671259378734	0.14960657566452684	-1.6145191588896526
C	-1.6332929004086263	0.29473296563271034	-0.40076503043282363
C	-1.0015176193810962	-0.9458664284214001	-0.4918020763911663
C	-0.8594093291758302	1.4114765841509014	-0.12676114785327963
C	0.36433376416350755	-1.0609629050867107	-0.3227077478093922
H	-1.5915998537067508	-1.830661219073207	-0.6872876740973399
C	0.5171007390464235	1.3137890110250074	0.04422775504468988
H	-1.3278532500212599	2.3826309625641597	-0.04178261364856997
C	1.1205387229342223	0.0741655673828901	-0.0555720069989998
H	0.8175596460203867	-2.039334413933556	-0.4003583339355013
H	1.0724348531105894	2.2135921616051757	0.2540396823171878
C	2.868239174784608	-1.0122741409868472	1.2792213830548007
H	2.4300430284402306	-1.9821734803994362	1.0730324952657604
H	3.944609206576541	-1.1054390693539369	1.39924442015001
H	2.4171395608168145	-0.5812068054000414	2.1683104837919323
C	3.198074323094313	-0.6695407321574529	-1.1272395933754569
H	2.9827286640252546	0.0058005495066316	-1.950246552532591
H	4.270546689577177	-0.7674416695336126	-0.9794216663078938
H	2.7574213921852144	-1.6413388546442436	-1.3185843619661826
C	3.292664368016723	1.2027933296318278	0.4023652437886134
H	3.1366646204653885	1.8787125204329973	-0.4326442863125317
H	2.9006712605059826	1.6268903536184018	1.321538721276042
H	4.3518828510208065	0.9912454272149671	0.5147375500544812
N	2.599313016337846	-0.09179188972833986	0.12314079733088668

Phenyl Pyruvic Acid Derivative Decay - Enol-pathway TS

C	-3.0806166418515906	0.5013696982095898	0.04581255547928395
C	-3.939787222146487	-0.5860374048350416	-0.08954397722856557
O	-5.2216471938875895	-0.23105875656512337	0.08140727068930799
H	-5.779384164596387	-0.9870174071584887	-0.12066780089322117
H	-3.457456151457462	1.497129090618796	0.291185592351541
H	-3.378493857801833	-0.10533375567713281	-1.1348049171201362
C	-1.6099690868761574	0.33545483880524946	0.02862659704931935
C	-1.0152045285691844	-0.9292785433201957	0.06076997818546413
C	-0.7891705852953462	1.4552048940206936	0.0001416343590977812
C	0.3579606142255419	-1.0607210869779709	0.03467601759143665
H	-1.6476788473967103	-1.8039417071476342	0.11320433317753789
C	0.5951178581781221	1.3365842823621261	-0.012467016232536052
H	-1.2294726399649087	2.4432950915494165	-0.012372286738835789
C	1.160438446287679	0.07480868861484827	-4.0788798849047516e-05
H	0.7836543256601685	-2.054187931319085	0.05929215187598624
H	1.1872020333829056	2.2370891272118745	-0.033395525590404186
C	3.0674717635858846	-0.8420705204493854	1.240475572937565
H	2.591477923344301	-1.8157742259375003	1.263836629961933
H	4.148622096519197	-0.9537340181872888	1.2225308139737836
H	2.7549372756176997	-0.25404000194022147	2.098575199107139
C	3.0495534899413634	-0.9139217043250498	-1.2117629203498324
H	2.7285957761388904	-0.37483454553735357	-2.098416202523224
H	4.130430449929023	-1.0287448186282517	-1.2005251279487217
H	2.5705728518270696	-1.8856511343184699	-1.173600665690491
C	3.391273736088321	1.1803743244566858	-0.048868422407865486
H	3.1223544251946302	1.7161963101138722	-0.9539228974081403
H	3.14583798674265	1.763539265446578	0.8331940543364447
H	4.452492879362689	0.9499428444995586	-0.056263462747959486
N	2.646725452637962	-0.1151524191630315	-0.00514620479122401

Phenyl Pyruvic Acid Derivative Decay - Aldehyde product

C	3.2248453821717167	0.6900533076477382	-0.5137507038837755
H	3.5625659164768155	0.5391668407041453	-1.544388790501367
H	3.515140943968642	1.7081852127809458	-0.2500307612043781
C	4.030309577122899	-0.27282472282790693	0.3442569280032513
O	3.5582623140397187	-1.2054770518422	0.9262604975333534
H	5.111926226303672	-0.05925887192137512	0.38541722290508684
C	1.7453461742026264	0.4883672850318218	-0.3952558215547653
C	0.9183851235707349	1.492910230619788	0.0952603304079867
C	1.1724053496295161	-0.730458548696225	-0.7373514046285218
C	-0.44341169309345135	1.291158181505275	0.24128078379028844
H	1.3395461136541624	2.4494886080507094	0.3740215790595385
C	-0.18957206251550746	-0.9514948524575855	-0.5973986172363742
H	1.7956260683315042	-1.532274479556469	-1.1071112957900773
C	-0.9904607473756285	0.06458993911330957	-0.10362547216439372
H	-1.0510260683926076	2.097005246749989	0.6283011479886568
H	-0.5827454092993898	-1.9168742988328518	-0.8717164934624115
C	-2.923935123552557	-1.489619425732854	-0.32573677719836364
H	-3.995818759224433	-1.539823515226686	-0.1586613157578935
H	-2.7058813048696613	-1.6370160060320915	-1.3788864173221815
H	-2.419416710886508	-2.234823349160381	0.2812832680657663
C	-3.217671152134382	0.8759752428393585	-0.7399060605178626
H	-4.282014335390355	0.7083045713421653	-0.5961031702641019
H	-2.9506580910052977	1.8760477427666715	-0.41796536618418784
H	-2.9427110241145393	0.7339773442914534	-1.7810676889501933
C	-2.8135444028353356	0.05252733502592438	1.5354607878201392
H	-2.2472733383754013	-0.67267617590789	2.1127673349427933
H	-2.5515785016218526	1.0584610716662723	1.8432650877285417
H	-3.8819931122076787	-0.10938311915806392	1.6533749690731152
N	-2.465137955039349	-0.12739917945885126	0.08543041026451945

Phenyl Pyruvic Acid Derivative Decay - Enol Product

C	-3.0579104469138945	-0.5128353680750728	-0.09683088232291359
H	-3.408983905504024	-1.5249468516300795	-0.25305111049960677
C	-3.9756413804530113	0.43642553792761196	0.09537903385175363
H	-3.716209063292447	1.4696708526026274	0.299681786960218
O	-5.284442070776174	0.14654516645137505	0.057028548742817514
H	-5.82013969978948	0.9216392247265218	0.24238679855152695
C	-1.6198192337600459	-0.297365349187071	-0.07271814494989784
C	-0.7687479170127003	-1.4091807700010817	-0.015712571388084615
C	-1.0176421145847991	0.9633012457686922	-0.11644393011523073
C	0.6039231393730427	-1.2723723800377307	0.01572322414862342
H	-1.198212030871289	-2.40139080259788	0.009084730629535104
C	0.3581055473959777	1.1164408434285076	-0.07875459054313447
H	-1.6233774530572704	1.8542254166441818	-0.19935441068632992
C	1.169939759556054	-0.004849345288880193	-0.011243715587435386
H	1.212286911621194	-2.1651320973110657	0.062183635937522734
H	0.7592266643471278	2.1166753403745058	-0.11567565847358052
C	3.13319225487839	1.522675469591953	-0.013399802770944661
H	2.7415937230610226	2.0507225667465483	0.8504201589011297
H	4.21866735733712	1.5114301628744886	0.019438117153491346
H	2.7953901902408553	1.9865384885597495	-0.9348414975522072
C	3.18714789856239	-0.5165273358532648	1.2859808334129608
H	2.9091219770962264	-1.564103297968951	1.3093128915263303
H	4.269595784593262	-0.41570604091956853	1.2952846736226264
H	2.7437894168830885	0.004337152563131705	2.1296110719322936
C	3.2521999596646105	-0.6022205117063028	-1.1626900159311377
H	2.9768358154300034	-1.6500939857151617	-1.1256438859635933
H	2.8523967574916296	-0.1446524197015853	-2.062889197442001
H	4.333595100557887	-0.4973209247612457	-1.1234830331689019
N	2.663067746596934	0.10497052949991605	0.023652848882346495

Methylhydroxycarbene

C	1.1086313202776528	-0.372888156623166	-1.5654270400465353e-31
C	0.0	0.6266203488817468	0.0
O	-1.1333557388771678	-0.048479062390889845	0.0
H	-1.844475395379819	0.6054596424388753	-3.1308540853848427e-31
H	0.7882924421775306	-1.4157841236664261	-4.174472112082533e-31
H	1.7356204792145151	-0.16211807696738256	0.8673574491292323
H	1.7356204792145151	-0.16211807696738256	-0.8673574491292323

Methylhydroxycarbene decay – Aldehyde pathway TS

C	1.1084376943372454	-0.4508023116287953	3.913567608053996e-32
C	-1.4687618002440926e-17	0.5388877314775579	-5.218090144071995e-32
O	-1.2176793861238764	0.038803765181714155	-7.827135226691537e-32
H	-1.0879962138048551	1.1898371877091276	0.0
H	0.7080621711384968	-1.4667304318204268	-2.0872360586871526e-31
H	1.735371490754607	-0.2810246909148493	0.8750802189686077
H	1.735371490754607	-0.2810246909148493	-0.8750802189686077

Methylhydroxycarbene decay – Enol pathway TS

C	1.1577267623536363	0.1941161691143368	-0.025926831773532416
C	-0.022160343038365515	-0.5328089194278716	-0.13285135150072258
O	-1.11602374066139	0.26347573321885465	0.0165285165514858
H	-1.8748350961521352	-0.32499032776641695	0.023156318627181406
H	2.082534149857366	-0.33959074763101726	-0.19272840294471122
H	1.192369665781681	1.2773037718555385	0.09880866626249735
H	0.7147226653587608	-0.6883720587402014	0.8912043860824418

Methylhydroxycarbene decay – Aldehyde product

C	1.1657086067705043	-0.14996293682582423	-1.1450248742040635e-07
H	1.7010629109030324	0.21619288924191443	-0.8762875103097992
H	1.1446194133355219	-1.2351516004244583	-1.1315974841023228e-05
H	1.701047146714006	0.21617699646282657	0.8763041370576746
C	-0.2279861896505409	0.40119036455141177	-9.680518918193358e-07
O	-1.2342176502782867	-0.2761098496433988	2.2466540475806512e-07
H	-0.29932274128294445	1.5042959439258508	-6.124268795195286e-07

Methylhydroxycarbene decay – Enol product

C	1.225233147346561	-0.18114498162525847	-4.517313584189572e-07
H	2.115760414148962	0.4239374368408941	-7.541801711948078e-07
H	1.3098197692067852	-1.2566325649136112	-4.689302918507202e-07
C	0.034653914335717975	0.4133368272451133	-3.03010214759109e-08
H	-0.062339787135591004	1.4921552799559947	0.0
O	-1.1321282805925792	-0.2968097713281639	5.03819285435105e-07
H	-1.8655365212556891	0.32186694396455023	8.47382443597466e-08

Rate Data

Rates are given in units of s^{-1}

a -> methylhydroxycarbene (Aldehyde Pathway)

b -> methylhydroxycarbene (Enol Pathway)

c -> Phenyl Pyruvic Acid Derivative (Aldehyde Pathway)

d -> Phenyl Pyruvic Acid Derivative (Enol Pathway)

e -> Deuterated Phenyl Pyruvic Acid Derivative (Enol Pathway)

Temperature (K)	a	b	c	d	e
1000	1.25e+07	2.80e+07	3.03e+06	1.52e+08	1.09e+08
955	6.34e+06	1.59e+07	1.38e+06	9.19e+07	6.52e+07
913	3.22e+06	9.02e+06	6.30e+05	5.56e+07	3.89e+07
875	1.65e+06	5.14e+06	2.89e+05	3.36e+07	2.32e+07
840	8.43e+05	2.93e+06	1.33e+05	2.04e+07	1.39e+07
808	4.33e+05	1.67e+06	6.13e+04	1.24e+07	8.30e+06
778	2.23e+05	9.58e+05	2.84e+04	7.54e+06	4.96e+06
750	1.16e+05	5.50e+05	1.32e+04	4.59e+06	2.97e+06
724	6.00e+04	3.16e+05	6.17e+03	2.80e+06	1.78e+06
700	3.13e+04	1.82e+05	2.89e+03	1.71e+06	1.07e+06
677	1.63e+04	1.05e+05	1.36e+03	1.05e+06	6.41e+05
656	8.59e+03	6.04e+04	6.43e+02	6.42e+05	3.85e+05
636	4.53e+03	3.49e+04	3.05e+02	3.94e+05	2.31e+05
618	2.40e+03	2.02e+04	1.46e+02	2.42e+05	1.39e+05
600	1.28e+03	1.17e+04	6.99e+01	1.49e+05	8.35e+04
583	6.82e+02	6.82e+03	3.37e+01	9.19e+04	5.03e+04
568	3.67e+02	3.97e+03	1.63e+01	5.67e+04	3.03e+04
553	1.98e+02	2.32e+03	7.97e+00	3.51e+04	1.82e+04
538	1.08e+02	1.35e+03	3.91e+00	2.17e+04	1.10e+04
525	5.89e+01	7.93e+02	1.94e+00	1.35e+04	6.61e+03
512	3.24e+01	4.65e+02	9.64e-01	8.37e+03	3.99e+03
500	1.80e+01	2.73e+02	4.84e-01	5.21e+03	2.40e+03
488	1.01e+01	1.61e+02	2.45e-01	3.25e+03	1.45e+03
477	5.67e+00	9.50e+01	1.25e-01	2.03e+03	8.76e+02
467	3.22e+00	5.62e+01	6.45e-02	1.27e+03	5.29e+02
457	1.85e+00	3.33e+01	3.36e-02	7.97e+02	3.19e+02
447	1.07e+00	1.98e+01	1.77e-02	5.01e+02	1.93e+02
438	6.29e-01	1.18e+01	9.41e-03	3.15e+02	1.17e+02
429	3.73e-01	7.05e+00	5.07e-03	1.99e+02	7.05e+01
420	2.24e-01	4.22e+00	2.76e-03	1.26e+02	4.26e+01
412	1.37e-01	2.54e+00	1.53e-03	7.99e+01	2.58e+01
404	8.43e-02	1.53e+00	8.53e-04	5.08e+01	1.56e+01
396	5.28e-02	9.24e-01	4.84e-04	3.24e+01	9.44e+00
389	3.35e-02	5.60e-01	2.78e-04	2.07e+01	5.71e+00
382	2.16e-02	3.41e-01	1.62e-04	1.33e+01	3.46e+00

375	1.42e-02	2.08e-01	9.59e-05	8.56e+00	2.09e+00
368	9.45e-03	1.27e-01	5.75e-05	5.53e+00	1.27e+00
362	6.40e-03	7.84e-02	3.49e-05	3.58e+00	7.68e-01
356	4.40e-03	4.84e-02	2.15e-05	2.33e+00	4.66e-01
350	3.07e-03	3.00e-02	1.34e-05	1.52e+00	2.82e-01
344	2.18e-03	1.87e-02	8.49e-06	1.00e+00	1.71e-01
339	1.57e-03	1.17e-02	5.44e-06	6.61e-01	1.04e-01
333	1.15e-03	7.38e-03	3.52e-06	4.39e-01	6.29e-02
328	8.50e-04	4.67e-03	2.31e-06	2.93e-01	3.82e-02
323	6.39e-04	2.97e-03	1.53e-06	1.97e-01	2.32e-02
318	4.87e-04	1.90e-03	1.03e-06	1.33e-01	1.40e-02
313	3.75e-04	1.22e-03	6.97e-07	9.06e-02	8.53e-03
309	2.93e-04	7.92e-04	4.77e-07	6.22e-02	5.18e-03
304	2.32e-04	5.16e-04	3.30e-07	4.31e-02	3.14e-03
300	1.85e-04	3.39e-04	2.30e-07	3.01e-02	1.91e-03
296	1.49e-04	2.24e-04	1.62e-07	2.12e-02	1.16e-03
292	1.22e-04	1.49e-04	1.15e-07	1.51e-02	7.04e-04
288	1.00e-04	9.98e-05	8.23e-08	1.09e-02	4.27e-04
284	8.33e-05	6.74e-05	5.94e-08	7.94e-03	2.60e-04
280	6.99e-05	4.58e-05	4.32e-08	5.86e-03	1.58e-04
276	5.91e-05	3.14e-05	3.16e-08	4.37e-03	9.59e-05
273	5.03e-05	2.17e-05	2.33e-08	3.31e-03	5.83e-05
269	4.32e-05	1.51e-05	1.73e-08	2.53e-03	3.54e-05
266	3.73e-05	1.06e-05	1.30e-08	1.97e-03	2.15e-05
262	3.25e-05	7.48e-06	9.75e-09	1.55e-03	1.31e-05
259	2.85e-05	5.33e-06	7.37e-09	1.23e-03	7.97e-06
256	2.51e-05	3.82e-06	5.61e-09	9.94e-04	4.84e-06
253	2.22e-05	2.76e-06	4.30e-09	8.12e-04	2.95e-06
250	1.98e-05	2.01e-06	3.31e-09	6.72e-04	1.79e-06
247	1.77e-05	1.47e-06	2.56e-09	5.62e-04	1.09e-06
244	1.60e-05	1.09e-06	1.99e-09	4.75e-04	6.64e-07
241	1.44e-05	8.07e-07	1.56e-09	4.06e-04	4.04e-07
239	1.31e-05	6.04e-07	1.22e-09	3.50e-04	2.46e-07
236	1.19e-05	4.55e-07	9.63e-10	3.05e-04	1.50e-07
233	1.09e-05	3.44e-07	7.63e-10	2.68e-04	9.11e-08
231	1.00e-05	2.63e-07	6.07e-10	2.37e-04	5.54e-08
228	9.25e-06	2.01e-07	4.85e-10	2.11e-04	3.38e-08
226	8.56e-06	1.55e-07	3.89e-10	1.90e-04	2.06e-08
223	7.94e-06	1.20e-07	3.13e-10	1.71e-04	1.25e-08
221	7.38e-06	9.40e-08	2.53e-10	1.56e-04	7.62e-09
219	6.89e-06	7.37e-08	2.05e-10	1.42e-04	4.64e-09
216	6.44e-06	5.81e-08	1.67e-10	1.31e-04	2.83e-09
214	6.04e-06	4.60e-08	1.37e-10	1.20e-04	1.72e-09
212	5.68e-06	3.66e-08	1.12e-10	1.12e-04	1.05e-09
210	5.35e-06	2.93e-08	9.21e-11	1.04e-04	6.39e-10
208	5.05e-06	2.35e-08	7.60e-11	9.69e-05	3.90e-10
206	4.77e-06	1.90e-08	6.29e-11	9.07e-05	2.37e-10
204	4.52e-06	1.54e-08	5.22e-11	8.53e-05	1.45e-10
202	4.29e-06	1.25e-08	4.34e-11	8.03e-05	8.82e-11
200	4.08e-06	1.02e-08	3.62e-11	7.59e-05	5.38e-11