[Supporting Information (SI)]

Experimental and Theoretical Study of Criegee Intermediate (CH_2OO) Reactions with n-Butyraldehyde and Isobutyraldehyde: Kinetics, Implications and Atmospheric Fate

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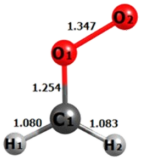
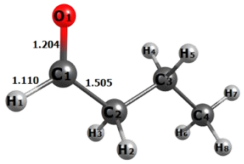
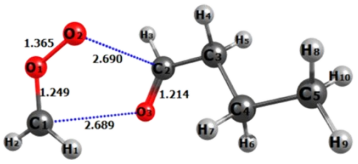


Criegee Intermediate



N-butyraldehyde



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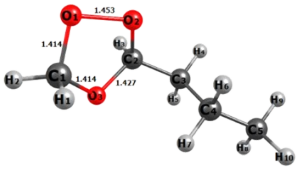

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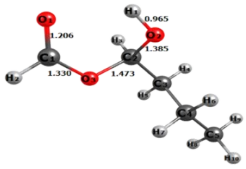

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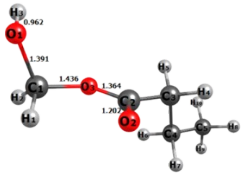

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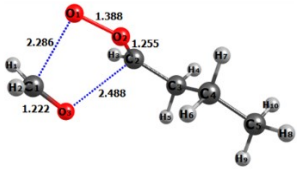

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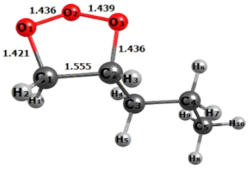

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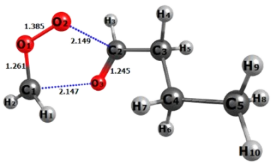

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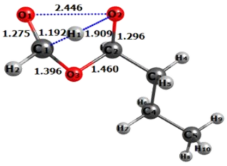

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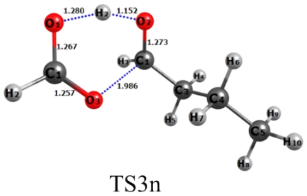

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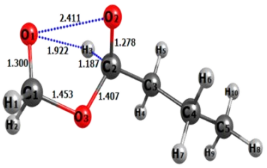

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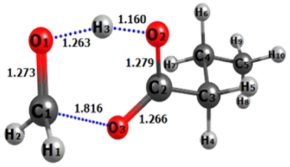

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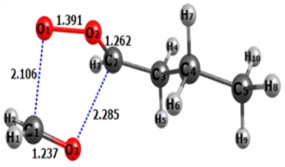

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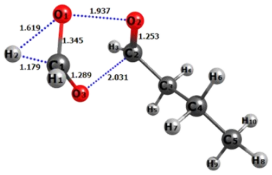

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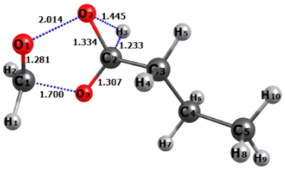

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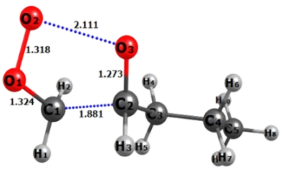

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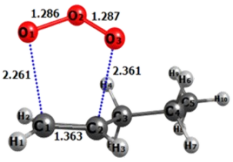

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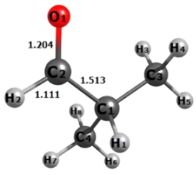
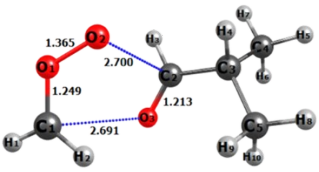


Iso-butyraldehyde



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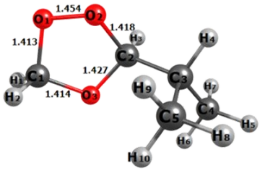

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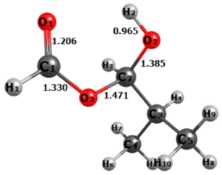

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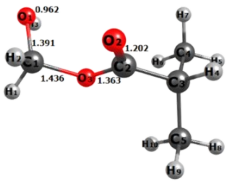

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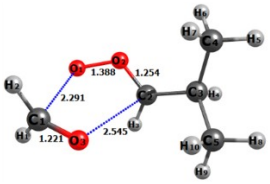

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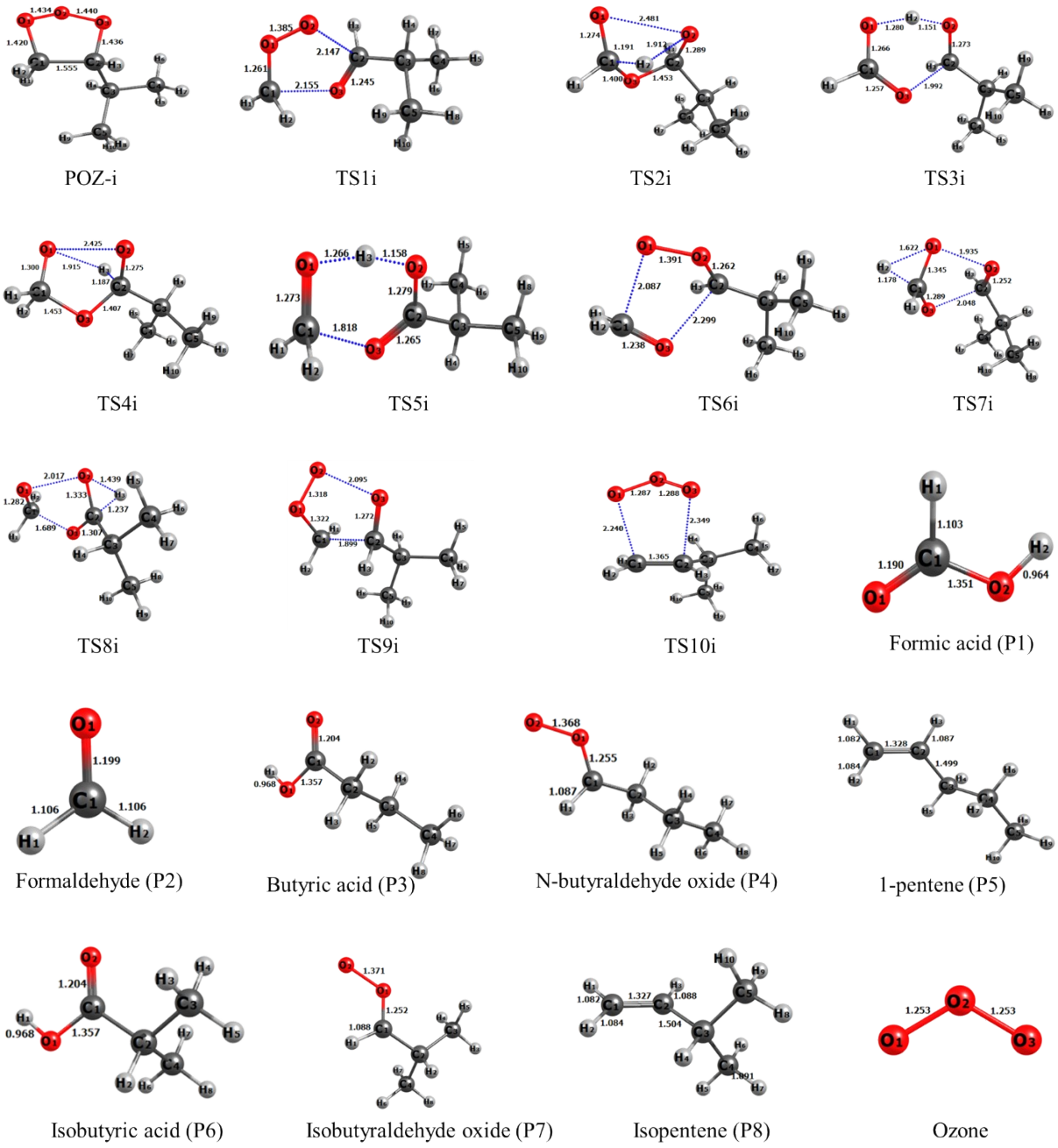


Figure S1. Optimized geometries along with relevant structural parameters of all the stationary points (viz. reactants, pre and post-reactive complexes (IM), transition states (TS) and products) for the reactions CH_2OO + nBD and CH_2OO + iBD obtained at B3LYP/6-311+G(2df,2p).

Table S1. Cartesian coordinates optimised at B3LYB/6-311+G(3df,2p) level of theory:

Table S1.1. Optimised parameters of CH_2OO.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	1.069420	-0.197420	0
2	H	1	1.973480	0.394200	0
3	H	1	1.029020	-1.279770	0
4	O	8	0.000000	0.456880	0
5	O	8	-1.177380	-0.198120	0

Table S1.2. Optimised parameters of nBD.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-1.459320	-0.218620	0.285180
2	O	8	-2.421330	0.110210	-0.360290
3	H	1	-1.519740	-1.095230	0.965920
4	C	6	1.010590	-0.503510	-0.138090
5	H	1	0.988710	-1.372560	0.524950
6	H	1	0.824310	-0.881540	-1.145950
7	C	6	-0.118930	0.463370	0.251030
8	H	1	0.076290	0.850640	1.258150
9	H	1	-0.171120	1.311350	-0.432060
10	C	6	2.390140	0.150140	-0.080260

11	H	1	2.617100	0.504030	0.926900
12	H	1	3.170830	-0.553640	-0.369640
13	H	1	2.449440	1.006930	-0.753080

Table S1.2. Optimised parameters of iBD.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.424730	0.011300	0.412360
2	H	1	0.591480	-0.042070	1.497030
3	C	6	-0.936770	-0.613910	0.202850
4	O	8	-1.894830	-0.061620	-0.272650
5	H	1	-1.008110	-1.674580	0.527060
6	C	6	0.480420	1.465900	-0.041100
7	H	1	0.314180	1.543100	-1.115720
8	H	1	-0.286090	2.063340	0.449730
9	H	1	1.454800	1.899340	0.185020
10	C	6	1.495320	-0.868770	-0.255060
11	H	1	2.492750	-0.508890	-0.004930
12	H	1	1.424440	-1.907900	0.069740
13	H	1	1.392880	-0.846520	-1.341060

Table S1.3. Optimised parameters of IM1n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.006010	1.042194	-0.688260
2	H	1	0.501667	1.215995	-1.653420
3	O	8	0.465093	1.490490	0.336584
4	O	8	1.519590	-1.173070	-0.712230
5	O	8	2.595051	-0.531790	-0.169730
6	C	6	2.506109	-0.126150	1.008718
7	H	1	3.370433	0.408492	1.378151
8	H	1	1.614552	-0.326320	1.585429
9	C	6	-1.311100	0.304067	-0.786380
10	H	1	-1.127080	-0.592850	-1.384580
11	C	6	-1.974860	-0.036210	0.542521
12	H	1	-1.299070	-0.669050	1.120755
13	H	1	-2.106380	0.877256	1.124894
14	H	1	-1.968900	0.930634	-1.404220
15	C	6	-3.318010	-0.742610	0.363965
16	H	1	-3.204820	-1.677560	-0.187930
17	H	1	-3.769970	-0.980490	1.327358
18	H	1	-4.025060	-0.118920	-0.186810

Table S1.6. Optimised parameters of SOZ-n.

Cartesian coordinate

Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.438190	-0.454600	0.694744
2	H	1	-0.858390	-1.006800	1.542005
3	O	8	-0.959020	0.874094	0.721858
4	O	8	-0.934130	-1.003950	-0.515950
5	O	8	-2.278300	-0.451230	-0.532540
6	C	6	-1.994370	0.902368	-0.240520
7	H	1	-2.905610	1.335478	0.172481
8	H	1	-1.657530	1.436165	-1.134060
9	C	6	1.077202	-0.492180	0.701124
10	H	1	1.378421	-1.543030	0.696580
11	C	6	1.759376	0.266960	-0.437600
12	H	1	1.451903	-0.158950	-1.393460
13	H	1	1.414727	1.302183	-0.432050
14	C	6	3.282873	0.229397	-0.322240
15	H	1	3.753177	0.774712	-1.140780
16	H	1	3.621810	0.679940	0.612713
17	H	1	3.658928	-0.795190	-0.349500
18	H	1	1.392836	-0.087500	1.666074

Table S1.4. Optimised parameters of IM2n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z

1	C	6	0.364757	0.431061	0.492710
2	H	1	0.905047	0.672098	1.410637
3	O	8	0.926864	-0.851210	0.034737
4	O	8	0.539447	1.416141	-0.465610
5	O	8	2.990626	0.064808	-0.033800
6	C	6	2.242323	-0.871980	-0.160820
7	H	1	1.481122	1.625654	-0.504250
8	H	1	2.562123	-1.876330	-0.463510
9	C	6	-1.107700	0.202248	0.758158
10	H	1	-1.490260	1.117384	1.216434
11	C	6	-1.939620	-0.150050	-0.476730
12	H	1	-1.829770	0.640142	-1.219920
13	H	1	-1.544200	-1.060310	-0.930460
14	C	6	-3.417280	-0.343150	-0.138150
15	H	1	-3.995620	-0.594050	-1.027650
16	H	1	-3.558530	-1.148570	0.585501
17	H	1	-3.848200	0.563841	0.290492
18	H	1	-1.192160	-0.586550	1.509027

Table S1.5. Optimised parameters of IM3n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.178625	0.538328	0.105015

2	H	1	3.224202	-1.192080	0.932183
3	O	8	0.922940	-0.589150	-0.080300
4	O	8	0.560965	1.642110	-0.177160
5	O	8	3.179005	-0.345050	0.478244
6	C	6	2.264759	-0.428220	-0.567130
7	H	1	2.433090	-1.301430	-1.197370
8	H	1	2.339621	0.495197	-1.131610
9	C	6	-1.185880	0.202950	0.650816
10	H	1	-1.548620	1.082326	1.181365
11	C	6	-2.169260	-0.174260	-0.471510
12	H	1	-2.219700	0.647694	-1.188440
13	H	1	-1.781250	-1.039930	-1.011650
14	H	1	-1.100730	-0.622550	1.358140
15	C	6	-3.566280	-0.480870	0.063883
16	H	1	-3.986960	0.379569	0.586873
17	H	1	-4.247450	-0.741850	-0.746400
18	H	1	-3.547270	-1.317770	0.764185

Table S1.6. Optimised parameters of IM4n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.438220	-0.454470	0.694963
2	H	1	-0.858360	-1.006490	1.542316

3	O	8	-0.959100	0.874238	0.721764
4	O	8	-0.933990	-1.003980	-0.515720
5	O	8	-2.27816	-0.451420	-0.532490
6	C	6	-1.994380	0.902287	-0.240840
7	H	1	-2.905620	1.335600	0.171943
8	H	1	-1.657430	1.435924	-1.134450
9	C	6	1.759318	0.266266	-0.438090
10	H	1	1.452318	-0.161010	-1.393480
11	H	1	1.414223	1.301354	-0.433980
12	C	6	1.077134	-0.491660	0.701489
13	H	1	1.378712	-1.542420	0.698295
14	H	1	1.392545	-0.085640	1.665950
15	C	6	3.282795	0.229508	-0.322200
16	H	1	3.753131	0.774070	-1.141220
17	H	1	3.621233	0.681283	0.612340
18	H	1	3.659312	-0.794940	-0.348150

Table S1.7. Optimised parameters of POZ-n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	1.551244	1.131635	0.022183
2	H	1	1.269137	1.646589	-0.898480
3	C	6	0.356176	0.309631	0.581854

4	O	8	0.835269	-1.041740	0.499031
5	O	8	2.560686	0.163833	-0.228900
6	C	8	1.777207	-0.985370	-0.587390
7	H	1	1.965623	1.836042	0.740388
8	C	6	-0.939310	0.524416	-0.186120
9	H	1	-0.773500	0.233854	-1.227050
10	C	6	-2.131250	-0.23768	0.393300
11	H	1	-2.287560	0.072928	1.430750
12	H	1	-1.891060	-1.302100	0.425058
13	H	1	0.215502	0.486670	1.649454
14	C	6	-3.416800	-0.022370	-0.403720
15	H	1	-4.249740	-0.574450	0.032113
16	H	1	-3.696570	1.032707	-0.429910
17	H	1	-3.301650	-0.358400	-1.435740
18	H	1	-1.155810	1.598533	-0.193620

Table S1.8. Optimised parameters of TS1n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.334940	0.531830	-0.353330
2	H	1	-0.226550	0.667085	-1.450510
3	O	8	-0.775910	-0.842310	-0.130690
4	O	8	-1.156710	1.395504	0.154708

5	O	8	-2.971420	-0.186780	-0.277270
6	C	6	-2.065750	-0.776590	0.398644
7	C	1	2.092212	-0.366500	-0.410940
8	H	1	1.712709	-1.384040	-0.316890
9	H	1	2.156918	-0.155120	-1.481450
10	H	1	-2.339090	-1.703070	0.927158
11	H	1	-1.841530	0.005302	1.269423
12	C	6	1.118631	0.605800	0.241303
13	H	1	1.433851	1.640036	0.103982
14	C	6	3.486172	-0.27267	0.214202
15	H	1	3.460315	-0.51554	1.277666
16	H	1	4.174133	-0.96785	-0.267510
17	H	1	3.902305	0.730938	0.113097
18	H	1	1.021279	0.41975	1.311785

Table S1.9. Optimised parameters of TS2n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.334940	0.531830	-0.353330
2	H	1	-0.226550	0.667085	-1.450510
3	O	8	-0.775910	-0.842310	-0.130690
4	O	8	-1.156710	1.395504	0.154708

5	O	8	-2.971420	-0.186780	-0.277270
6	C	6	-2.065750	-0.776590	0.398644
7	C	6	2.092212	-0.366500	-0.410940
8	H	1	1.712709	-1.384040	-0.316890
9	H	1	2.156918	-0.155120	-1.481450
10	H	1	-2.339090	-1.703070	0.927158
11	H	1	-1.841530	0.005302	1.269423
12	C	6	1.118631	0.605800	0.241303
13	H	1	1.433851	1.640036	0.103982
14	C	6	3.486172	-0.272670	0.214202
15	H	1	3.460315	-0.515540	1.277666
16	H	1	4.174133	-0.967850	-0.267510
17	H	1	3.902305	0.730938	0.113097
18	H	1	1.021279	0.419750	1.311785

Table S1.10. Optimised parameters of TS3n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.228451	0.632804	0.659141
2	H	1	0.802839	0.673065	1.585833
3	O	8	1.139511	-1.102240	0.339738
4	O	8	0.623592	1.326887	-0.332080
5	O	8	2.747625	0.265896	-0.431700

6	C	6	2.277362	-0.874550	-0.144490
7	H	1	1.740954	1.056428	-0.406240
8	H	1	2.922950	-1.742570	-0.336520
9	C	6	-1.202880	0.239545	0.789490
10	H	1	-1.688390	1.070570	1.318985
11	C	6	-1.922750	-0.045930	-0.527260
12	H	1	-1.846750	0.827248	-1.175390
13	H	1	-1.402180	-0.856540	-1.039710
14	H	1	-1.252170	-0.615820	1.465587
15	C	6	-3.389190	-0.417660	-0.315790
16	H	1	-3.881330	-0.624080	-1.266170
17	H	1	-3.488860	-1.308080	0.307784
18	H	1	-3.938870	0.390090	0.171652

Table S1.11. Optimised parameters of TS4n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.362140	-0.306160	0.192778
2	H	1	-1.021150	-0.523210	1.155925
3	O	8	-0.931080	0.937501	-0.137140
4	O	8	-0.686100	-1.289890	-0.556100
5	O	8	-2.748130	-0.400830	0.321051

6	C	6	-2.370540	0.742409	-0.168310
7	H	1	-2.751230	1.611687	0.402734
8	H	1	-2.710600	0.894638	-1.214650
9	C	6	2.063659	0.100059	-0.462780
10	H	1	1.988912	-0.703660	-1.196760
11	H	1	1.759286	1.018576	-0.966810
12	C	6	1.093225	-0.189380	0.689033
13	H	1	1.351304	-1.128290	1.178094
14	H	1	1.122583	0.605278	1.434645
15	C	6	3.502207	0.229588	0.033766
16	H	1	4.180456	0.436576	-0.794690
17	H	1	3.603841	1.043138	0.754306
18	H	1	3.840546	-0.688110	0.517861

Table S1.12. Optimised parameters of TS5n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.232740	-0.072590	0.423815
2	H	1	-1.730860	1.126238	0.101431
3	O	8	-0.958300	-1.040280	0.051225
4	O	8	-0.681360	1.112928	0.595864
5	O	8	-2.678900	0.667965	-0.596730

6	C	6	-2.685570	-0.544730	-0.208180
7	H	1	-2.942230	-1.320240	-0.931550
8	H	1	-2.954960	-0.784770	0.825952
9	C	6	2.075521	0.196612	-0.534340
10	H	1	1.759542	-0.319240	-1.443480
11	H	1	1.869457	1.257014	-0.686100
12	C	6	1.232722	-0.311170	0.650067
13	H	1	1.394714	-1.377300	0.801797
14	H	1	1.521378	0.221073	1.558074
15	C	6	3.570405	-0.019160	-0.309750
16	H	1	3.803787	-1.076890	-0.177020
17	H	1	4.148103	0.343572	-1.159990
18	H	1	3.917521	0.511720	0.578288

Table S1.13. Optimised parameters of TS6n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.237730	-0.352210	0.775000
2	H	1	-0.897190	-0.206910	1.619379
3	O	8	-1.497420	1.412852	0.053586
4	O	8	-0.668600	-1.030590	-0.198510
5	O	8	-2.049070	-1.197430	-0.206200
6	C	6	-2.516590	0.849913	-0.362940

7	H	1	-3.383070	0.679020	0.287651
8	H	1	-2.699220	0.739713	-1.437960
9	C	6	1.982333	-0.165760	-0.471380
10	H	1	1.969808	-1.224040	-0.736340
11	H	1	1.483629	0.360677	-1.286090
12	C	6	1.185155	0.048922	0.814482
13	H	1	1.646865	-0.478960	1.659028
14	H	1	1.185313	1.104615	1.104309
15	C	6	3.423989	0.320582	-0.336680
16	H	1	3.975651	0.162544	-1.262870
17	H	1	3.463360	1.386536	-0.106070
18	H	1	3.952540	-0.210590	0.457176

Table S1.14. Optimised parameters of TS7n..

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.316547	0.784178	0.580043
2	H	1	0.855642	1.027268	1.497550
3	O	8	1.128545	-1.073970	0.697044
4	O	8	0.768191	1.173629	-0.522010
5	O	8	2.509356	0.332482	-0.402340
6	C	6	1.968969	-0.891030	-0.263330
7	H	1	3.097686	-1.126080	-0.017240

8	H	1	1.780389	-1.428130	-1.211280
9	C	6	-1.827920	-0.128530	-0.504350
10	H	1	-1.710420	0.560474	-1.341160
11	H	1	-1.314540	-1.049320	-0.785160
12	C	6	-1.148250	0.452813	0.732217
13	H	1	-1.624870	1.398603	1.019003
14	H	1	-1.245180	-0.211460	1.591454
15	C	6	-3.310090	-0.412360	-0.264930
16	H	1	-3.777180	-0.831230	-1.156370
17	H	1	-3.452410	-1.125930	0.548704
18	H	1	-3.853430	0.498242	-0.004920

Table S1.15. Optimised parameters of TS8n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.363073	0.384434	0.482282
2	H	1	0.396043	1.202309	1.404323
3	O	8	0.814003	-0.811320	0.755984
4	O	8	1.317478	1.297850	0.295975
5	O	8	2.219862	0.070896	-1.021160
6	C	6	2.245163	-0.875520	-0.158980
7	H	1	2.972697	-0.842100	0.657937
8	H	1	2.069869	-1.879070	-0.563580

9	C	6	-2.099300	-0.293500	0.370913
10	H	1	-1.788440	-1.334330	0.466950
11	H	1	-2.284510	0.066789	1.386658
12	C	6	-0.961070	0.513252	-0.254410
13	H	1	-0.756870	0.164673	-1.271270
14	H	1	-1.218210	1.570839	-0.322090
15	C	6	-3.387720	-0.205150	-0.445510
16	H	1	-3.242290	-0.593870	-1.454840
17	H	1	-4.187050	-0.782110	0.019545
18	H	1	-3.732830	0.826360	-0.535860

Table S1.16. Optimised parameters of TS9n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	O	8	0.700432	-1.231960	0.077913
2	C	6	0.202230	-0.142100	0.506319
3	C	6	1.486717	1.133191	-0.004340
4	O	8	2.582739	0.425873	0.220914
5	O	8	2.621729	-0.635050	-0.559930
6	H	1	1.426475	2.003166	0.638025
7	C	6	-1.062920	0.407851	-0.162920
8	H	1	-0.952680	0.308744	-1.244450
9	C	6	-2.303650	-0.359970	0.307745

10	H	1	-2.175810	-1.414530	0.056906
11	H	1	-2.369130	-0.307950	1.398113
12	H	1	1.198381	1.226978	-1.044010
13	H	1	0.237193	0.022517	1.598146
14	H	1	-1.181430	1.470804	0.070165
15	C	6	-3.594860	0.174763	-0.309520
16	H	1	-4.459620	-0.390770	0.038602
17	H	1	-3.757440	1.222224	-0.048110
18	H	1	-3.570280	0.105468	-1.398350

Table S1.16. Optimised parameters of TS10n.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	O	8	0.700432	-1.231960	0.077913
2	C	6	0.202230	-0.142100	0.506319
3	C	6	1.486717	1.133191	-0.004340
4	O	8	2.582739	0.425873	0.220914
5	O	8	2.621729	-0.635050	-0.559930
6	H	1	1.426475	2.003166	0.638025
7	C	6	-1.062920	0.407851	-0.162920
8	H	1	-0.952680	0.308744	-1.244450
9	C	6	-2.303650	-0.359970	0.307745
10	H	1	-2.175810	-1.414530	0.056906

11	H	1	-2.369130	-0.307950	1.398113
12	H	1	1.198381	1.226978	-1.044010
13	H	1	0.237193	0.022517	1.598146
14	H	1	-1.181430	1.470804	0.070165
15	C	6	-3.594860	0.174763	-0.30952
16	H	1	-4.459620	-0.390770	0.038602
17	H	1	-3.757440	1.222224	-0.048110
18	H	1	-3.570280	0.105468	-1.398350

Table S1.17. Optimised parameters of IM1i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.432120	-0.153590	0.766290
2	H	1	0.220270	-1.102160	1.292220
3	O	8	-0.142570	0.863870	1.091870
4	O	8	-1.555850	-1.053230	-0.823080
5	O	8	-2.529830	-0.537860	-0.018220
6	C	6	-2.626140	0.704870	0.068660
7	C	6	2.818630	-0.702340	0.417010
8	H	1	3.592210	-0.899260	-0.324770
9	H	1	3.190860	0.066980	1.09555
10	H	1	2.668790	-1.617310	0.991990
11	H	1	-3.38830	1.061460	0.747850

12	H	1	-1.980360	1.341310	-0.519110
13	C	6	1.521050	-0.245750	-0.276010
14	H	1	1.203920	-1.048600	-0.948710
15	C	6	1.700490	1.045770	-1.065400
16	H	1	2.483170	0.927300	-1.815150
17	H	1	0.780420	1.323000	-1.577940
18	H	1	1.978160	1.871260	-0.409780

Table S1.18. Optimised parameters of SOZ-i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.037670	-0.276280	-0.548260
2	H	1	-0.094800	-1.000840	-1.368100
3	O	8	-0.568460	-0.887350	0.627040
4	O	8	-0.915210	0.805780	-0.814100
5	O	8	-2.196980	0.211170	-0.471280
6	C	6	-1.874840	-0.367890	0.776330
7	C	6	2.344060	-0.944410	-0.216640
8	H	1	3.374120	-0.592650	-0.161760
9	H	1	2.129660	-1.504650	0.693780
10	H	1	2.27048	-1.63127	-1.06102
11	H	1	-2.59693	-1.16524	0.95291
12	H	1	-1.89005	0.38075	1.5739

13	C	6	1.38449	0.24142	-0.36504
14	H	1	1.62391	0.76091	-1.29807
15	C	6	1.51227	1.22851	0.79691
16	H	1	2.53464	1.60242	0.85685
17	H	1	0.84764	2.08171	0.67399
18	H	1	1.27669	0.74395	1.74443

Table S1.19. Optimised parameters of IM2i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.041720	0.230368	-0.502100
2	H	1	-0.379680	-0.240950	-1.427980
3	O	8	-0.655950	-0.550990	0.582346
4	O	8	-0.441760	1.555025	-0.437720
5	O	8	-2.709720	-0.137970	-0.262680
6	C	6	-1.981570	-0.653720	0.547942
7	C	6	1.946254	-1.315700	-0.541800
8	H	1	3.035338	-1.356910	-0.533980
9	H	1	1.582112	-1.960590	0.257996
10	H	1	1.605766	-1.731090	-1.492000
11	H	1	-1.375110	1.593485	-0.681330
12	H	1	-2.332050	-1.280490	1.376777
13	C	6	1.469557	0.126415	-0.350410

14	H	1	1.861780	0.730616	-1.173290
15	C	6	1.967725	0.727615	0.966780
16	H	1	3.057789	0.72592	0.988183
17	H	1	1.626716	1.753934	1.087767
18	H	1	1.615265	0.147616	1.819798

Table S1.20. Optimised parameters of IM3i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.144120	-0.532700	-0.370330
2	H	1	2.681025	1.582937	0.321487
3	O	8	0.619882	0.040875	0.601206
4	O	8	0.287136	-1.308720	-1.180560
5	O	8	2.721380	0.741821	-0.143680
6	C	6	2.031282	-0.223340	0.583195
7	C	6	-1.706350	1.428014	-0.570120
8	H	1	-2.757210	1.717404	-0.598570
9	H	1	-1.214300	2.012851	0.206292
10	H	1	-1.260050	1.688999	-1.529840
11	H	1	2.319768	-0.236480	1.634155
12	H	1	2.217060	-1.178470	0.103647
13	C	6	-1.588890	-0.076260	-0.285410

14	H	1	-2.096330	-0.625470	-1.078310
15	C	6	-2.218940	-0.450360	1.063179
16	H	1	-3.276970	-0.186660	1.062131
17	H	1	-2.141190	-1.520370	1.257663
18	H	1	-1.736830	0.081346	1.882555

Table S1.21. Optimised parameters of IM4i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.190120	-0.335510	-0.684410
2	H	1	0.305038	0.166756	-1.507110
3	O	8	1.351705	1.415165	0.333345
4	O	8	0.473128	-1.184520	-0.041800
5	O	8	1.819173	-1.289430	-0.362180
6	6	6	2.393280	0.784515	0.422447
7	6	6	-1.904430	1.405165	-0.321560
8	H	1	-2.974330	1.571261	-0.203250
9	H	1	-1.377970	1.865132	0.512101
10	H	1	-1.581270	1.901769	-1.235980
11	H	1	3.147090	0.793854	-0.376420
12	H	1	2.692412	0.295076	1.358751
13	C	6	-1.624150	-0.109860	-0.367970

14	H	1	-2.164980	-0.509800	-1.238310
15	C	6	-2.097000	-0.838540	0.889549
16	H	1	-3.162840	-0.666730	1.033271
17	H	1	-1.929660	-1.912220	0.824062
18	H	1	-1.571050	-0.469530	1.769672

Table S1.22. Optimised parameters of POZ-i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	1.018819	1.165953	0.128235
2	H	1	0.717467	1.643656	-0.805880
3	C	6	0.021506	0.039520	0.522388
4	O	8	0.819330	-1.147340	0.388265
5	O	8	2.260526	0.497029	-0.032610
6	O	8	1.833526	-0.765940	-0.560860
7	H	1	1.163591	1.911436	0.906954
8	C	6	-1.253300	0.004247	-0.323750
9	H	1	-0.941000	-0.045370	-1.371410
10	C	6	-2.090290	-1.236940	-0.005490
11	H	1	-2.430140	-1.223740	1.032987
12	H	1	-2.975340	-1.275520	-0.641380
13	H	1	-1.519480	-2.150450	-0.161540
14	H	1	-0.230000	0.086642	1.584536

15	C	6	-2.068290	1.285367	-0.110900
16	H	1	-2.382190	1.378687	0.931480
17	H	1	-1.510990	2.185535	-0.373590
18	H	1	-2.969640	1.270187	-0.723480

Table S1.23. Optimised parameters of TS1i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.219230	-0.728670	0.013050
2	H	1	0.070360	-1.637270	-0.585720
3	O	8	-0.338140	-0.632520	1.121610
4	O	8	-1.243150	0.210600	-1.248270
5	O	8	-2.313380	-0.187410	-0.464870
6	C	6	-2.253410	0.265900	0.710420
7	C	6	2.682270	-0.707300	-0.081560
8	H	1	3.565490	-0.186620	-0.452100
9	H	1	2.798260	-0.849220	0.993840
10	H	1	2.654480	-1.691580	-0.551480
11	H	1	-2.977310	-0.151930	1.397910
12	H	1	-1.677920	1.150710	0.927830
13	C	6	1.413570	0.109810	-0.393390
14	H	1	1.352160	0.232800	-1.477260
15	C	6	1.440960	1.480370	0.276410

16	H	1	2.329620	2.033530	-0.029180
17	H	1	0.568330	2.069380	-0.003090
18	H	1	1.458260	1.384280	1.361950

Table S1.24. Optimised parameters of TS2i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.028110	-0.070040	-0.710270
2	H	1	0.030570	-0.762070	-1.576080
3	O	8	-0.584070	-0.815080	0.406210
4	O	8	-0.703150	0.994010	-0.982170
5	O	8	-2.724540	-0.161980	-0.125990
6	C	6	-1.800250	-0.213250	0.748840
7	C	6	2.235050	-1.123620	-0.114600
8	H	1	3.295370	-0.93350	0.061200
9	H	1	1.840030	-1.652750	0.751350
10	H	1	2.154360	-1.780610	-0.981160
11	H	1	-2.086210	-0.447060	1.786510
12	H	1	-1.412560	0.912310	0.791140
13	C	6	1.512370	0.197930	-0.334670
14	H	1	1.883760	0.681990	-1.239200
15	C	6	1.636550	1.153150	0.842690

16	H	1	1.224830	0.720060	1.754450
17	H	1	2.69219	1.360180	1.026960
18	H	1	1.137910	2.100710	0.648570

Table S1.25. Optimised parameters of TS3i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.124280	0.350560	-0.694050
2	H	1	-0.186500	-0.256100	-1.546810
3	O	8	-0.806440	-1.011380	0.422770
4	O	8	-0.537110	1.403760	-0.424540
5	O	8	-2.588930	0.241030	-0.135340
6	C	6	-2.035880	-0.748260	0.429740
7	C	6	2.104090	-1.180690	-0.501240
8	H	1	1.646340	-1.876040	0.199960
9	H	1	1.907510	-1.541060	-1.512160
10	H	1	3.182430	-1.197220	-0.347300
11	H	1	-1.626950	1.033510	-0.428580
12	H	1	-2.691720	-1.439830	0.976490
13	C	6	1.563360	0.235590	-0.291000
14	H	1	2.062570	0.899710	-1.012560
15	C	6	1.825120	0.775340	1.116230

16	H	1	2.895810	0.790660	1.318070
17	H	1	1.437890	1.785290	1.231890
18	H	1	1.346620	0.138490	1.859890

Table S1.26. Optimised parameters of TS4i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.079610	-0.288500	-0.266460
2	H	1	0.591562	0.347175	-1.127730
3	O	8	0.642957	0.394550	0.826483
4	O	8	0.542711	-1.453630	-0.499310
5	O	8	2.415899	0.082824	-0.610040
6	C	6	2.075386	0.452971	0.588618
7	C	6	-1.800030	1.431240	-0.412570
8	H	1	-2.877640	1.558550	-0.523320
9	H	1	-1.501590	1.899475	0.524555
10	H	1	-1.314060	1.964915	-1.229850
11	H	1	2.317726	1.510768	0.809899
12	H	1	2.577701	-0.144850	1.378367
13	C	6	-1.456600	-0.054260	-0.421490
14	H	1	-1.703430	-0.487180	-1.391120
15	C	6	-2.191130	-0.835140	0.6754650

16	H	1	-3.268190	-0.730660	0.5374670
17	H	1	-1.939880	-1.893610	0.6392040
18	H	1	-1.938200	-0.452430	1.6640050

Table S1.27. Optimised parameters of TS5i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.044660	-0.077830	-0.144420
2	H	1	-1.430990	-0.349680	1.093255
3	O	8	-0.794130	0.241359	-1.036070
4	O	8	-0.294040	-0.546580	0.996483
5	O	8	-2.547370	0.144105	0.759230
6	C	6	-2.509510	-0.035400	-0.500510
7	C	6	2.314601	-1.148720	-0.116640
8	H	1	3.366159	-0.989990	-0.355390
9	H	1	2.237046	-1.406520	0.938380
10	H	1	1.961867	-1.998800	-0.701090
11	H	1	-2.974870	0.711153	-1.146090
12	H	1	-2.516610	-1.052200	-0.907580
13	C	6	1.515907	0.122272	-0.429800
14	H	1	1.590688	0.348528	-1.493460
15	C	6	2.027925	1.329401	0.373912

16	H	1	3.076720	1.509807	0.138508
17	H	1	1.468458	2.234238	0.136864
18	H	1	1.944376	1.144066	1.444282

Table S1.28. Optimised parameters of TS6i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.113690	-0.283810	-0.679490
2	H	1	0.322494	0.268889	-1.500810
3	O	8	1.084765	1.327702	0.438534
4	O	8	0.600327	-1.159110	-0.116140
5	O	8	1.958103	-1.053870	-0.400250
6	C	6	2.221414	0.837584	0.440458
7	C	6	-2.009290	1.277757	-0.385850
8	H	1	-3.091170	1.330871	-0.272330
9	H	1	-1.538280	1.831371	0.423178
10	H	1	-1.742580	1.762008	-1.325130
11	H	1	2.943970	1.067056	-0.352270
12	H	1	2.639683	0.392818	1.350576
13	C	6	-1.563310	-0.194780	-0.360100
14	H	1	-2.058160	-0.697660	-1.204550
15	C	6	-1.947440	-0.908290	0.936591

16	H	1	-3.023390	-0.835940	1.089742
17	H	1	-1.675690	-1.962050	0.917071
18	H	1	-1.448540	-0.445980	1.787776

Table S1.29. Optimised parameters of TS7i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.065370	-0.277810	-0.781400
2	H	1	0.152083	0.372505	-1.631600
3	O	8	0.759356	1.171366	0.408249
4	O	8	0.694031	-1.241160	-0.532770
5	O	8	2.344698	-0.249320	-0.345810
6	C	6	1.841590	0.511625	0.642383
7	C	6	-2.155180	1.084381	-0.435170
8	H	1	-3.228140	1.009390	-0.258110
9	H	1	-1.730170	1.782321	0.283301
10	H	1	-2.011910	1.498206	-1.434240
11	H	1	2.850175	1.082594	0.428989
12	H	1	1.973709	0.099158	1.659838
13	C	6	-1.505260	-0.293210	-0.296300
14	H	1	-1.987660	-0.967470	-1.017700
15	C	6	-1.662420	-0.893200	1.099878

16	H	1	-2.719910	-0.995500	1.343210
17	H	1	-1.199290	-1.875400	1.167814
18	H	1	-1.203760	-0.243650	1.844802

Table S1.30. Optimised parameters of TS8i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-0.039940	0.005208	0.480148
2	H	1	0.218716	-0.501320	1.578419
3	O	8	-0.808540	1.062325	0.484319
4	O	8	-0.695000	-1.140060	0.669308
5	O	8	-1.985670	-0.630080	-0.793900
6	C	6	-2.235790	0.483441	-0.209900
7	H	1	-2.879850	0.493816	0.675224
8	H	1	-2.388630	1.335628	-0.882460
9	C	6	1.238441	0.038144	-0.364900
10	H	1	0.852633	0.042021	-1.390200
11	C	6	2.019675	1.331952	-0.125730
12	H	1	2.420512	1.365784	0.889483
13	H	1	2.861575	1.391814	-0.814990
14	H	1	1.393568	2.209441	-0.271410
15	C	6	2.095516	-1.20977	-0.165400

16	H	1	2.946508	-1.189600	-0.845640
17	H	1	2.491764	-1.259400	0.852028
18	H	1	1.529469	-2.119480	-0.353550

Table S1.31. Optimised parameters of TS9i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	O	8	0.565659	-1.331790	0.187520
2	C	6	-0.088710	-0.277720	0.466012
3	C	6	1.112061	1.096477	-0.059830
4	O	8	2.253277	0.507832	0.255888
5	O	8	2.421931	-0.594860	-0.445230
6	H	1	0.950466	1.995010	0.521237
7	C	6	-1.372310	0.030825	-0.335560
8	H	1	-1.110360	-0.025850	-1.395080
9	C	6	-2.389730	-1.078880	-0.035560
10	H	1	-3.304340	-0.923060	-0.609260
11	H	1	-1.981220	-2.055470	-0.288350
12	H	1	-2.658840	-1.087300	1.023102
13	H	1	0.862590	1.097682	-1.113890
14	H	1	-0.160150	-0.007220	1.536244
15	C	6	-1.955720	1.407802	-0.013760

16	H	1	-1.316010	2.228411	-0.340920
17	H	1	-2.919390	1.537420	-0.506400
18	H	1	-2.123220	1.519946	1.060030

Table S1.32. Optimised parameters of TS10i.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	O	8	-1.407510	1.146612	0.474345
2	C	6	0.287874	-0.464520	0.694941
3	C	6	-0.523220	-1.527740	0.419682
4	O	8	-2.384400	-0.565370	-0.373030
5	O	8	-1.919900	0.616845	-0.581880
6	C	6	1.302615	0.075279	-0.277460
7	H	1	0.835224	0.089052	-1.268140
8	H	1	-1.119490	-1.987070	1.191593
9	C	6	1.749519	1.495856	0.075313
10	H	1	2.223953	1.518584	1.059136
11	H	1	2.477185	1.861630	-0.649520
12	H	1	0.904641	2.181432	0.092618
13	H	1	-0.451900	-2.056520	-0.520690
14	H	1	0.335987	-0.101800	1.714496
15	C	6	2.517550	-0.873630	-0.354830

16	H	1	3.242086	-0.498100	-1.078550
17	H	1	3.016412	-0.944720	0.613310
18	H	1	2.224322	-1.878720	-0.655680

Table S1.33. Optimised parameters of Formic acid (P1).

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.133818	0.361049	0.000043
2	H	1	0.042063	1.459768	-0.000079
3	O	8	1.172698	-0.219860	-0.000014
4	O	8	-1.056020	-0.278450	-0.000004
5	H	1	-1.778430	0.360447	-0.000036

Table S1.34. Optimised parameters of Formaldehyde (P2).

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	O	8	0	0	0.672848
2	C	6	0	0	-0.526580
3	H	1	0	0.938333	-1.111650
4	H	1	0	-0.938330	-1.111650

Table S1.35. Optimised parameters of Butyric acid (P3).

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	-2.701560	0.012117	0.011388
2	H	1	-2.884510	0.753550	0.791053
3	H	1	-2.923690	-0.971040	0.429602
4	H	1	-3.411050	0.197198	-0.795360
5	C	6	-1.263410	0.085939	-0.496840
6	H	1	-1.114200	-0.645510	-1.293630
7	H	1	-1.073110	1.068627	-0.931720
8	C	6	-0.238980	-0.178430	0.621838
9	H	1	-0.399450	-1.167090	1.048624
10	H	1	-0.356800	0.566688	1.409621
11	C	6	1.174187	-0.134040	0.103941
12	O	8	1.835511	-1.086180	-0.221330
13	O	8	1.640467	1.136280	0.004468
14	H	1	2.533559	1.083236	-0.365260

Table S1.36. Optimised parameters of n-Butyraldehyde oxide (P4).

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	1.567124	0.545660	-0.052030
2	H	1	1.553666	1.296743	0.741170
3	H	1	1.291162	1.062457	-0.972870

4	C	6	0.509598	-0.536060	0.250549
5	H	1	0.797716	-1.062030	1.167840
6	H	1	0.469732	-1.272710	-0.552030
7	C	6	-0.841430	0.033947	0.451402
8	H	1	-1.086780	0.742481	1.238881
9	O	8	-1.770570	-0.284250	-0.329360
10	O	8	-3.010810	0.261556	-0.142180
11	C	6	2.969855	-0.043880	-0.183050
12	H	1	3.699437	0.735057	-0.402700
13	H	1	3.278989	-0.539490	0.738605
14	H	1	3.016218	-0.778950	-0.987800

Table S1.37. Optimised parameters of 1-Pentene (P5).

Cartesian coordinate					
Center No.		Atomic No.	X	Y	Z
1	C	6	-2.426330	-0.194980	-0.076810
2	H	1	-2.688810	-0.242160	0.981859
3	H	1	-3.209220	0.366864	-0.587340
4	H	1	-2.444250	-1.214910	-0.465580
5	C	6	-1.056160	0.449697	-0.278870
6	H	1	-1.076420	1.478412	0.091623
7	H	1	-0.830680	0.515568	-1.345970
8	C	6	0.075345	-0.316770	0.423379

9	H	1	-0.168070	-0.392190	1.489341
10	H	1	0.119461	-1.339920	0.041378
11	C	6	1.415376	0.337267	0.270244
12	H	1	1.494200	1.349787	0.658226
13	C	6	2.480470	-0.212330	-0.300600
14	H	1	2.452604	-1.217880	-0.703760
15	H	1	3.418959	0.319082	-0.383870

Table S1.38. Optimised parameters of Isobutyric acid (P6).

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	O	8	-1.110880	-1.130300	0.676780
2	C	6	-0.782050	-0.191820	-0.001610
3	C	6	0.635017	0.177794	-0.391190
4	C	6	1.560690	-1.034230	-0.314290
5	H	1	2.569508	-0.752720	-0.616540
6	H	1	1.601704	-1.427310	0.700578
7	H	1	1.221058	-1.838400	-0.966040
8	C	6	1.119688	1.331581	0.506948
9	H	1	1.155329	1.018167	1.551053
10	H	1	2.124762	1.632135	0.211653
11	H	1	0.467636	2.200092	0.429338
12	H	1	0.592023	0.547253	-1.418000

13	O	8	-1.685990	0.693516	-0.491410
14	H	1	-2.55713	0.415118	-0.174170

Table S1.39. Optimised parameters of Isobutyraldehyde oxide (P7).

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.450491	-0.474100	-0.345380
2	O	8	1.339479	0.279480	0.113287
3	C	6	-0.965460	-0.022110	-0.417050
4	H	1	-1.232440	-0.072630	-1.481490
5	C	6	-1.175200	1.408474	0.078245
6	H	1	-0.558350	2.118375	-0.470060
7	H	1	-2.219240	1.692108	-0.048060
8	H	1	-0.924350	1.497707	1.135006
9	C	6	-1.864290	-1.038270	0.317667
10	H	1	-2.911820	-0.781520	0.164396
11	H	1	-1.709870	-2.053750	-0.047590
12	H	1	-1.663840	-1.027550	1.389137
13	H	1	0.769327	-1.460700	-0.674350
14	O	8	2.632688	-0.173980	0.165724

Table S1.40. Optimised parameters of Isopentene (P8).

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	C	6	0.949812	0.000158	0.413180
2	C	6	2.146063	0.000019	-0.161590
3	C	6	-0.369710	-0.000051	-0.307990
4	H	1	-0.165560	-0.000018	-1.382650
5	H	1	3.057453	-0.000110	0.421108
6	C	6	-1.175000	-1.264660	0.028318
7	H	1	-1.388660	-1.317170	1.098271
8	H	1	-2.129410	-1.269320	-0.500710
9	H	1	-0.628360	-2.166500	-0.247190
10	H	1	2.257532	-0.000150	-1.239620
11	H	1	0.887496	0.000120	1.499512
12	C	6	-1.175130	1.264621	0.028275
13	H	1	-2.129430	1.269264	-0.50092
14	H	1	-1.388910	1.316919	1.098204
15	H	1	-0.628410	2.166427	-0.24714

Table S1.41. Optimised parameters of Ozone.

Cartesian coordinate					
Center No.	Atom	Atomic No.	X	Y	Z
1	O	8	0	0	0.427990
2	O	8	0	1.076416	-0.214000

3	O	8	0	-1.076420	-0.214000

Table S2. Vibrational frequencies (cm^{-1}) for the reactants, transition states, intermediates at B3LYP/6-311+G(2df,2p) level of theory:

Table S2.1. Normal mode frequencies of CH_2OO, nBD, IM1n, SOZ-n, IM2n, IM3n, IM4n and POZ-n.

CH_2OO	nBD	IM1n	SOZ-n	IM2n	IM3n	IM4n	POZ-n
530.15	81.53	32.68	69.26	71.79	17.39	69.38	65.29
674.69	172.88	47.77	84.09	79.76	62.28	84.26	92.71
925.57	192.43	66.01	102.05	94.34	84.67	102.09	114.84
949.84	245.31	96.23	203.64	194.17	86.19	203.73	169.39
1244.87	344.68	122.63	**244.94**	226.27	194.58	244.96	246.15
1403.5	669.28	158.64	309.49	**244.95**	242.97	309.51	307.77
1543.3	693.02	193.41	317.52	286.25	287.28	317.55	359.32
3121.96	793.18	215.14	341.32	311.52	314.29	341.36	400.89
3272.47	852.81	**244.36**	657.52	372.47	**373.61**	657.53	512.70
	952.93	254.19	700.12	501.11	413.50	700.12	695.03
	962.85	346.91	737.95	560.98	560.83	737.93	713.71
	1044.39	527.04	746.95	665.71	645.80	746.97	739.26
	1133.81	674.74	834.65	744.87	754.91	834.65	765.85
	1157.19	678.63	847.45	776.64	759.69	847.47	844.77

	1257.20	698.36	885.73	839.58	845.12	885.83	891.68
	1318.86	799.80	936.32	864.86	899.99	936.31	906.55
	1326.10	855.16	948.46	915.33	911.28	948.41	922.66
	1397.20	897.69	997.22	975.21	976.09	997.16	969.61
	1417.87	954.18	1036.23	1039.88	1038.95	1036.20	1005.44
	1423.09	967.14	1068.42	1049.23	1053.50	1068.27	1034.66
	1452.29	992.93	1129.55	1103.85	1085.80	1129.52	1043.96
	1496.56	1045.05	1133.42	1123.95	1112.10	1133.42	1075.56
	1506.11	1134.88	1147.00	1163.09	1113.27	1146.95	1131.97
	1513.25	1150.60	1162.15	1219.38	1214.47	1162.10	1171.24
	1802.75	1243.81	1218.85	1252.19	1274.51	1218.79	1236.31
	2864.76	1259.55	1270.42	1280.54	1291.75	1270.42	1269.79
	2992.61	1318.91	1325.79	1335.47	1315.63	1325.80	1278.05
	3009.32	1326.13	1330.73	1344.34	1333.31	1330.72	1326.98
	3024.57	1396.99	1354.26	1391.92	1380.53	1354.17	1338.05
	3043.84	1417.09	1393.55	1399.12	1396.09	1393.53	1348.94
	3063.07	1419.47	1405.78	1411.81	1420.26	1405.74	1385.20
	3088.27	1423.90	1415.77	1422.04	1439.91	1415.74	1404.61
	3092.74	1452.70	1425.08	1457.47	1486.85	1425.06	1421.60
		1496.39	1478.32	1480.48	1500.63	1478.32	1478.77
		1505.58	1501.72	1501.38	1504.00	1501.71	1499.30
		1512.40	1505.63	1505.55	1510.93	1505.63	1505.48
		1567.10	1517.77	1517.49	1515.12	1517.76	1508.01
		1754.78	1529.05	1762.43	1803.07	1529.07	1514.47

		2929.57	3004.36	3023.71	3027.84	3004.70	3003.99
		2988.46	3011.92	3029.93	3032.63	3011.87	3014.06
		3024.58	3024.57	3039.48	3055.33	3024.57	3025.98
		3038.44	3031.53	3044.08	3059.26	3031.55	3036.92
		3044.43	3045.23	3049.46	3060.50	3045.22	3041.50
		3063.45	3054.97	3059.81	3088.52	3054.97	3056.64
		3087.46	3069.82	3071.61	3094.04	3069.81	3066.02
		3090.37	3091.96	3091.50	3108.96	3091.94	3086.22
		3136.41	3092.72	3094.92	3154.83	3092.70	3092.75
		3281.49	3092.95	3774.29	3824.02	3092.95	3117.52

Table S2.2. Normal mode frequencies of TS1n, TS2n, TS3n, TS4n, TS5n, TS6n, TS7n, TS8n, TS9n and TS10n.

TS1n	TS2n	TS3n	TS4n	TS5n	TS6n	TS7n	TS8n	TS9n	TS10n
253.83i	959.32i	972.82i	808.44i	999.95i	130.97i	767.66i	1182.47i	420.90i	172.07i
35.72	70.31	63.20	72.69	26.43	55.36	70.23	60.67	62.62	51.84
73.74	101.32	73.65	83.59	74.15	78.58	76.79	76.86	91.32	63.01
78.41	118.36	99.39	137.50	82.25	88.09	105.69	122.72	111.45	89.30
185.31	180.68	207.63	220.31	176.41	147.75	169.15	178.77	146.26	149.92
191.80	232.59	224.47	**240.45**	216.78	176.99	219.63	**243.60**	**244.96**	188.18
246.87	**244.57**	**251.56**	288.34	**243.70**	**243.76**	**245.81**	271.68	289.67	213.73
280.03	300.72	264.05	308.79	304.75	322.24	277.38	291.58	309.47	239.86
354.73	415.12	322.58	343.83	345.71	342.34	314.84	330.95	364.53	357.83

406.48	472.67	391.47	364.01	487.07	355.88	374.87	386.85	467.94	397.16
449.44	510.28	454.39	545.36	546.31	399.68	461.19	446.52	509.56	451.21
548.24	630.38	648.07	629.67	577.95	487.65	524.60	573.18	565.52	477.07
679.33	711.33	700.93	725.14	747.27	670.53	669.79	622.81	602.14	653.41
733.96	758.01	751.34	750.78	760.96	686.83	712.13	742.15	756.79	742.75
759.25	810.79	834.54	786.85	804.04	725.33	744.83	775.30	865.23	753.07
827.33	862.74	857.31	820.47	894.56	838.77	848.03	885.68	889.29	873.40
862.40	896.29	874.87	880.32	908.18	866.11	864.14	894.43	904.78	880.06
911.31	925.13	981.98	912.50	948.01	947.97	881.29	910.63	948.65	953.00
965.08	946.75	1044.25	942.08	976.80	961.92	973.84	935.19	1002.08	957.02
980.07	1007.65	1049.65	1000.17	1039.32	1005.87	1012.40	991.39	1041.52	992.66
1039.14	1032.03	1069.62	1033.93	1111.35	1047.13	1044.77	1045.17	1069.20	1044.26
1048.83	1067.45	1133.52	1058.54	1115.95	1119.32	1112.99	1111.48	1094.46	1075.12
1132.63	1110.25	1170.38	1109.53	1222.97	1141.84	1126.18	1126.19	1130.97	1099.77
1137.00	1134.79	1259.97	1125.60	1252.97	1156.45	1135.12	1171.78	1171.81	1113.65
1228.61	1177.29	1311.73	1138.71	1287.99	1244.08	1211.81	1208.37	1235.56	1122.52
1260.05	1187.14	1329.48	1231.11	1308.01	1257.01	1258.64	1245.27	1262.14	1182.70
1315.30	1244.24	1339.68	1255.06	1314.26	1327.88	1310.85	1261.11	1268.47	1260.70
1327.54	1254.66	1373.40	1275.13	1329.39	1330.36	1322.71	1309.74	1306.07	1298.18
1393.72	1273.67	1378.15	1309.10	1381.46	1359.77	1329.34	1330.54	1329.38	1301.70
1396.07	1291.07	1401.53	1316.84	1418.65	1412.81	1364.13	1339.85	1359.04	1327.82
1402.54	1323.39	1416.69	1344.69	1421.20	1424.37	1389.76	1384.18	1381.93	1389.63
1420.36	1377.48	1422.56	1366.45	1445.06	1442.88	1398.27	1412.66	1418.81	1420.61
1462.91	1383.53	1453.37	1387.31	1490.44	1485.53	1421.42	1422.88	1459.76	1456.67

1500.70	1418.27	1499.77	1418.37	1500.98	1498.84	1460.38	1480.42	1477.25	1466.47
1505.32	1480.98	1506.19	1476.28	1504.22	1506.82	1499.57	1500.04	1484.30	1499.79
1515.01	1500.29	1514.74	1499.52	1515.00	1513.45	1505.71	1503.45	1498.25	1505.33
1547.70	1502.63	1569.23	1501.12	1606.58	1553.14	1512.73	1505.35	1503.99	1514.03
1599.58	1515.65	1635.75	1513.60	1648.58	1646.26	1526.98	1516.39	1512.75	1586.38
2980.77	2094.63	1835.57	2122.47	1776.34	2966.84	2413.37	2185.51	2896.76	2985.08
2997.05	2840.93	2991.68	2850.07	2994.68	2995.16	2901.78	2981.02	3008.56	3009.94
3024.42	2963.83	3010.89	2877.97	3028.81	3028.64	3000.03	3018.92	3020.59	3022.71
3036.35	3025.88	3025.64	3026.72	3034.60	3032.70	3025.97	3027.91	3026.56	3026.50
3053.02	3029.32	3048.06	3040.63	3052.76	3035.82	3047.16	3032.55	3054.06	3060.45
3066.56	3050.69	3059.92	3058.05	3064.39	3048.15	3057.68	3044.36	3071.33	3085.97
3087.82	3068.90	3067.62	3065.75	3084.27	3070.44	3065.89	3062.32	3089.08	3093.19
3090.07	3090.18	3075.05	3089.09	3090.16	3094.66	3079.04	3081.35	3092.49	3156.44
3146.16	3094.81	3094.09	3091.99	3096.33	3100.40	3093.38	3094.21	3107.92	3166.24
3287.25	3107.20	3096.85	3109.74	3109.39	3200.35	3096.58	3096.40	3227.92	3251.20

Table S2.3. Normal mode frequencies of iBD, IM1i, SOZ-I, IM2i, IM3i, IM4i and POZ-i

iBD	IM1i	SOZ-i	IM2i	IM3i	IM4i	POZ-i
95.52	29.33	75.30	80.28	26.73	39.69	76.34
201.05	44.99	99.13	89.99	66.23	84.46	99.93
228.12	73.99	196.58	177.42	83.71	92.62	196.93
270.88	90.37	208.23	214.34	195.09	129.94	219.57
342.93	143.73	**240.85**	234.99	215.12	191.87	238.65
400.82	184.29	258.69	244.65	243.00	210.14	313.24

639.25	205.36	330.81	263.25	252.17	220.35	349.72
792.18	213.97	360.74	296.15	309.12	264.66	381.64
914.63	**232.70**	446.41	358.94	343.70	298.99	445.50
926.80	276.81	593.50	460.83	**378.17**	320.68	492.13
946.21	352.29	707.92	515.82	509.46	359.90	689.23
974.70	417.51	746.51	**559.22**	535.35	453.37	718.75
1129.43	526.83	823.94	618.64	644.87	464.00	766.38
1154.64	648.01	883.30	771.23	775.34	539.12	820.08
1201.82	678.75	915.82	840.84	807.66	602.63	895.36
1305.29	796.65	934.15	863.60	900.36	832.29	920.86
1355.26	897.26	947.87	939.08	944.04	926.58	938.09
1407.79	913.71	972.44	960.99	962.12	934.47	961.92
1412.44	931.60	992.36	973.83	973.72	945.70	984.47
1434.81	948.55	1063.77	1048.65	1045.60	976.44	994.69
1490.31	974.37	1091.44	1109.34	1063.81	980.03	1026.32
1494.29	992.49	1137.97	1131.85	1111.38	1110.09	1033.09
1508.36	1123.21	1148.70	1136.37	1116.74	1145.93	1134.56
1512.73	1148.74	1161.19	1206.52	1190.94	1154.73	1184.64
1801.51	1199.84	1210.65	1218.95	1255.16	1208.23	1195.50
2856.51	1243.88	1220.20	1269.82	1289.68	1254.27	1247.13
2975.58	1305.12	1327.90	1349.98	1351.60	1294.27	1294.27
3030.96	1366.72	1346.18	1368.46	1353.35	1349.59	1318.67
3042.00	1404.83	1371.14	1394.23	1396.04	1377.87	1349.26
3091.28	1413.47	1397.37	1400.20	1403.78	1414.12	1357.93

3100.18	1417.51	1407.61	1407.57	1424.18	1433.55	1396.15
3103.59	1434.31	1410.66	1423.30	1441.32	1492.28	1408.65
3112.83	1491.49	1433.61	1458.29	1494.40	1494.80	1430.34
	1493.90	1494.57	1495.46	1496.46	1506.74	1493.79
	1508.02	1499.26	1499.18	1507.17	1513.61	1497.90
	1513.22	1508.42	1509.36	1510.88	1515.36	1505.00
	1567.05	1520.85	1522.20	1517.97	1566.27	1510.84
	1754.30	1529.43	1762.89	1799.41	1708.23	1518.08
	2922.94	3000.58	3025.51	3035.53	2955.10	3013.54
	3023.70	3012.01	3031.93	3038.22	2961.18	3023.87
	3029.53	3019.73	3039.18	3061.28	3018.79	3028.34
	3040.21	3034.00	3040.67	3065.30	3046.07	3039.94
	3090.32	3042.32	3042.95	3096.41	3048.58	3047.67
	3097.78	3093.72	3091.27	3098.90	3110.14	3081.42
	3101.58	3094.74	3098.05	3106.43	3112.48	3086.41
	3108.20	3098.80	3104.35	3113.41	3117.37	3096.44
	3136.46	3104.28	3119.13	3155.67	3128.65	3114.36
	3281.50	3115.51	3775.97	3824.50	3179.23	3121.53

Note: ‘i’ stands for imaginary frequency

Table S2.4. Normal mode frequencies of TS1i, TS2i, TS3i, TS4i, TS5i, TS6i, TS7i, TS8i, TS9i and TS10i.

TS1i	TS2i	TS3i	TS4i	TS5i	TS6i	TS7i	TS8i	TS9i	TS10i
239.33i	936.73i	962.51i	824.45i	989.93i	138.91i	755.32i	1192.22i	428.76i	181.07i
40.96	86.29	66.08	68.61	20.39	47.46	71.05	52.33	69.71	44.48

63.18	99.68	99.38	172.82	85.57	83.99	111.84	112.00	84.71	75.37
140.28	180.08	155.49	186.01	168.10	128.25	142.01	193.11	183.74	134.00
212.18	205.89	205.13	214.68	211.08	191.61	198.98	211.47	218.55	191.84
231.63	214.67	**219.32**	**239.18**	216.55	214.99	212.39	**229.98**	247.69	225.56
243.49	**231.26**	262.52	259.02	**251.28**	**231.43**	**237.92**	269.66	292.52	246.65
284.67	314.80	268.13	298.27	265.07	287.33	264.50	315.87	314.98	263.96
299.19	359.94	334.54	327.76	297.42	333.08	333.88	325.49	356.90	339.30
382.19	460.55	367.80	372.54	413.47	366.06	363.17	368.59	410.73	370.69
404.62	476.93	414.72	466.70	530.66	420.80	432.13	401.90	474.98	419.84
514.94	508.45	481.43	537.39	545.45	466.83	481.28	493.42	521.08	491.06
562.81	632.37	642.49	637.08	585.02	508.09	531.52	548.18	574.16	497.56
652.89	728.23	697.39	649.67	761.84	604.14	622.71	619.72	600.77	722.26
756.74	776.25	812.70	781.12	799.48	698.76	710.51	787.18	823.50	745.64
805.27	824.47	849.34	833.41	860.98	836.93	813.24	826.50	889.64	802.97
908.83	879.31	935.97	886.85	929.14	927.29	873.89	893.80	907.12	922.88
919.97	932.54	963.31	939.73	944.93	944.21	935.35	914.04	936.36	939.15
942.16	940.66	977.62	942.40	969.16	949.08	951.43	940.73	969.63	957.09
968.69	958.28	1027.26	957.94	974.71	978.55	973.26	972.35	978.55	968.21
983.01	1000.20	1069.37	981.19	1113.36	983.53	994.63	997.52	1068.33	997.67
1043.45	1055.36	1151.06	1042.56	1115.11	1106.23	1107.61	1116.17	1092.36	1016.80
1111.41	1089.21	1164.59	1108.27	1193.73	1147.68	1123.16	1134.45	1135.57	1097.22
1136.19	1140.99	1212.66	1132.40	1222.77	1160.03	1146.83	1168.91	1171.84	1111.68
1198.36	1157.48	1304.94	1138.60	1286.80	1209.59	1209.63	1192.83	1188.70	1119.61
1229.33	1188.97	1327.96	1195.00	1311.10	1243.01	1212.17	1208.31	1241.70	1186.10

1318.50	1207.13	1349.21	1236.85	1340.17	1295.99	1318.02	1263.73	1269.71	1209.01
1369.35	1262.30	1373.80	1276.25	1347.71	1345.64	1322.45	1315.48	1312.24	1295.82
1397.24	1280.62	1379.53	1314.98	1403.49	1371.50	1335.62	1334.53	1346.06	1320.96
1398.26	1311.24	1406.14	1345.53	1411.07	1412.80	1369.65	1338.70	1355.53	1337.71
1403.07	1365.27	1407.88	1349.41	1420.36	1431.22	1396.13	1393.37	1404.16	1402.39
1420.64	1386.28	1431.10	1365.08	1458.29	1482.54	1406.00	1413.02	1424.00	1422.56
1492.67	1403.48	1493.72	1402.21	1493.61	1492.59	1427.31	1431.80	1455.39	1455.43
1496.27	1421.80	1498.76	1424.79	1496.25	1495.88	1491.23	1494.51	1485.18	1494.01
1506.54	1483.95	1506.96	1486.46	1506.69	1506.69	1496.32	1497.40	1492.89	1494.34
1518.56	1495.61	1517.77	1496.57	1521.67	1513.98	1503.05	1501.53	1495.44	1505.98
1548.23	1499.07	1564.62	1501.05	1607.17	1543.46	1511.21	1506.72	1511.16	1517.52
1599.82	1515.61	1635.66	1514.77	1649.60	1641.40	1519.52	1517.65	1515.04	1581.09
2983.19	2096.75	1834.78	2125.48	1772.67	2957.65	2415.19	2167.67	2881.98	2998.75
3028.82	2846.75	2963.35	2850.91	2994.35	2966.53	2900.95	2978.85	3024.87	3026.90
3036.45	2957.88	3009.81	2877.05	3038.32	3031.89	2972.91	3012.73	3026.08	3031.36
3039.11	3032.96	3039.34	3035.25	3040.94	3046.17	3038.83	3028.01	3032.46	3085.21
3091.32	3038.66	3046.35	3039.18	3064.58	3048.87	3045.41	3035.81	3081.50	3091.95
3095.25	3054.50	3060.04	3062.99	3083.81	3108.05	3052.81	3040.58	3086.62	3102.64
3099.64	3089.20	3098.01	3094.40	3100.19	3113.05	3095.39	3088.99	3094.17	3118.09
3108.15	3093.08	3107.09	3100.22	3103.41	3118.97	3105.63	3094.87	3109.24	3156.81
3145.92	3112.82	3119.84	3111.18	3110.50	3132.11	3121.16	3122.60	3116.27	3160.91
3287.33	3118.97	3124.65	3118.86	3118.18	3194.20	3122.88	3122.83	3233.13	3251.31

Table S2.5. Normal mode frequencies of formic acid (P1), formaldehyde (P2), butyric acid (P3), n-butyraldehyde oxide (P4), 1-pentene (P5), isobutyric acid (P6), isobutyraldehyde oxide (P7), isopentane (P8) and ozone.

Formic acid (P1)	Formal dehyde (P2)	Butyric acid (P3)	N-butyral dehyde oxide (P4)	1-Pentene (P5)	Iso butyric acid (P6)	Iso butyral dehyde oxide (P7)	Iso pentene (P8)	Ozone
533.21	1200.41	26.78	66.43	96.90	36.10	86.34	98.52	748.52
661.12	1264.24	90.41	89.50	102.48	117.67	189.99	222.98	1209.08
1035.86	1530.74	185.37	169.52	230.23	153.12	196.01	239.66	1259.78
1105.50	1817.03	243.32	244.39	245.84	207.18	222.18	312.84	
1269.04	2887.10	329.09	301.10	383.79	214.76	258.55	321.71	
1415.83	2942.95	431.17	337.76	436.94	330.12	334.82	346.77	
1859.95		581.94	384.68	645.22	444.36	437.10	504.69	
2963.13		621.28	580.64	751.22	580.91	444.38	697.29	
		742.05	749.03	878.38	658.98	603.68	801.11	
		758.33	848.83	889.64	815.43	826.62	930.62	
		876.66	882.22	952.44	862.74	928.33	933.02	
		896.64	944.87	953.16	979.70	930.04	952.89	
		914.43	950.50	1026.50	1030.29	941.85	963.87	
		1038.46	1021.05	1035.81	1105.09	971.69	1008.29	
		1073.79	1042.62	1051.84	1110.20	975.38	1035.74	

		1113.04	1106.10	1114.61	1173.08	1109.32	1115.19	
		1199.74	1178.44	1198.79	1199.19	1140.51	1185.29	
		1261.42	1259.25	1268.37	1216.96	1205.36	1218.60	
		1300.73	1295.75	1303.75	1281.05	1301.87	1322.50	
		1327.37	1328.56	1324.26	1382.27	1343.20	1338.20	
		1363.06	1358.58	1335.44	1421.73	1374.90	1343.06	
		1382.57	1381.64	1381.55	1464.89	1411.62	1400.71	
		1420.69	1422.48	1417.88	1472.34	1433.11	1420.11	
		1488.05	1474.81	1458.82	1483.01	1492.34	1462.08	
		1500.82	1498.66	1486.83	1495.43	1496.15	1492.97	
		1504.13	1504.58	1498.38	1500.38	1508.06	1493.71	
		1515.55	1513.25	1503.86	1504.46	1513.87	1505.65	
		1807.82	1566.52	1513.82	1808.96	1565.84	1514.27	
		3028.32	3003.84	1702.76	3036.86	2971.87	1700.84	
		3034.14	3030.09	2995.02	3042.72	3037.40	3013.31	
		3055.60	3033.50	3017.14	3046.41	3047.15	3021.05	
		3061.38	3059.48	3024.74	3062.63	3103.02	3025.40	
		3089.59	3087.02	3034.44	3107.83	3107.66	3077.99	
		3094.98	3096.83	3053.30	3114.02	3111.57	3084.37	
		3111.88	3101.78	3083.82	3116.25	3117.46	3095.17	
		3753.82	3136.89	3089.06	3153.19	3131.44	3096.57	
				3114.67			3105.70	
				3129.47			3128.69	
				3209.22			3208.21	

Table S3. Theoretically calculated relative zero-point energy correction (ΔE_{ZPE}), reaction energy (ΔE^0_r), change in reaction enthalpy (ΔH^0), Gibbs' free energy change (ΔG^0), entropy (S^0) and zero-point energy corrected activation barrier heights ($\Delta E_{r,ZPE}$) for all the stationary points at CCSD(T)-F12/cc-pVTZ-F12//B3LYP/6-311+G(2df,2p).

(CH_2OO + nBD)						
B3LYP/6-311+G(2df,2p)					CCSD(T)-F12/cc-pVTZ-F12	
Stationary Points	ΔE_{ZPE} kcal mol^{-1}	ΔH^0 kcal mol^{-1}	ΔG^0 kcal mol^{-1}	S^0 cal K^{-1} mol^{-1}	ΔE^0_r [a] kcal mol^{-1}	$\Delta E_{r,ZPE}$ [b] kcal mol^{-1}
CH_2OO + nBD		0	0	137.05	0	0
TS1n	2.17	-2.40	9.94	95.66	-8.49	-6.32
TS2n	-0.31	-1.02	12.55	91.52	-12.12	-12.43
TS3n	1.62	-104.82	-91.80	93.36	-111.34	-109.72
TS4n	-0.44	-1.65	11.97	91.37	-12.37	-12.81
TS5n	1.88	-103.82	-91.29	95.00	-110.88	-109.00
TS6n	1.99	-6.43	5.95	95.51	-10.93	-8.95
TS7n	0.29	-4.52	8.36	93.86	-9.19	-8.90
TS8n	0.27	-4.95	8.15	93.10	-10.26	-10.00
TS9n	2.40	24.18	37.49	92.41	15.53	17.94
TS10n	1.28	61.45	74.08	94.69	55.00	56.28
IM1n	1.26	-4.25	5.29	105.02	-9.50	-8.24
SOZ-n	5.41	-40.80	-26.88	90.36	-56.48	-51.08
IM2n	5.31	-117.63	-104.61	93.36	-132.68	-127.37
IM3n	5.25	-117.40	-106.11	99.19	-131.06	-125.81
IM4n	1.68	-6.21	4.60	100.79	-10.75	-9.07
POZ-n	4.55	7.16	21.02	90.57	-6.17	-1.62
Formic acnid + nBD	1.40	-109.47	-109.45	136.98	-114.16	-112.76
Formaldehyde + Butyric acid	1.16	-110.64	-110.52	136.65	-117.26	-116.10
Formaldehyde +	-0.51	0.62	0.95	135.93	0.47	-0.05

Butyraldehyde oxide						
Ozone + 1-pentene	0.15	60.84	61.33	135.40	54.09	54.24
(CH_2OO + nBD)						
B3LYP/6-311+G(2df,2p)					CCSD(T)-F12/cc-pVTZ-F12	
Stationary Points	ΔE_{ZPE} kcal mol^{-1}	ΔH^0 kcal mol^{-1}	ΔG^0 kcal mol^{-1}	S^0 cal K^{-1} mol^{-1}	$\Delta E^{0,a}_r$ kcal mol^{-1}	$\Delta E_{r,\,ZPE}{}^b$ kcal mol^{-1}
CH_2OO + iBD		0	0	136.65	0	0
TS1i	2.14	-2.38	10.15	94.61	-7.95	-5.80
TS2i	-0.58	-1.65	12.02	90.80	-11.73	-12.30
TS3i	1.51	-104.82	-91.56	92.19	-110.91	-109.39
TS4i	-0.60	-1.99	11.84	90.27	-12.06	-12.66
TS5i	1.77	-103.75	-91.13	94.33	-110.19	-108.42
TS6i	2.00	-6.30	6.26	94.53	-10.50	-8.50
TS7i	0.15	-4.79	8.30	92.73	-8.99	-8.84
TS8i	0.27	-5.15	8.35	91.37	-10.44	-10.17
TS9i	2.27	24.81	38.39	91.11	16.47	18.73
TS10i	1.47	61.80	74.31	94.69	56.78	58.25
IM1i	1.24	-4.11	5.35	104.895	-8.71	-7.47
SOZ-i	5.30	-41.01	-26.85	89.157	-56.19	-50.89
IM2i	5.18	-117.77	-104.49	92.119	-132.30	-127.11
IM3i	5.16	-117.08	-105.33	97.25	-130.16	-125.00
IM4i	1.66	-6.17	4.78	99.94	-10.28	-8.62
POZ-i	4.49	7.46	21.62	89.16	-5.65	-1.17
Formic acid + Isobutyraldehyde	1.40	-109.47	-109.45	136.58	-114.16	-112.76
Formaldehyde + Isobutyric_acid	1.04	-110.97	-110.43	134.84	-116.90	-115.87
Formaldehyde + Isobutyraldehyde_oxide	-0.58	0.61	1.21	134.64	1.20	0.62
Ozone + Isopentene	0.05	60.65	61.27	134.55	54.68	54.73

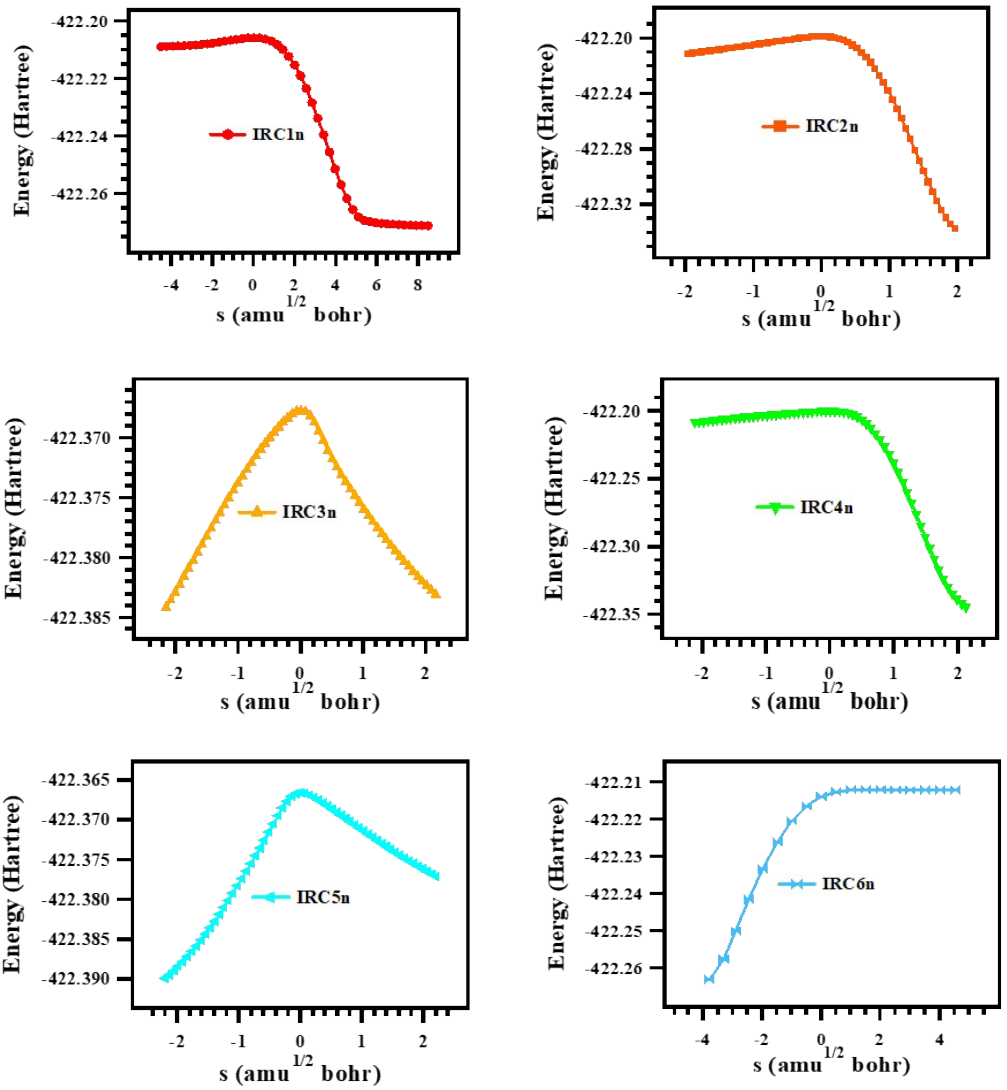
[a] ΔE^0_r = Energy change at CCSD(T)-F12/cc-pVTZ-F12

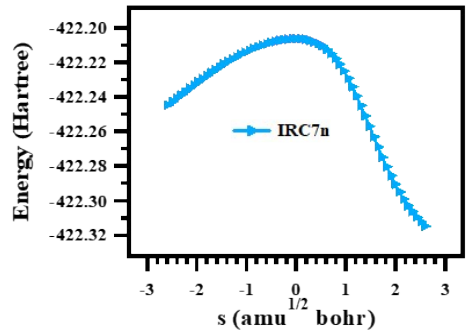
[b] $\Delta E_{r,\,ZPE} = \Delta E^0_r + \Delta E_{ZPE}$

Table S4. T1-Diagnostics values of reactants, reactive complexes (IM), transition states (TS) and products obtained at CCSD(T)-F12/cc-pVTZ-F12 level of theory.

Species	T1-Diagnostic value	Species	T1-Diagnostic value
CH_2OO	0.043112131	iBD	0.012731293
nBD	0.012623929	IM1i	0.027224446
IM1n	0.027157005	SOZ-i	0.012617156
SOZ-n	0.012549977	IM2i	0.013609582
IM2n	0.013547092	IM3i	0.013325027
IM3n	0.013311760	IM4i	0.024923300
IM4	0.024748782	POZ-i	0.014289088
POZ-n	0.014291561	TS1i	0.026150244
TS1n	0.026104868	TS2i	0.023171854
TS2n	0.024182981	TS3i	0.016862784
TS3n	0.016796795	TS4i	0.028025537
TS4n	0.027074759	TS5i	0.016234474
TS5n	0.016184984	TS6i	0.024417166
TS6n	0.024343955	TS7i	0.032212839
TS7n	0.032011717	TS8i	0.027642102
TS8n	0.027464283	TS9i	0.016919572
TS9n	0.017132855	TS10i	0.018328136
TS10n	0.017980666	Isobutyric acid (P6)	0.013359081
Formic acid (P1)	0.016366012	Isobutyraldehyde	0.029453086

		oxide (P7)	
Formaldehyde (P2	0.015418823	Isopentene (P8)	0.009874978
Butyric acid (P3)	0.013310703	Ozone	0.026341348
N-butyraldehyde oxide (P4)	0.030034881		
1-Pentene (P5)	0.009880719		




Energy (Hartree)
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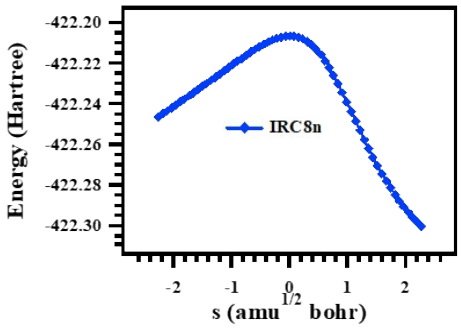
-422.22
-422.24
-422.26
-422.28
-422.30
-422.32
IRC7n
-3 -2 -1 0 1 2 3
s (amu 1/2 bohr)


Energy (Hartree)
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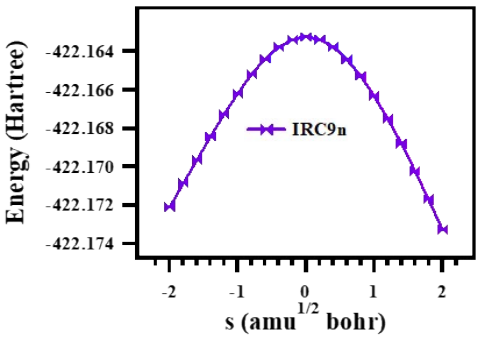
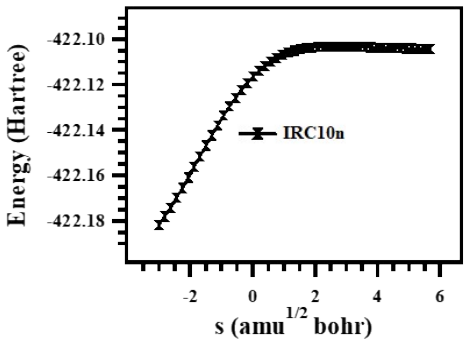
-422.24
-422.26
-422.28
-422.30
IRC8n
-2 -1 0 1 2
s (amu 1/2 bohr)


Energy (Hartree)
-422.164
-422.166
-422.168
-422.170
-422.172
-422.174
IRC9n
-2 -1 0 1 2
s (amu 1/2 bohr)


Energy (Hartree)
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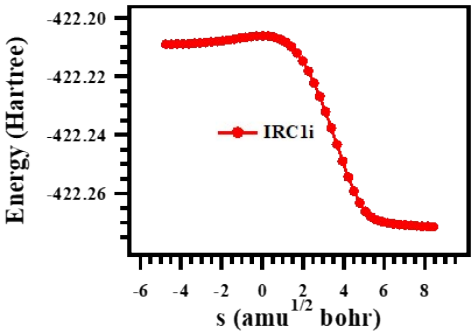
-422.14
-422.16
-422.18
IRC10n
-2 0 2 4 6
s (amu 1/2 bohr)


Energy (Hartree)
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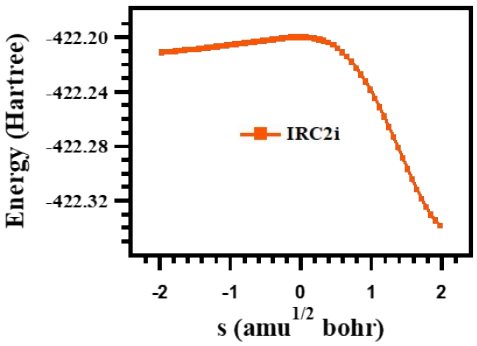
-422.24
-422.26
IRC1i
-6 -4 -2 0 2 4 6 8
s (amu 1/2 bohr)


Energy (Hartree)
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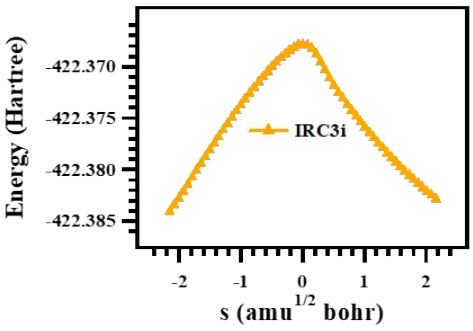
-422.32
IRC2i
-2 -1 0 1 2
s (amu 1/2 bohr)


Energy (Hartree)
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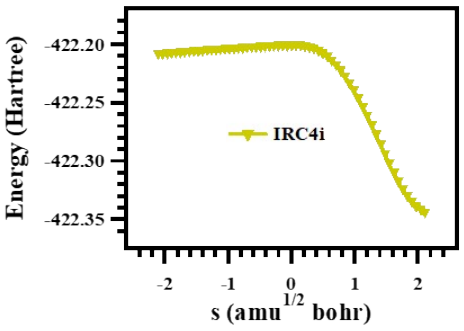
-422.375
-422.380
-422.385
IRC3i
-2 -1 0 1 2
s (amu 1/2 bohr)


Energy (Hartree)
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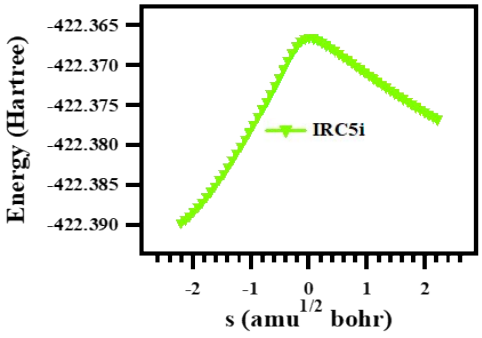
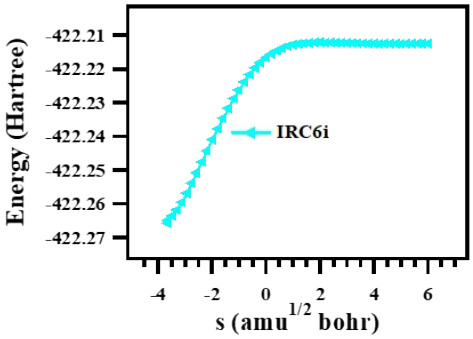
-422.25
-422.30
-422.35
IRC4i
-2 -1 0 1 2
s (amu 1/2 bohr)


Energy (Hartree)
-422.365
-422.370
-422.375
-422.380
-422.385
-422.390
IRC5i
-2 -1 0 1 2
s (amu 1/2 bohr)


Energy (Hartree)
-422.21
-422.22
-422.23
-422.24
-422.25
-422.26
-422.27
IRC6i
-4 -2 0 2 4 6
s (amu 1/2 bohr)

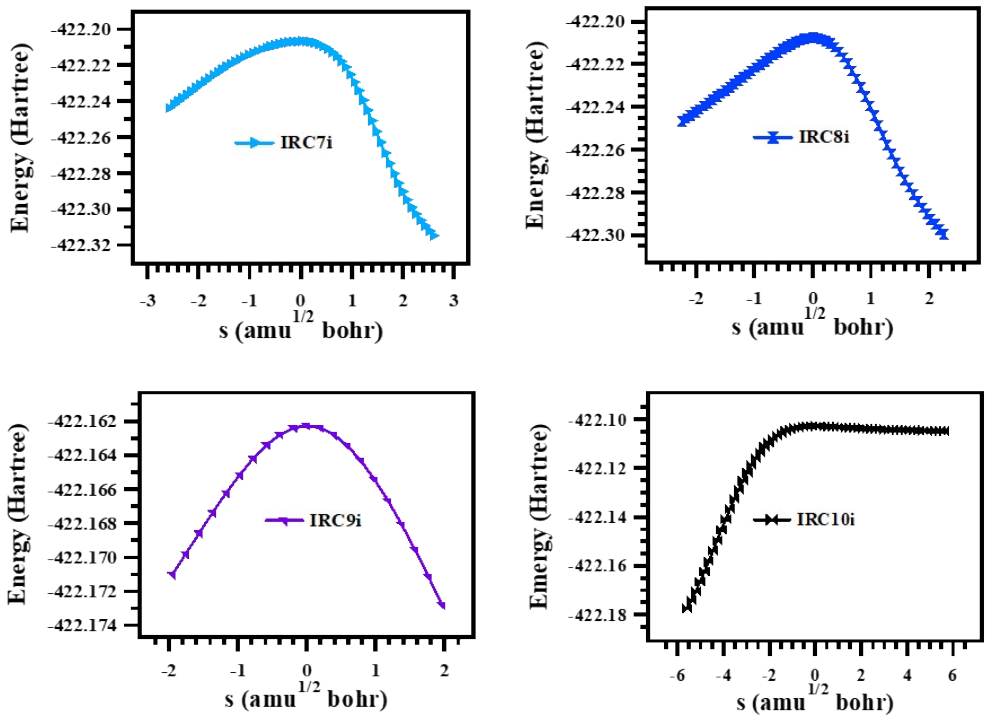


Figure S2. Intrinsic Reaction Coordinate (IRC) plots for CH_2OO + nBD and CH_2OO + iBD obtained at B3LYP/6-311+G(2df,2p) level of theory. Left side is the reactant and right side is the product well. No fitting was performed.

Section S2: MESMER Simulation:

Master equation (ME) simulation was performed using MESMER code (6.1), in which the Rice-Ramsperger-Kassel-Marcus (RRKM) theory was employed to treat the consecutive reaction steps.[1,2] ME simulations were performed in lot of studies to determine the temperature and pressure dependent kinetics of CH_2OO reactions and the product distribution, in recent past.[3-5] This simulation involves the distribution of thermal energies among the energy grains for individual states along the PES. The molecular collision enables the energy transfer among these energy grains. The equation for this energy transfer process was given by,

$$\frac{d}{dt}p = Mp \qquad \text{(ES1)}$$

where, p is the population vector of the grains and M is a matrix for the energy transfer rates between grains. For bimolecular reaction in pseudo-1st order condition, p can be expressed as

time population of the reactant which is not in excess concentration in the reaction mixture. Equation ES1 is a standard eigenvalue problem, solving which by diagonalising matrix *M*, one gets corresponding set of eigen solutions. The Bartis-Widom[6] method is used by the MESMER code to calculate the phenomenological rate coefficients for the consecutive reaction steps using these set of eigen values.[7,8]

Exponential down model was employed in order to describe the collisional energy transfer process as per the equation,

$$\langle \Delta E \rangle_{down,\,T} = \langle \Delta E \rangle_{down,\,298\,K} \left(\frac{T}{300} \right)^{n} \quad \text{(ES2)}$$

where, $<\Delta E>_{down,T}$ is the downward energy transfer due to the collision of the reactants to the bat gas molecules, $<\Delta E>_{down,298K}$ is the standard value at 298 K for a specific bath gas, *n* is a constant specific to each bath gas. The values of the latter two constants for N_2 were 200 cm^{-1} and 0.85.[9,10] The L-J parameters for the bath gas (N_2) was set to be default as in the MESMER code, and for the intermediates, were calculated using following equations[11],

$$\sigma = 2.44 \left(\frac{T_c}{p_c} \right)^{\frac{1}{3}} \quad \text{(ES3)}$$

$$\epsilon = 0.77 k T_c \quad \text{(ES4)}$$

The critical constants for temperature and pressure in Equation ES4 were calculated using Joback's group contribution method for the intermediates.[12] The σ and ϵ values calculated are given in Table S5.

Table S5. The L-J parameters calculated**.**

Species	σ **(in Å)**	ϵ **(in kT)**	**Species**	σ **(in Å)**	ϵ **(in kT)**
CH_2OO + nBD			CH_2OO + iBD		

IM1	5.89	454.88	IM1	5.90	459.99
SOZ	5.89	454.88	SOZ	5.90	459.99
IM2	5.88	452.31	IM2	5.88	457.40
IM3	5.95	434.55	IM3	5.99	448.23

The entrance channel for the title reactions is the bimolecular association of the CH_2OO to the C=O group of the nBD and iBD. This association step is a barrierless process, and is treated using Inverse Laplace Transformation (ILT), included in the MESMER code. The Arrhenius parameters used for the ILT method were taken from the liner least-square fit of the experimental data as per Equation ES5.

$$k(T) = A\left(\frac{T}{298K}\right)^n \quad \text{(ES5)}$$

The values for A and n were taken to be 2.53×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and -1.49 respectively for R4 and 2.14×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and -1.49 respectively for R5. It should be noted that the value n from the fit obtained were 3.16 and 3.62 for R4 and R5 respectively, but MESMER code allows the lowest value of -1.49. Hence the highest possible negative curvature with n = -1.49 was employed the ILT method. Whereas, the excess concentration values for nBD and iBD were 1.13×10^{15} and 1.14×10^{15} molecule cm^{-3} respectively. The MESMER parameters namely "energy above the Top hill" and "Energy grain" were assigned to be 25 kT and 40 cm^{-1} respectively.

Table S6. Pseudo-1st order rate coefficients at temperatures in the range of 253-318 K for (a) CH_2OO + nBD and (b) CH_2OO + iBD reactions, respectively. Standard deviations are given in 1σ obtained from the fittings in Figure 1.

(a) CH_2OO + nBD						
[nBD] (10^{15} molecule cm^{-3})	$k_{pseudo}^{253\,K} \pm 2\sigma$ **s^{-1}**	$k_{pseudo}^{268\,K} \pm 2$ **s^{-1}**	$k_{pseudo}^{283\,K} \pm 2$ **s^{-1}**	$k_{pseudo}^{298\,K} \pm 2\sigma$ **s^{-1}**	$k_{pseudo}^{308\,K} \pm 2\sigma$ **s^{-1}**	$k_{pseudo}^{318\,K} \pm 2\sigma$ **s^{-1}**
0.38	3386.3 ± 65.0	3524.0 ± 73.9	3328.9 ± 66.0	3049.9 ± 83.5	2769.8 ± 68.3	2451.7 ± 86.6
0.76	5370.0 ± 216.0	4732.0 ± 227.0	5362.5 ± 68.6	3805.4 ± 76.9	3520.7 ± 71.2	3143.7 ± 59.1
1.13	6807.5 ± 261.0	6173.4 ± 186.0	5306.2 ± 105.5	4756.3 ± 135.0	4288.4 ± 137.0	3791.1 ± 104.0
1.49	8282.4 ± 357.0	4799.4 ± 305.0	6386.2 ± 192.0	5852.7 ± 111.0	5004.2 ± 104.0	4601.7 ± 111.0
1.85	9765.9 ± 532.0	8850.0 ± 153.0	7467.5 ± 369.0	6753.3 ± 207.0	5908.6 ± 144.0	5266.2 ± 137.0
2.20	11180.0 ± 518.0	10003 ± 310.0	8884.4 ± 278.0	7782.2 ± 205.0	6928.4 ± 150.0	6106.9 ± 214.0
(b) CH_2OO + iBD						
[iBD] (10^{15} molecule cm^{-3})	$k_{pseudo}^{253\,K} \pm 2\sigma$ **s^{-1}**	$k_{pseudo}^{268\,K} \pm 2$ **s^{-1}**	$k_{pseudo}^{283\,K} \pm 2$ **s^{-1}**	$k_{pseudo}^{298\,K} \pm 2\sigma$ **s^{-1}**	$k_{pseudo}^{308\,K} \pm 2\sigma$ **s^{-1}**	$k_{pseudo}^{318\,K} \pm 2\sigma$ **s^{-1}**
0.38	3146.9 ± 85.5	3122.0 ± 58.3	3053.3 ± 54.4	3020.1 ± 124.0	2944.6 ± 34.9	2871.4 ± 86.6
0.76	4349.9 ± 244.0	4029.1 ± 113.0	3881.4 ± 87.4	3775.4 ± 123.0	3512.1 ± 41.9	3348.0 ± 126.0
1.14	5892.6	5193.6	4714.4	4340.2	4135.6	3881.1

	± 314.0.	± 500.0	± 245.0	± 180.0	± 92.1	± 75.6
1.52	7214.8 ± 358.0	6239.3 ± 361.0	5786.6 ± 448.0	5251.5 ± 180.0	4855.6 ± 80.0	4480.2 ± 120.0
1.89	8691.9 ± 262.0	7679.1 ± 344.0	6978.4 ± 372.0	6213.1 ± 195.0	5715.2 ± 221.0	5166.4 ± 78.7
2.26	10390.0 ± 591.0	9029.9 ± 471.0	8042.9 ± 172.0	7160.0 ± 253.0	6416.3 ± 226.0	5946.4 ± 116.0

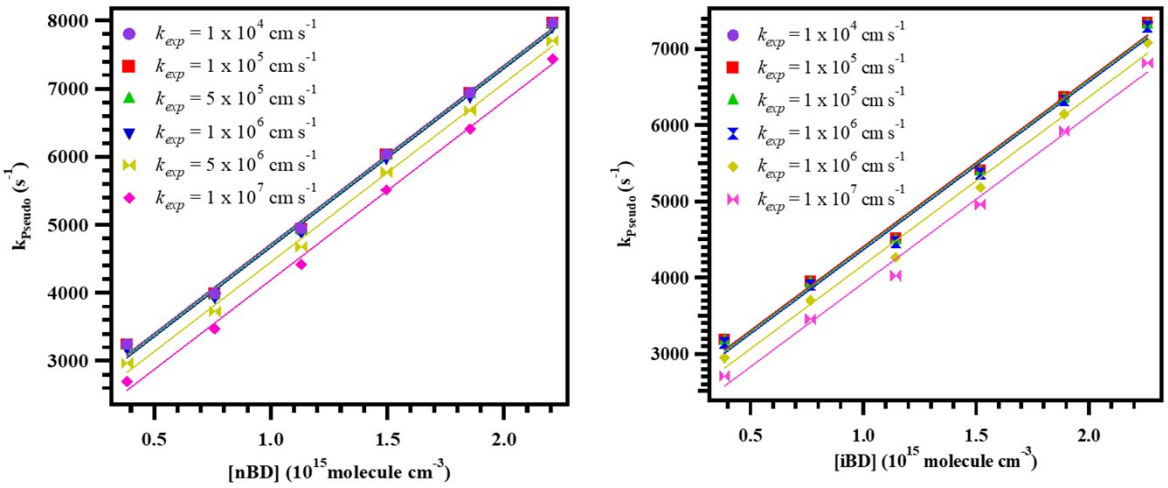


Figure S3. Sensitivity analysis of k_{exp} on the bimolecular rate coefficients.

Section S3. Thermochemistry:

The change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) for all the reaction pathways are given in Table S7. There are identical products formed in different pathways, such as Pathways 1 and 4 and Pathways 2 and 5, which give the same thermodynamic parameters. Highly negative free energies for Pathways 1, 2, 4 and 5 make them thermodynamically favourable over Pathways 3 and 6. Again, only the net change of free energy or enthalpy does not provide a clear picture of the feasibility of the pathways. These pathways contain several consecutive steps, each of which behaves thermodynamically

different. The thermodynamic parameters for each consecutive pathway are given in Table S7. It is worth mentioning that there exists an equilibrium between the reactants and the vdW complexes, which is common in reactions associated with loose TSs, as in this case. The formation of vdW complexes, namely IM1n (ΔH^0 = -4.25 kcal mol^{-1}) and IM1i (ΔH^0 = -4.11 kcal mol^{-1}), were found to be exothermic in nature, which governs how the equilibrium changes with the temperature.

Table S7. Thermochemical parameters obtained at B3LYP/6-311+G(2df,2p) level, for reactions R4 and R5. All parameters are given in kcal mol^{-1}.

	CH_2OO + nBD				**CH_2OO + iBD**		
Pathways	**ΔG^0**	**ΔH^0**	**$T\Delta S^0$**	**Pathways**	**ΔG^0**	**ΔH^0**	**$T\Delta S^0$**
Pathway 1 & 4	-109.45	-109.47	-0.02	Pathway 1 & 4	-109.45	-109.47	-0.02
Pathway 2 & 5	-110.52	-110.64	-0.12	Pathway 2 & 5	-110.43	-110.97	-0.12
Pathway 3	0.95	0.62	-0.33	Pathway 3	1.21	0.61	-0.33
Pathway 6	61.33	60.84	-0.49	Pathway 6	61.27	60.65	-0.49

Table S8. Equilibrium constant for the reaction CH_2OO + nBD ↔ IM1n and CH_2OO + iBD ↔ IM1i calculated at B3LYP/6-311+G(2df,2p) level of theory.

Temperature (K)	K_{eq}^{nBD} **(cm^3 molecule^{-1})**	K_{eq}^{iBD} **(cm^3 molecule^{-1})**

200	1.63×10^{-18}	2.55×10^{-19}
225	1.83×10^{-19}	3.56×10^{-20}
250	3.19×10^{-20}	7.42×10^{-21}
275	8.17×10^{-21}	2.20×10^{-21}
298	2.86×10^{-21}	8.58×10^{-22}
325	1.02×10^{-21}	3.44×10^{-22}
350	4.64×10^{-22}	1.70×10^{-22}

Table S9. Calculated CVT and CVT/SCT rate coefficients showing the tunnelling effect for IM1 → SOZ step in both the reactions.

Temp	**IM1n → SOZ-n**		**IM1i → SOZ-i**	
	k_{uni}^{CVT} **(s^{-1})**	$k_{uni}^{CVT/SCT}$ **(s^{-1})**	k_{uni}^{CVT} **(s^{-1})**	$k_{uni}^{CVT/SCT}$ **(s^{-1})**
200	2.22×10^{08}	2.41×10^{09}	2.22×10^{08}	2.41×10^{09}
225	4.34×10^{08}	2.70×10^{09}	4.34×10^{08}	2.70×10^{09}
250	7.33×10^{08}	3.05×10^{09}	7.33×10^{08}	3.05×10^{09}
268	9.99×10^{08}	3.34×10^{09}	9.99×10^{08}	3.34×10^{09}
275	1.11×10^{09}	3.46×10^{09}	1.11×10^{09}	3.46×10^{09}
298	1.53×10^{09}	3.86×10^{09}	1.53×10^{09}	3.86×10^{09}
300	1.57×10^{09}	3.90×10^{09}	1.57×10^{09}	3.90×10^{09}
325	2.08×10^{09}	4.36×10^{09}	2.08×10^{09}	4.36×10^{09}
350	2.64×10^{09}	4.83×10^{09}	2.64×10^{09}	4.83×10^{09}

Table S10. Rate coefficients for the reaction of CH_2OO + nBD and CH_2OO + iBD obtained from CVT/SCT and MESMER calculations.

Temperature (K)	CH_2OO + nBD		CH_2OO + iBD	
	$k_{nBD}^{CVT/SCT-HR}$ (cm^3 molecule^{-1} s^{-1})	k_{nBD}^{MESMER} (cm^3 molecule^{-1} s^{-1})	$k_{iBD}^{CVT/SCT-HR}$ (cm^3 molecule^{-1} s^{-1})	k_{iBD}^{MESMER} (cm^3 molecule^{-1} s^{-1})
200	4.80×10^{-10}	4.00×10^{-12}	6.07×10^{-10}	3.37×10^{-12}
225	1.04×10^{-10}	3.20×10^{-12}	9.49×10^{-11}	2.60×10^{-12}
250	3.05×10^{-11}	2.59×10^{-12}	2.23×10^{-11}	2.04×10^{-12}
275	1.19×10^{-11}	2.12×10^{-12}	7.48×10^{-12}	1.61×10^{-12}
298	5.62×10^{-12}	1.78×10^{-12}	3.26×10^{-12}	1.31×10^{-12}
325	2.73×10^{-12}	1.45×10^{-12}	1.47×10^{-12}	1.04×10^{-12}
350	1.56×10^{-12}	1.22×10^{-12}	8.07×10^{-13}	8.42×10^{-13}

Section S4. Error Propagation:

The experimental error associated with the measurement of the concentration of the sample (nBD/iBD) was propagated to get the upper and lower limit of the rate coefficients. The maximum possible error due to the flow calibration through the MFCs, in the concentration measurement was assumed to be ± 10 %. The upper and lower limit of the rate coefficients were determined by plotting the corresponding k_{pseudo} values against the concentration (± 10 %) of nBD and iBD, which are given in Table S11.

Table S11. Error (Ek_n) propagation of the reactions CH_2OO + nBD and CH_2OO + iBD.

T	CH_2OO + nBD			CH_2OO + iBD		
	k_{nBD}	k_{nBD} (± 10%)	Ek_{nBD} (± 10%)	k_{iBD}	k_{iBD} (± 10%)	Ek_{iBD} (± 10%)
K	cm^3 molecule^{-1} s^{-1}					

(Concentration -10%)						
253	4.20×10^{-12}	4.66×10^{-12}	9.22×10^{-13}	3.86×10^{-12}	4.28×10^{-12}	4.20×10^{-13}
268	3.61×10^{-12}	4.00×10^{-12}	7.85×10^{-13}	3.16×10^{-12}	3.51×10^{-12}	3.55×10^{-13}
283	2.99×10^{-12}	3.31×10^{-12}	6.48×10^{-13}	2.65×10^{-12}	2.99×10^{-12}	3.38×10^{-13}
298	2.63×10^{-12}	2.92×10^{-12}	5.75×10^{-13}	2.20×10^{-12}	2.45×10^{-12}	2.47×10^{-13}
308	2.24×10^{-12}	2.49×10^{-12}	4.99×10^{-13}	1.88×10^{-12}	2.09×10^{-12}	2.09×10^{-13}
318	1.99×10^{-12}	2.21×10^{-12}	4.40×10^{-13}	1.63×10^{-12}	1.81×10^{-12}	1.83×10^{-13}
(Concentration +10%)						
253	4.20×10^{-12}	3.82×10^{-12}	7.68×10^{-13}	3.86×10^{-12}	3.50×10^{-12}	3.59×10^{-13}
268	3.61×10^{-12}	3.28×10^{-12}	6.66×10^{-13}	3.16×10^{-12}	2.88×10^{-12}	2.84×10^{-13}
283	2.99×10^{-12}	2.71×10^{-12}	5.53×10^{-13}	2.65×10^{-12}	2.44×10^{-12}	2.05×10^{-13}
298	2.63×10^{-12}	2.39×10^{-12}	4.82×10^{-13}	2.20×10^{-12}	2.00×10^{-12}	1.98×10^{-13}
308	2.24×10^{-12}	2.04×10^{-12}	4.04×10^{-13}	1.88×10^{-12}	1.71×10^{-12}	1.71×10^{-13}
318	1.99×10^{-12}	1.81×10^{-12}	3.61×10^{-13}	1.63×10^{-12}	1.48×10^{-12}	1.47×10^{-13}

These uncertainties are given as error bars in Figure 5 of the manuscript where Figure 2 reflects only fitting error comes from the temporal profiles of CH_2OO in Figure 1.

Table S12. Rate coefficients obtained from MESMER calculations for product formation pathways from SOZs at 760 Torr.

Temperature	$k_{MESMER}^{SOZ-n\rightarrow P}$ **(s^{-1})**				
	Pathway 1	**Pathway 2**	**Pathway 3**	**Pathway 4**	**Pathway 5**
200	1.36×10^{-06}	1.38×10^{-05}	1.05×10^{-30}	8.17×10^{-31}	4.67×10^{-27}
225	1.48×10^{-04}	7.94×10^{-04}	2.09×10^{-31}	1.82×10^{-28}	1.32×10^{-24}

250	7.94×10^{-04}	2.25×10^{-02}	2.87×10^{-24}	3.91×10^{-24}	7.00×10^{-22}
275	1.49×10^{-01}	3.68×10^{-01}	8.08×10^{-21}	8.72×10^{-21}	3.63×10^{-19}
298	1.70×10^{00}	3.29×10^{00}	3.64×10^{-18}	3.42×10^{-18}	6.96×10^{-17}
325	1.92×10^{01}	2.97×10^{01}	1.61×10^{-15}	1.34×10^{-15}	1.60×10^{-14}
350	1.31×10^{02}	1.71×10^{02}	1.99×10^{-13}	1.51×10^{-13}	1.28×10^{-12}
375	6.96×10^{02}	7.86×10^{02}	1.30×10^{-11}	9.25×10^{-12}	6.06×10^{-11}
400	2.99×10^{03}	3.01×10^{03}	5.10×10^{-10}	3.43×10^{-10}	1.83×10^{-09}
Temperature	$k_{MESMER}^{SOZ-i \rightarrow P}$ **(s^{-1})**				
	Pathway 1	**Pathway 2**	**Pathway 3**	**Pathway 4**	**Pathway 5**
200	1.56×10^{-06}	2.12×10^{-05}	2.35×10^{-31}	1.08×10^{-31}	1.82×10^{-26}
225	1.58×10^{-04}	1.08×10^{-03}	5.83×10^{-28}	1.13×10^{-27}	4.15×10^{-24}
250	6.65×10^{-03}	2.78×10^{-02}	1.99×10^{-24}	5.27×10^{-24}	1.81×10^{-21}
275	1.47×10^{-01}	4.24×10^{-01}	5.74×10^{-21}	1.14×10^{-20}	8.19×10^{-19}
298	1.64×10^{00}	3.59×10^{00}	2.68×10^{-18}	4.43×10^{-18}	1.45×10^{-16}
325	1.82×10^{01}	3.08×10^{01}	1.23×10^{-15}	1.71×10^{-15}	3.10×10^{-14}
350	1.23×10^{02}	1.70×10^{02}	1.55×10^{-13}	1.92×10^{-13}	2.36×10^{-12}
375	6.46×10^{03}	7.54×10^{02}	1.04×10^{-11}	1.16×10^{-11}	1.07×10^{-10}
400	2.88×10^{03}	2.80×10^{03}	4.14×10^{-10}	4.29×10^{-10}	3.11×10^{-09}

Section S5. Cumulative Atmospheric Lifetime:

$$\frac{1}{T_{cum}} = \frac{1}{T_{OH}} + \frac{1}{T_{Cl(MBl)}} + \frac{1}{T_{CH_2OO}} \quad \text{(ES6)}$$

$$\tau_x = \frac{1}{([x] \times k_x)} \quad \text{(ES7)}$$

Where, τ_x is the atmospheric lifetime, $[x]$ is the mixing ratio and k_x is the corresponding rate coefficient. The mixing ratio values considered in this calculation were [OH] = 1.0×10^6 molecule cm^{-3} [13], [Cl(MBL)] = 1.3×10^5 molecule cm^{-3} [14], [CH_2OO] = 10^4 molecule cm^{-3} [15] and the rate coefficients were k(OH + nBD) = $5.7\times10^{-12}\times\exp\{411/T\}$ and k(OH + iBD) = $6.8\times10^{-12}\times\exp\{393/T\}$ cm^3 $molecule^{-1}$ s^{-1} [16], k(Cl + nBD) = $3.09\times10^{-11}\times\exp\{446/T\}$ cm^3 $molecule^{-1}$ s^{-1} [17], k(CH_2OO + nBD) = $11.51\times10^{-14}\times\exp\{918.1/T\}$ and k(CH_2OO + iBD) = $6.23\times10^{-14}\times\exp\{1051.4/T\}$ cm^3 $molecule^{-1}$ s^{-1} (this study). The rate coefficients for Cl + iBD were taken to be same as for Cl + nBD, as there were no temperature dependent rate coefficients available for the same.

Table S13. Comparison of the rate of the reactions CH_2OO + nBD with OH + nBD and CH_2OO + iBD with OH + iBD.

Rate ratio(υ) CH_2OO + nBD		[OH] (molecule cm^{-3})		
		1.00×10^4	**1.00×10^5**	**1.00×10^6**
[CH_2OO] (molecule cm^{-3})	**1.00×10^4**	0.1162	0.01162	0.001162
	5.00×10^4	0.581	0.0581	0.00581
	1.00×10^5	1.162	0.1162	0.01162

Rate ratio(υ) CH_2OO + iBD		[OH] (molecule cm^{-3})		
		1.00×10^4	**1.00×10^5**	**1.00×10^6**
[CH_2OO] (molecule cm^{-3})	**1.00×10^4**	0.0865	0.00865	0.000865
	5.00×10^4	0.4325	0.04325	0.004325
	1.00×10^5	0.865	0.0865	0.00865

Where,

$$v = \frac{k_{(CH_2OO+s)}[CH_2OO][s]}{k_{(OH+s)}[OH][s]} = \frac{k_{(CH_2OO+s)}[CH_2OO]}{k_{(OH+s)}s[OH]}$$

(ES8)

The rate coefficients used are, $k^{298\ K}$ (OH + nBD) = 2.26 ×10^{-11} and $k^{298\ K}$ (OH + iBD) = 2.54 ×10^{-11} cm^3 $molecule^{-1}$ s^{-1} [15], $k^{298\ K}$ (CH_2OO + nBD) = 2.63 ×10^{-12} and $k^{298\ K}$ (CH_2OO + iBD) = 2.20 ×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (this study).

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