Supporting Information: Temperature-Dependent Kinetics of the Reactions of the Criegee Intermediate CH_2OO with Aliphatic Aldehydes

Jonas J. Enders,[1] Zachary A. Cornwell,[1] Aaron W. Harrison,[2] and Craig Murray[1,1]

1. *Department of Chemistry, University of California, Irvine, Irvine CA 92697, USA*
2. *Department of Chemistry, Austin College, Sherman, TX 75090, USA*

[1] Email: craig.murray@uci.edu; Telephone: +1-949-824-4218

Reactant Concentrations

The concentrations of the liquid aldehydes CH_3CHO and C_2H_5CHO present in the flow reactor can be estimated based on the mole fraction of the aldehyde and the gas flow rates using the equation

$$[\mathrm{X}]_{\mathrm{est}} = \chi F P_{\mathrm{tot}} \frac{N_{\mathrm{A}}}{RT}$$

where χ is the mole fraction of X in the gas flow, F is the fractional contribution of the flow of X to the total flow rate, P_{tot} is the total pressure in the flow reactor (Torr), N_{A} is the Avogadro constant (6.02×10^{23} mol^{-1}), R is the gas constant (62.4×10^{3} Torr cm^3 mol^{-1} K^{-1}), and T is the temperature of the flow reactor (K). Absorbance measurements are done in the flow cell using an LED centered at 280 nm, covering the wavelength range 275–305 nm, to find the concentration in the flow reactor of each aldehyde experimentally. Plots of $[\mathrm{X}]_{\mathrm{exp}}$ versus $[\mathrm{X}]_{\mathrm{est}}$, shown in Figure S1 and Figure S2, are used to determine temperature-independent scale factors with which to correct the estimated aldehyde concentrations.

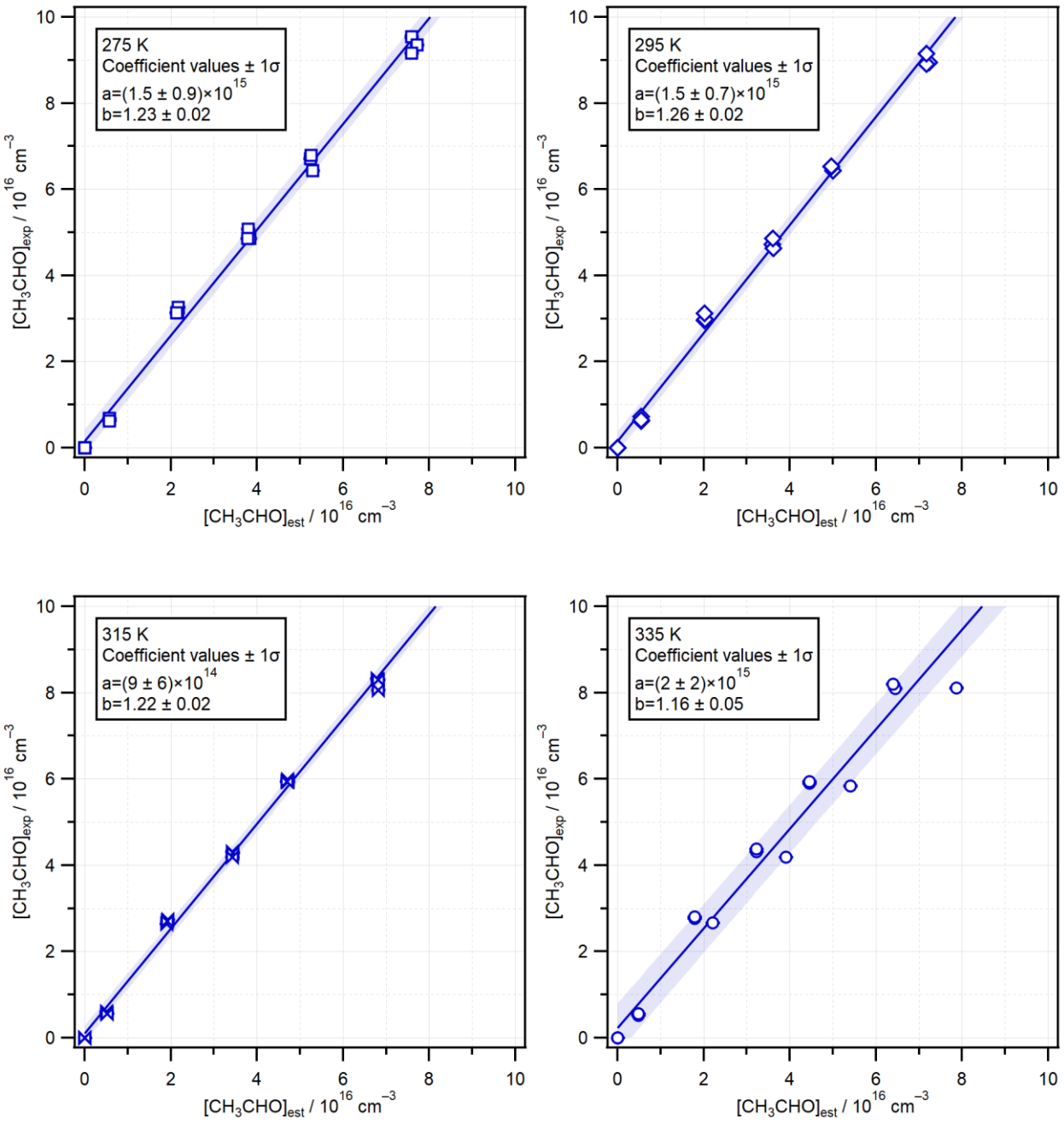


Figure S1: Experimental CH_3CHO concentrations plotted against estimated concentration values for derivation of a concentration scale factor at 4 temperatures over 275–335 K.

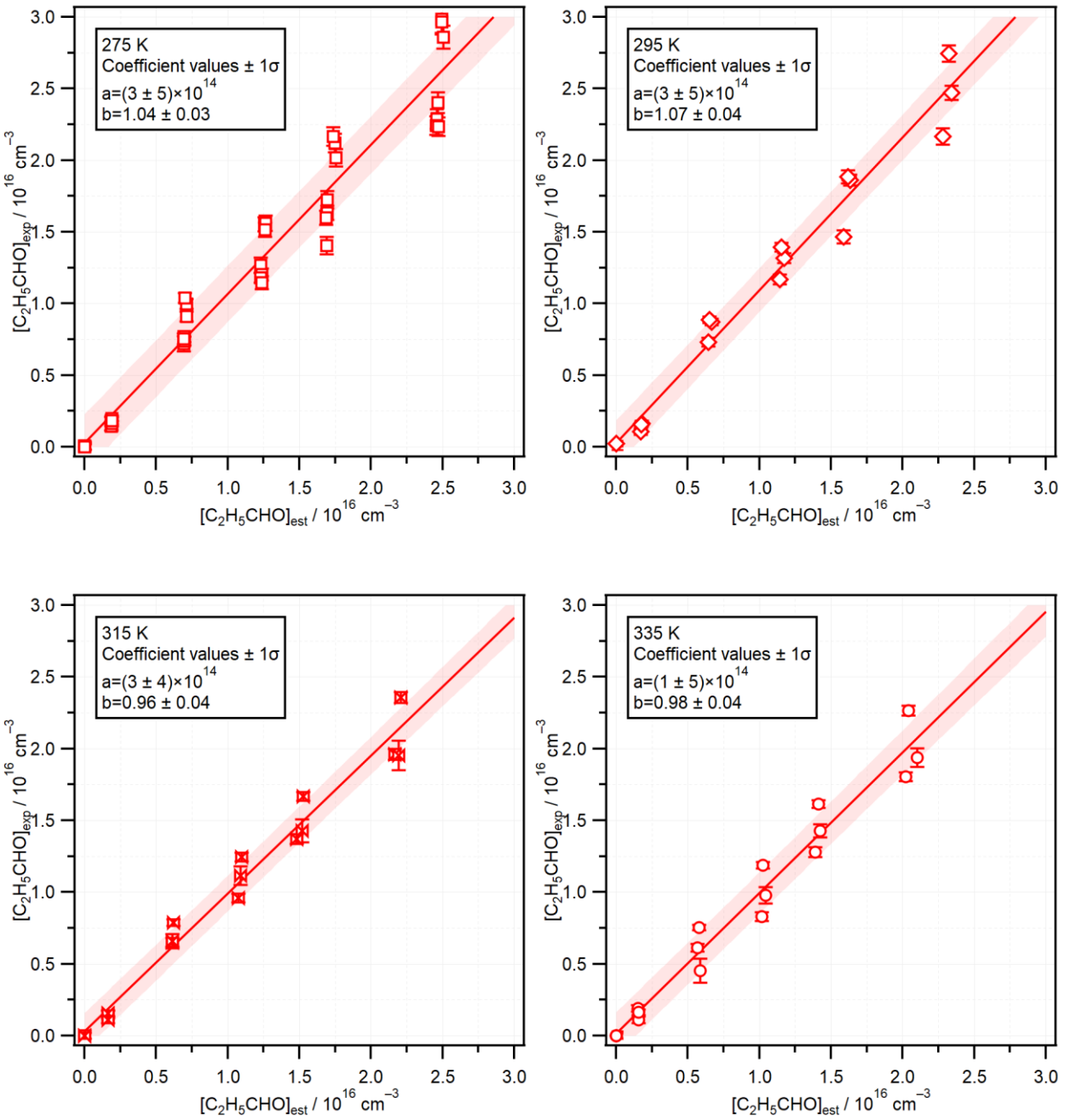


Figure S2: Experimental C_2H_5CHO concentrations plotted against estimated concentration values for derivation of a concentration scale factor at 4 temperatures over 275–335 K.

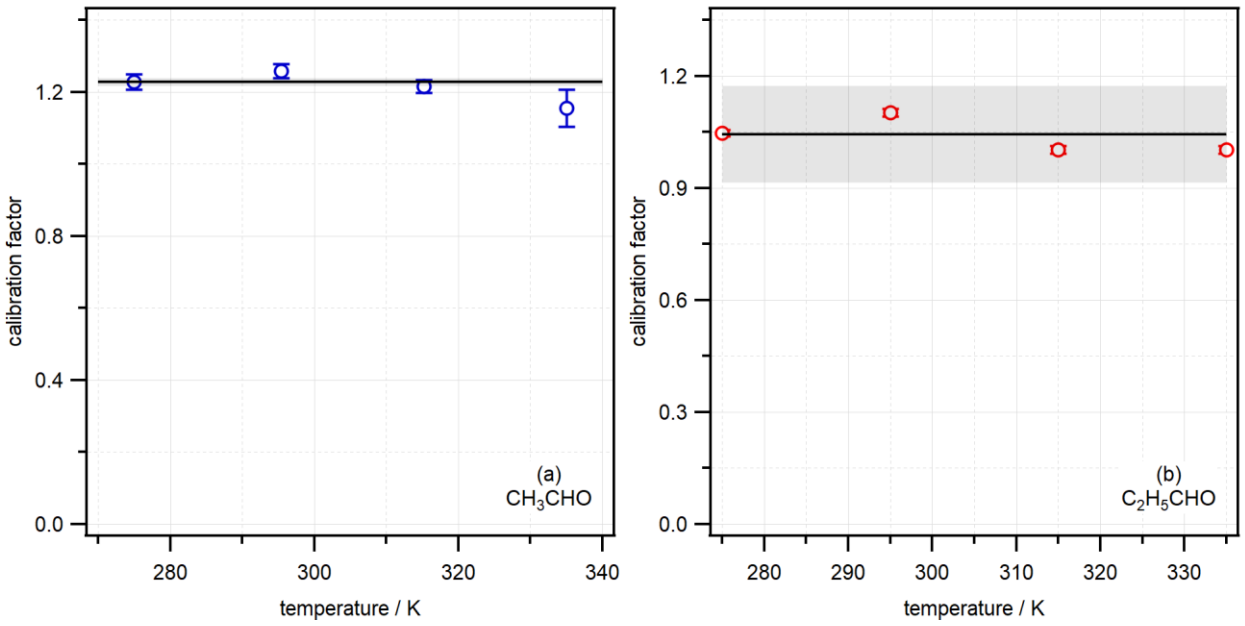


Figure S3: Scale factors determined from gradient of calibration plots shown above across temperature range 275–335 K. Solid lines represent the temperature-independent average, with shaded areas showing the estimated experimental uncertainty, based on variability in measurements.

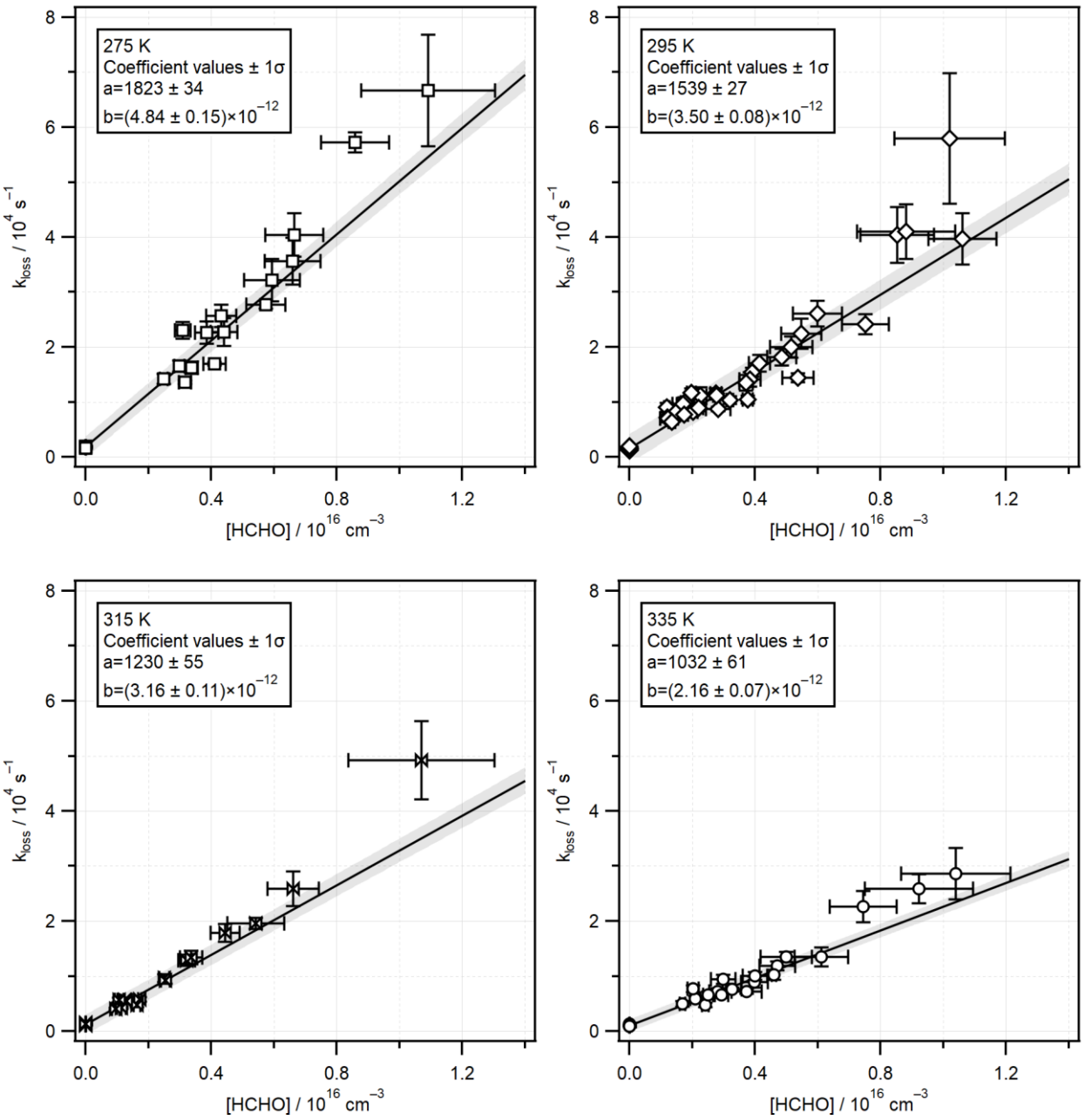


Figure S4: Compilation of pseudo-first order plots for the reaction of CH_2OO with HCHO in the temperature range 275–335 K. Shaded areas represent the statistical uncertainty in the linear fits.

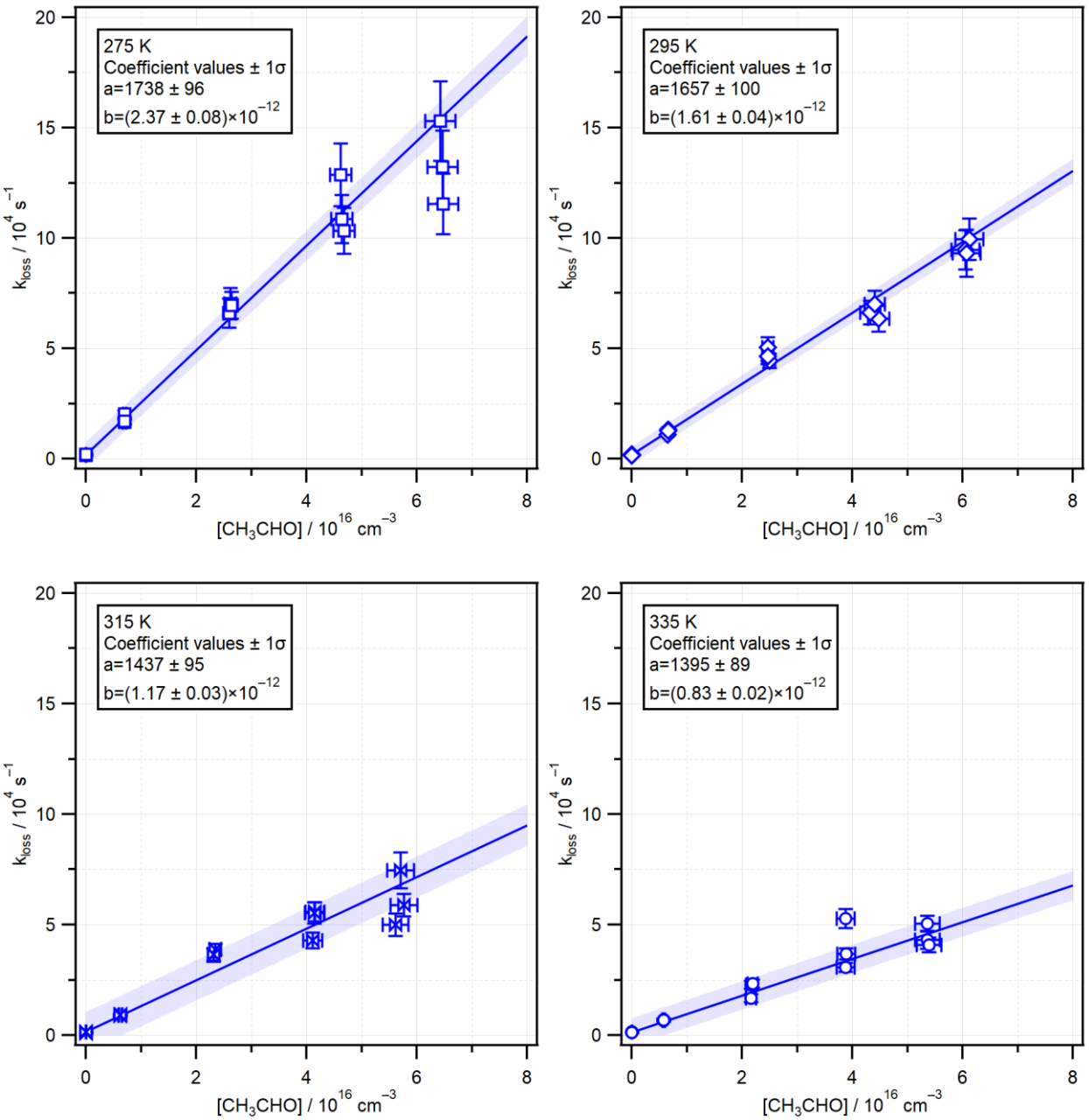


Figure S5: Compilation of pseudo-first order plots for the reaction of CH_2OO with CH_3CHO in the temperature range 275–335 K. Shaded areas represent the statistical uncertainty in the linear fits.

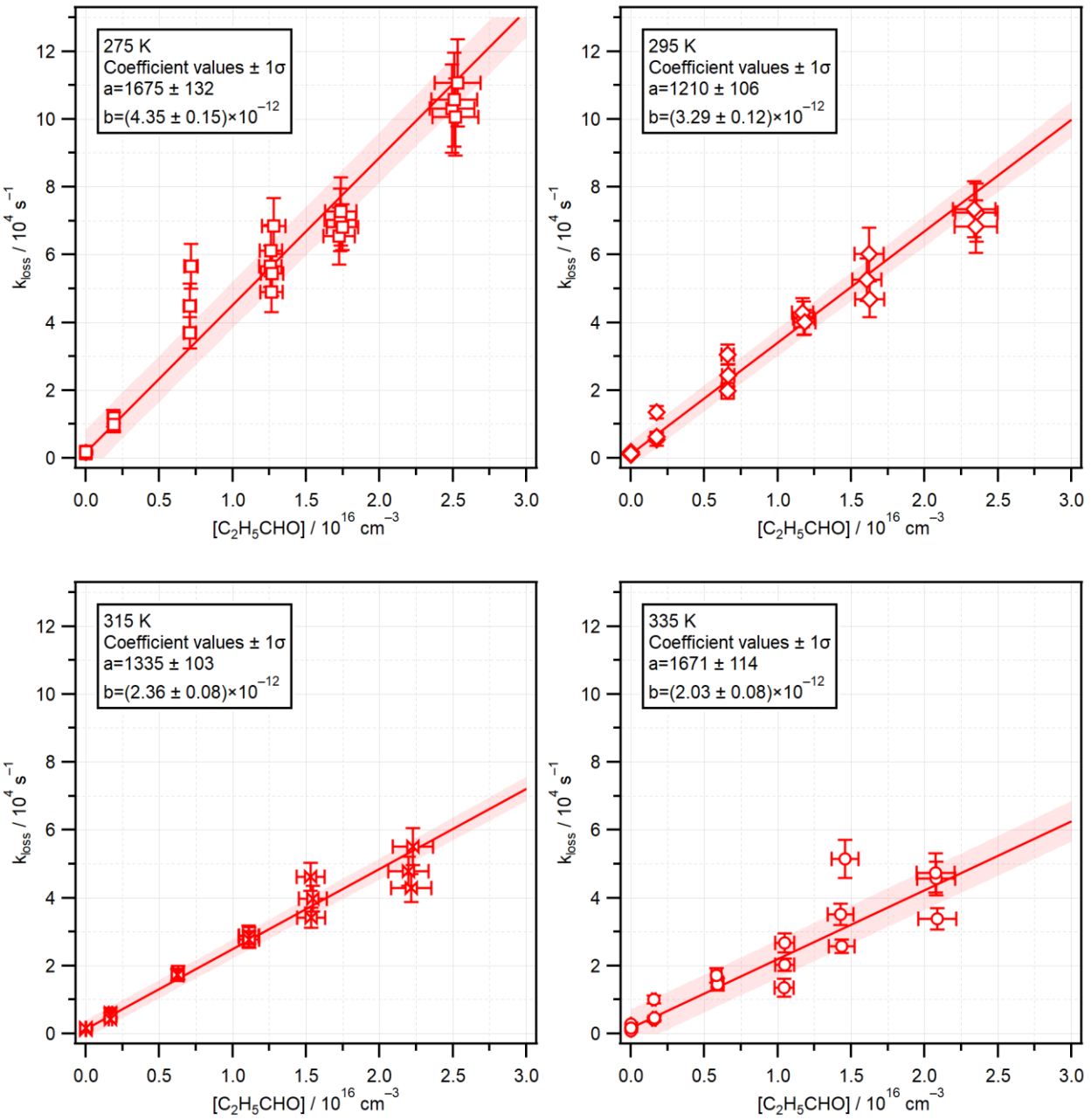


Figure S6: Compilation of pseudo-first order plots for the reaction of CH_2OO with C_2H_5CHO in the temperature range 275–335 K. Shaded areas represent the statistical uncertainty in the linear fits.

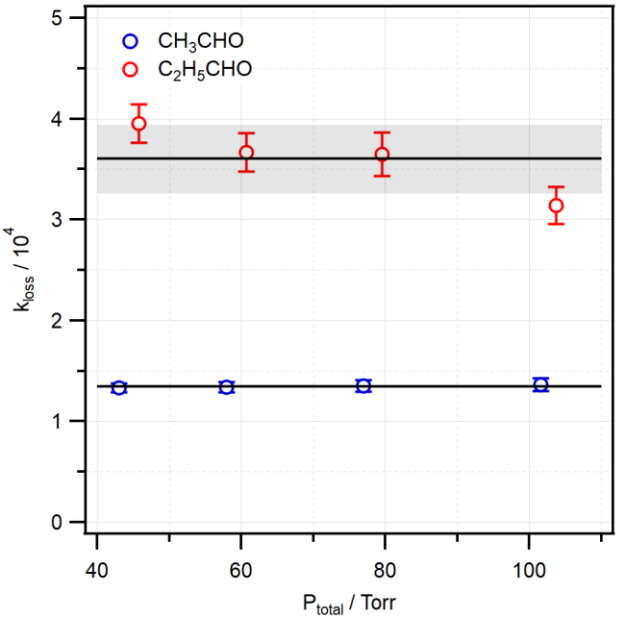
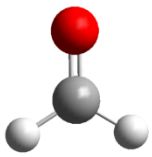


Figure S7: CH_2OO loss rates in the presence of CH_3CHO ($[CH_3CHO]=(6.8\pm0.4)\times10^{15}$ cm^{-3}) and C_2H_5CHO ($[C_2H_5CHO]=(1.1\pm0.1)\times10^{16}$ cm^{-3}) at 295 K. Total pressure was varied by changing the flow of N_2 buffer gas while holding all other flows constant. The solid lines represent the average of the loss rates determined at each pressure. Shaded areas represent 1σ uncertainties.

Cartesian Coordinates (Å) for CBS-QB3 Optimized Geometries and Relative Energies

CH_2OO + HCHO

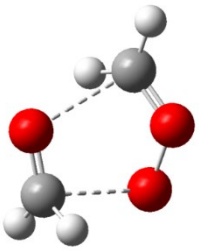
HCHO



```
C         0.000000    0.000000   -0.526260
O         0.000000    0.000000    0.673989
H         0.000000    0.939196   -1.117174
H         0.000000   -0.939196   -1.117174

Temperature=               298.150000 Pressure=                    1.000000
E(ZPE)=                      0.026228 E(Thermal)=                  0.029097
E(SCF)=                   -113.909678 DE(MP2)=                    -0.390356
DE(CBS)=                    -0.039154 DE(MP34)=                   -0.014891
DE(CCSD)=                   -0.009663 DE(Int)=                     0.012654
DE(Empirical)=              -0.019324
CBS-QB3 (0 K)=            -114.344185 CBS-QB3 Energy=           -114.341315
CBS-QB3 Enthalpy=         -114.340371 CBS-QB3 Free Energy=      -114.365186
```

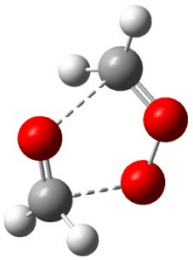
vdW



```
O        -1.211003   -0.164732   -0.380067
O        -0.586441   -1.228034    0.215945
C         1.545849   -0.361267   -0.042510
O         1.326194    0.840339   -0.056626
C        -1.116223    0.942494    0.206134
H        -0.685138    0.999668    1.195866
H        -1.551035    1.780510   -0.325523
H         1.805089   -0.898176    0.884886
O         1.623327   -0.949946   -0.970993

Temperature=               298.150000 Pressure=                    1.000000
E(ZPE)=                      0.060614 E(Thermal)=                  0.066979
E(SCF)=                   -302.544268 DE(MP2)=                    -1.028347
DE(CBS)=                    -0.102473 DE(MP34)=                   -0.033623
DE(CCSD)=                   -0.034046 DE(Int)=                     0.032116
DE(Empirical)=              -0.048529
CBS-QB3 (0 K)=            -303.698556 CBS-QB3 Energy=           -303.692190
CBS-QB3 Enthalpy=         -303.691246 CBS-QB3 Free Energy=      -303.728406
```

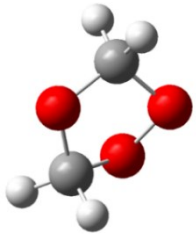
TS



```
O         1.647135    0.556673    0.192417
O         0.640835    0.519303    1.128595
C        -0.909262   -0.145979   -0.295896
O        -0.236590   -0.648905   -1.195653
C         1.907690   -0.549742   -0.350378
H         1.541650   -1.469921    0.081253
H         2.616697   -0.502360   -1.168539
H        -1.272372    0.890617   -0.362234
H        -1.338473   -0.750975    0.518015

Temperature=               298.150000 Pressure=                    1.000000
E(ZPE)=                      0.060872 E(Thermal)=                  0.066270
E(SCF)=                   -302.540944 DE(MP2)=                    -1.031751
DE(CBS)=                    -0.102758 DE(MP34)=                   -0.032716
DE(CCSD)=                   -0.034309 DE(Int)=                     0.032154
DE(Empirical)=              -0.048488
CBS-QB3 (0 K)=            -303.697939 CBS-QB3 Energy=           -303.692541
CBS-QB3 Enthalpy=         -303.691596 CBS-QB3 Free Energy=      -303.726584
```

SOZ

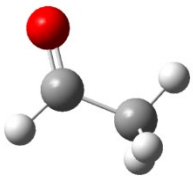


O	1.370429	0.570039	0.515060
O	0.189596	-0.024782	1.140136
C	-0.610717	-0.226328	-0.006972
O	0.277496	-0.669614	-1.021217
C	1.572808	-0.352504	-0.535197
H	2.069922	-1.260787	-0.174760
H	2.161652	0.161825	-1.297840
H	-1.099042	0.704418	-0.318820
H	-1.334831	-1.003557	0.247191

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.066961	E(Thermal)=	0.071272
E(SCF)=	-302.626706	DE(MP2)=	-1.030493
DE(CBS)=	-0.103384	DE(MP34)=	-0.030449
DE(CCSD)=	-0.027698	DE(Int)=	0.031501
DE(Empirical)=	-0.048995		
CBS-QB3 (0 K)=	-303.769263	CBS-QB3 Energy=	-303.764952
CBS-QB3 Enthalpy=	-303.764008	CBS-QB3 Free Energy=	-303.796451

CH_2OO + CH_3CHO

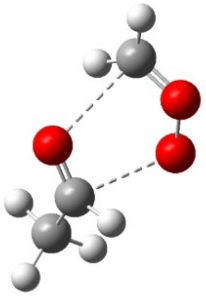
CH_3CHO



C	0.235625	0.397296	-0.000013
C	-1.168728	-0.147737	0.000021
O	1.233053	-0.276639	-0.000047
H	-1.155258	-1.237514	-0.000373
H	-1.707749	0.221890	0.879208
H	0.305332	1.508807	0.000137
H	-1.708124	0.222574	-0.878641

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.054659	E(Thermal)=	0.058565
E(SCF)=	-152.971417	DE(MP2)=	-0.559171
DE(CBS)=	-0.055480	DE(MP34)=	-0.027129
DE(CCSD)=	-0.014148	DE(Int)=	0.018444
DE(Empirical)=	-0.028223		
CBS-QB3 (0 K)=	-153.582464	CBS-QB3 Energy=	-153.578558
CBS-QB3 Enthalpy=	-153.577614	CBS-QB3 Free Energy=	-153.607406

vdW (*exo*-)



O	-1.695042	-0.357803	-0.299502
O	-0.730572	-1.289337	-0.045302
C	1.209069	0.285444	-0.490266
O	0.648424	1.317780	-0.172789
C	-1.778308	0.625405	0.475052
H	-1.144798	0.681470	1.350190
H	-2.523054	1.363147	0.202232
C	2.162281	-0.466371	0.397887
H	1.904092	-1.526936	0.409620
H	3.175676	-0.374318	-0.010921
H	2.142395	-0.059055	1.408968
H	1.104955	-0.116295	-1.515384

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.087907	E(Thermal)=	0.096059
E(SCF)=	-341.608124	DE(MP2)=	-1.194458
DE(CBS)=	-0.118487	DE(MP34)=	-0.046949
DE(CCSD)=	-0.038428	DE(Int)=	0.037898
DE(Empirical)=	-0.057450		

```
CBS-QB3 (0 K)=            -342.938090 CBS-QB3 Energy=              -342.929938
CBS-QB3 Enthalpy=         -342.928994 CBS-QB3 Free Energy=         -342.970918
```

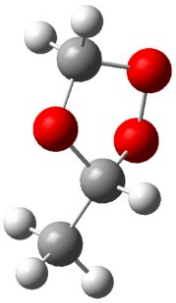
TS (*exo*-)

```
O       -1.577855   -0.411303   -0.243859
O       -0.512206   -1.275331   -0.093524
C        1.013251    0.232188   -0.518278
O        0.367431    1.269478   -0.299960
C       -1.539181    0.575059    0.543750
H       -0.948546    0.528800    1.446588
H       -2.277590    1.344552    0.351074
C        2.033445   -0.314876    0.444379
H        2.091532   -1.402380    0.380354
H        3.014596    0.096222    0.176289
H        1.801403   -0.009658    1.465577
H        1.054555   -0.174507   -1.540246
```

```
Temperature=              298.150000 Pressure=                  1.000000
E(ZPE)=                     0.088865 E(Thermal)=                0.095589
E(SCF)=                  -341.598577 DE(MP2)=                  -1.203481
DE(CBS)=                   -0.119105 DE(MP34)=                 -0.044775
DE(CCSD)=                  -0.039342 DE(Int)=                   0.037947
DE(Empirical)=             -0.057335
CBS-QB3 (0 K)=           -342.935803 CBS-QB3 Energy=          -342.929079
CBS-QB3 Enthalpy=        -342.928134 CBS-QB3 Free Energy=     -342.966530
```

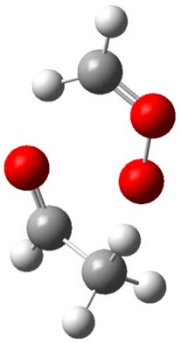
SOZ (*exo*-)

```
O       -1.396687   -0.740443   -0.144720
O       -0.024967   -1.110722    0.182940
C        0.681942   -0.033885   -0.418078
O       -0.117145    1.118451   -0.145494
C        2.051871    0.069450    0.208000
H        2.632274   -0.831359   -0.001586
H        2.575499    0.928993   -0.213871
H        1.959108    0.201294    1.286682
C       -1.381830    0.617710    0.250962
H       -1.499005    0.714096    1.336818
H       -2.191331    1.112445   -0.291062
H        0.721959   -0.183411   -1.504092
```



```
Temperature=              298.150000 Pressure=                  1.000000
E(ZPE)=                     0.094323 E(Thermal)=                0.100047
E(SCF)=                  -341.683965 DE(MP2)=                  -1.201899
DE(CBS)=                   -0.119522 DE(MP34)=                 -0.042405
DE(CCSD)=                  -0.032693 DE(Int)=                   0.037261
DE(Empirical)=             -0.057850
CBS-QB3 (0 K)=           -343.006750 CBS-QB3 Energy=          -343.001026
CBS-QB3 Enthalpy=        -343.000082 CBS-QB3 Free Energy=     -343.035917
```

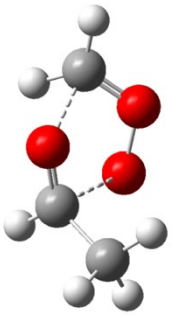
vdW (*endo*-)



O	-1.501860	-0.494251	-0.416534
O	-0.835904	-1.191340	0.549843
C	1.274122	0.331040	0.448358
O	0.698247	1.340511	0.091753
C	-1.839883	0.686669	-0.162600
H	-1.640634	1.107238	0.814370
H	-2.330814	1.209029	-0.974706
H	1.296144	0.045241	1.516695
C	2.065000	-0.559653	-0.470545
H	3.119219	-0.544192	-0.170869
H	1.705080	-1.586067	-0.375175
H	1.971715	-0.218937	-1.502082

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.087691	E(Thermal)=	0.095969
E(SCF)=	-341.608643	DE(MP2)=	-1.193574
DE(CBS)=	-0.118459	DE(MP34)=	-0.047102
DE(CCSD)=	-0.038375	DE(Int)=	0.037891
DE(Empirical)=	-0.057465		
CBS-QB3 (0 K)=	-342.938037	CBS-QB3 Energy=	-342.929759
CBS-QB3 Enthalpy=	-342.928814	CBS-QB3 Free Energy=	-342.971182

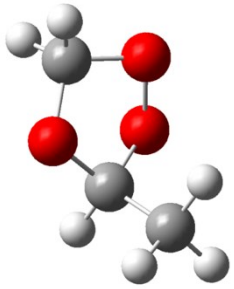
TS (*endo*-)



O	-1.370766	-0.555364	-0.454673
O	-0.534666	-1.248383	0.401232
C	1.020225	0.366620	0.443175
O	0.359493	1.294571	-0.040663
C	-1.726219	0.571490	-0.013322
H	-1.647514	0.791851	1.041619
H	-2.274389	1.189615	-0.714854
H	1.029165	0.199476	1.532008
C	2.075264	-0.360778	-0.345449
H	3.024056	0.178323	-0.230694
H	2.211491	-1.378238	0.020940
H	1.809078	-0.371607	-1.402606

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.088786	E(Thermal)=	0.095572
E(SCF)=	-341.599683	DE(MP2)=	-1.201743
DE(CBS)=	-0.119012	DE(MP34)=	-0.045129
DE(CCSD)=	-0.039045	DE(Int)=	0.037944
DE(Empirical)=	-0.057356		
CBS-QB3 (0 K)=	-342.935238	CBS-QB3 Energy=	-342.928451
CBS-QB3 Enthalpy=	-342.927507	CBS-QB3 Free Energy=	-342.965989

SOZ (*endo*-)

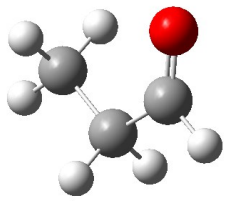


O	1.038821	-0.793593	0.535147
O	0.074228	-1.091514	-0.520471
C	-0.719315	0.099694	-0.518924
O	0.198283	1.151178	-0.211689
C	1.408676	0.508822	0.141077
H	2.093408	0.478584	-0.715551
H	1.858122	0.993271	1.009823
H	-1.069753	0.200660	-1.550873
C	-1.852674	0.063130	0.484515
H	-2.363368	1.028539	0.502291
H	-2.571575	-0.712684	0.211030
H	-1.457610	-0.146816	1.479372

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.094273	E(Thermal)=	0.099915
E(SCF)=	-341.682335	DE(MP2)=	-1.202375
DE(CBS)=	-0.119541	DE(MP34)=	-0.042439
DE(CCSD)=	-0.032762	DE(Int)=	0.037267
DE(Empirical)=	-0.057839		
CBS-QB3 (0 K)=	-343.005751	CBS-QB3 Energy=	-343.000108
CBS-QB3 Enthalpy=	-342.999164	CBS-QB3 Free Energy=	-343.034789

$CH_2OO + C_2H_5CHO$

C_2H_5CHO

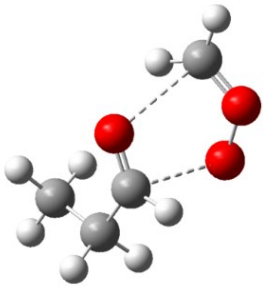


C	0.252324	0.415368	-0.021788
C	-1.148415	-0.145221	0.053363
O	1.111907	0.231962	0.801919
H	-1.316790	-0.711215	-0.873424
H	0.456614	1.037005	-0.922997
H	-1.838230	0.707775	-0.012025
C	-1.417651	-0.995369	1.291194
H	-1.264770	-0.414710	2.202880
H	-2.443180	-1.371011	1.289193
H	-0.737875	-1.848530	1.332882

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.083148	E(Thermal)=	0.088170
E(SCF)=	-192.018777	DE(MP2)=	-0.729883
DE(CBS)=	-0.071657	DE(MP34)=	-0.039443
DE(CCSD)=	-0.018998	DE(Int)=	0.024224
DE(Empirical)=	-0.037071		
CBS-QB3 (0 K)=	-192.808458	CBS-QB3 Energy=	-192.803435
CBS-QB3 Enthalpy=	-192.802491	CBS-QB3 Free Energy=	-192.8357798

vdW (*exo*-)

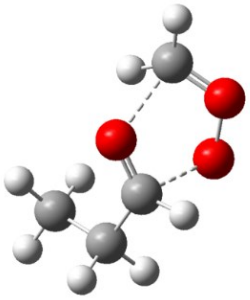
O	-2.090571	-0.389865	-0.129786
O	-1.058064	-1.283618	-0.136667
C	0.671653	0.424253	-0.919037
O	0.211070	1.377158	-0.319038
C	-2.055694	0.543153	0.707861
H	-1.257219	0.589929	1.436270
H	-2.872693	1.251207	0.638930
C	1.841374	-0.403084	-0.444930
H	1.603021	-1.452298	-0.643639
H	2.676494	-0.155725	-1.117629
C	2.225787	-0.175105	1.013231
H	3.133867	-0.726546	1.267482
H	2.395994	0.884439	1.213329
H	1.426026	-0.518174	1.673167
H	0.296309	0.162466	-1.926732



Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.116203	E(Thermal)=	0.125630
E(SCF)=	-380.655374	DE(MP2)=	-1.365532
DE(CBS)=	-0.134569	DE(MP34)=	-0.059334
DE(CCSD)=	-0.043389	DE(Int)=	0.043666
DE(Empirical)=	-0.066290		
CBS-QB3 (0 K)=	-382.164618	CBS-QB3 Energy=	-382.155191
CBS-QB3 Enthalpy=	-382.154247	CBS-QB3 Free Energy=	-382.199700

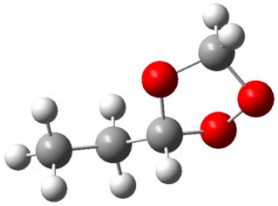
TS (*exo*-)

O	1.939383	0.454051	0.047251
O	0.817257	1.262179	0.132690
C	-0.441821	-0.099444	-0.957875
O	0.062106	-1.188789	-0.627505
C	1.780098	-0.671956	0.599006
H	1.026979	-0.806771	1.360760
H	2.575789	-1.384976	0.414451
C	-1.759806	0.396463	-0.405849
H	-1.745565	1.489904	-0.414881
H	-2.520801	0.096661	-1.141403
C	-2.110662	-0.151060	0.974964
H	-3.115429	0.157575	1.272660
H	-2.068196	-1.241854	0.982430
H	-1.407973	0.224512	1.722146
H	-0.101629	0.401407	-1.877120



Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.117347	E(Thermal)=	0.125304
E(SCF)=	-380.644682	DE(MP2)=	-1.375288
DE(CBS)=	-0.135283	DE(MP34)=	-0.056966
DE(CCSD)=	-0.044476	DE(Int)=	0.043715
DE(Empirical)=	-0.066179		
CBS-QB3 (0 K)=	-382.161813	CBS-QB3 Energy=	-382.153855
CBS-QB3 Enthalpy=	-382.152911	CBS-QB3 Free Energy=	-382.194731

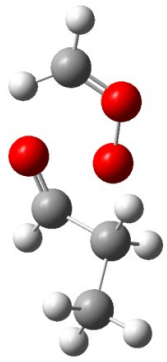
SOZ (*exo*-)



O	-1.990005	-0.435359	-0.241949
O	-0.776830	-1.159783	0.119491
C	0.216493	-0.262400	-0.357339
O	-0.293702	1.038082	-0.052422
C	1.523110	-0.546126	0.355801
H	1.787362	-1.591707	0.168195
H	1.348659	-0.436516	1.429332
C	-1.662403	0.846151	0.257374
H	-1.813457	0.897350	1.342206
H	-2.291189	1.563293	-0.275502
H	0.304156	-0.354227	-1.447996
C	2.647059	0.382885	-0.111121
H	2.384352	1.427290	0.067981
H	3.572508	0.165659	0.426444
H	2.846339	0.262270	-1.179910

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.122551	E(Thermal)=	0.129612
E(SCF)=	-380.730314	DE(MP2)=	-1.373120
DE(CBS)=	-0.135648	DE(MP34)=	-0.054642
DE(CCSD)=	-0.037673	DE(Int)=	0.043030
DE(Empirical)=	-0.066699		
CBS-QB3 (0 K)=	-382.232515	CBS-QB3 Energy=	-382.225453
CBS-QB3 Enthalpy=	-382.224509	CBS-QB3 Free Energy=	-382.263877

vdW (*endo*-)

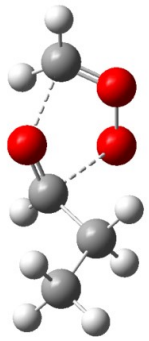


O	-1.999373	-0.603614	-0.417974
O	-1.260748	-1.241521	0.536267
C	0.701558	0.502290	0.436458
O	0.018151	1.446703	0.092388
C	-2.450173	0.535732	-0.150073
H	-2.282193	0.966320	0.828455
H	-2.997824	1.013961	-0.953022
H	0.752693	0.204209	1.502209
C	1.595604	-0.287395	-0.487983
H	1.223554	-1.316487	-0.485290
H	1.486257	0.116130	-1.497422
C	3.060509	-0.256930	-0.024492
H	3.680470	-0.881696	-0.670961
H	3.465769	0.758165	-0.049763
H	3.162056	-0.635331	0.996887

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.116039	E(Thermal)=	0.125659
E(SCF)=	-380.654532	DE(MP2)=	-1.364053
DE(CBS)=	-0.134564	DE(MP34)=	-0.059496
DE(CCSD)=	-0.043268	DE(Int)=	0.043660
DE(Empirical)=	-0.066314		
CBS-QB3 (0 K)=	-382.162529	CBS-QB3 Energy=	-382.152908
CBS-QB3 Enthalpy=	-382.151964	CBS-QB3 Free Energy=	-382.198606

TS (*endo*-)

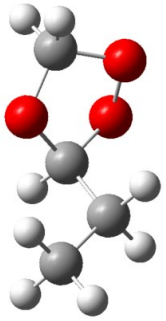
O	-1.907096	-0.470422	-0.497311
O	-1.165637	-1.232881	0.384660
C	0.513848	0.248466	0.508950
O	-0.047783	1.238291	0.023231
C	-2.201089	0.675065	-0.060631
H	-2.143079	0.885794	0.997521
H	-2.671715	1.335630	-0.779544
H	0.477711	0.067070	1.596432
C	1.537400	-0.550647	-0.260609
H	1.554731	-1.574321	0.119435
H	1.229570	-0.576698	-1.308231
C	2.928253	0.095550	-0.126013
H	3.675204	-0.486864	-0.670470
H	2.925245	1.110699	-0.529740
H	3.245990	0.148196	0.919783



Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.117152	E(Thermal)=	0.125263
E(SCF)=	-380.645828	DE(MP2)=	-1.372697
DE(CBS)=	-0.135074	DE(MP34)=	-0.057409
DE(CCSD)=	-0.044040	DE(Int)=	0.043703
DE(Empirical)=	-0.066199		
CBS-QB3 (0 K)=	-382.160391	CBS-QB3 Energy=	-382.152279
CBS-QB3 Enthalpy=	-382.151335	CBS-QB3 Free Energy=	-382.193574

SOZ (*endo*-)

O	-1.634563	-0.448109	-0.659252
O	-0.906575	-1.134049	0.406448
C	0.213577	-0.262632	0.589255
O	-0.299575	1.050125	0.350415
C	-1.613861	0.861435	-0.138872
H	-2.345568	0.972560	0.671043
H	-1.813308	1.542084	-0.968596
H	0.483021	-0.368346	1.645984
C	1.373080	-0.578679	-0.340482
H	1.681179	-1.610516	-0.141676
H	0.997199	-0.541571	-1.366367
C	2.553265	0.378840	-0.157768
H	3.364668	0.129618	-0.845142
H	2.247911	1.409474	-0.348508
H	2.954232	0.329185	0.859580



Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.122546	E(Thermal)=	0.129514
E(SCF)=	-380.728580	DE(MP2)=	-1.373752
DE(CBS)=	-0.135679	DE(MP34)=	-0.054663
DE(CCSD)=	-0.037746	DE(Int)=	0.043039
DE(Empirical)=	-0.066684		
CBS-QB3 (0 K)=	-382.231519	CBS-QB3 Energy=	-382.224550
CBS-QB3 Enthalpy=	-382.223606	CBS-QB3 Free Energy=	-382.262683

CBS-QB3 Relative Energies, Enthalpies, and Free Energies of *endo*- Pathways

Table S1 Relative energies, including zero-point contributions, Δ(E+ZPE) at 0 K, standard enthalpies ΔH° at 298 K, and standard free energies ΔG° at 298 K calculated at the CBS-QB3 levels for the SOZ *endo*- pathway for reactions of CH_2OO with, acetaldehyde and propionaldehyde. All energies are reported in kcal mol^{-1}.

	Δ(E+ZPE) {ΔH°} [ΔG°] / kcal mol^{-1}	
	CH_3CHO	C_2H_5CHO
vdW	–7.8 {–7.7} [+2.2]	–6.9 {–6.6} [+2.8]
TS_{SOZ}	–6.1 {–6.9} [+5.4]	–5.5 {–6.3} [+5.9]
SOZ	–50.3 {–51.9} [–37.8]	–50.1 {–51.6} [–37.5]