Supplementary Information:

Theoretical investigation on the reaction mechanism and kinetics of Criegee intermediate with ethylene and acetylene

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Cartesian coordinates of all the optimized geometries on M06-2X/AUG-cc-pVTZ level.

C_2H_4 + CH_2OO reaction

CH_2OO

O	-0.007248	-0.459800	0.000006
C	-1.053886	0.203122	-0.000016
H	-0.984282	1.285139	0.000040
H	-1.972841	-0.366750	0.000021
O	1.167303	0.192660	-0.000002

C_2H_4

C	-0.660958	-0.000009	0.000004
C	0.660957	-0.000022	-0.000006
H	-1.227831	0.921836	0.000010
H	-1.227651	-0.922007	-0.000022
H	1.227977	-0.921717	0.000028
H	1.227509	0.922073	-0.000005

ComA

C	-1.580174	-0.762131	0.013288
C	-1.972579	0.500517	-0.086698
H	-1.520667	-1.267785	0.967633
H	-1.287120	-1.340391	-0.851766
H	-2.038159	0.999110	-1.045801
H	-2.270858	1.073133	0.783348
O	1.369571	0.141511	-0.401674
C	0.952236	1.105853	0.255734
H	0.576385	0.935386	1.256477
H	1.024473	2.072087	-0.225933

O	1.270310	-1.083633	0.154437

ComInsW

C	-0.888281	1.002182	0.512650
H	-0.710228	0.558389	1.485152
H	-0.704930	2.038621	0.261660
O	-1.344617	0.295573	-0.394612
O	-1.558848	-1.015897	-0.127259
C	1.666202	-0.646661	0.380096
C	2.078806	0.292486	-0.458745
H	0.772933	-1.232238	0.183863
H	2.212969	-0.861704	1.290015
H	1.540745	0.501625	-1.375592
H	2.975864	0.869859	-0.274142

ComInsO

C	-1.078238	1.040028	0.383373
H	-0.729220	0.784086	1.376506
H	-1.191008	2.046639	0.003285
O	-1.385797	0.130774	-0.397702
O	-1.235463	-1.145650	0.021758
H	1.126048	-0.254831	-1.382830
C	1.834757	0.149195	-0.669719
C	1.835813	-0.264624	0.588038
H	2.544032	0.121753	1.310595
H	1.123026	-1.010340	0.920708
H	2.543212	0.884114	-1.030871

IMA

C	-1.176484	0.266719	-0.126194
C	0.000155	1.244044	-0.000079
H	-2.008910	0.485116	0.538546
H	-1.527987	0.194264	-1.156734
H	0.082558	1.877058	-0.879851
H	-0.082071	1.877462	0.879420
O	0.651648	-0.986009	-0.288708
C	1.176507	0.266455	0.126360
H	1.527594	0.193764	1.157030
H	2.009261	0.484744	-0.538009
O	-0.651837	-0.985955	0.288592

IMRO

C	-1.142736	0.109605	-0.518221
C	1.142734	0.109619	0.518201
H	0.744185	-0.623444	1.244190
H	1.896759	0.685235	1.069777
O	1.734925	-0.656491	-0.447780
O	-1.734926	-0.656483	0.447794

H	-1.896735	0.685208	-1.069832
C	-0.000004	0.972144	0.000000
H	-0.365588	1.616026	0.801614
H	0.365552	1.616055	-0.801605
H	-0.744124	-0.623503	-1.244128

IMIso

C	1.107457	0.354880	0.415732
C	-1.338932	0.211413	-0.139395
H	0.770600	-1.414890	-0.269126
H	-2.268571	0.684537	-0.504792
O	-1.353009	-0.933646	0.231613
O	1.468900	-0.759911	-0.368456
H	1.964207	1.026619	0.419444
C	-0.108332	1.071711	-0.147722
H	0.070325	1.380763	-1.182578
H	-0.333198	1.985862	0.410458
H	0.908353	0.057542	1.449653

TSA

C	-1.391313	-0.740546	0.010281
C	-1.516643	0.595071	-0.109050
H	-1.494365	-1.234627	0.965515
H	-1.275099	-1.380290	-0.850744
H	-1.548104	1.067105	-1.082013
H	-1.801813	1.206598	0.737655
O	1.228265	0.092590	-0.392009
C	0.759341	1.063988	0.258475
H	0.532264	0.927363	1.305844
H	0.890559	2.035092	-0.200855
O	0.970266	-1.109130	0.162804

TSD3

C	1.146236	0.097212	0.324885
C	0.286849	1.167513	-0.270438
H	1.891809	0.759128	-0.294050
H	1.359812	0.228173	1.393214
H	0.355431	2.171911	0.140951
H	0.213330	1.109869	-1.351189
O	-1.148270	-0.878862	-0.094488
C	-1.302950	0.330425	0.199263
H	-1.841827	0.978122	-0.515601
H	-1.408646	0.625914	1.252912
O	0.979431	-1.051641	-0.174073

TSRO

C	1.205738	0.257089	0.243713
C	-1.205739	0.257088	-0.243710

H	-1.411737	0.132768	-1.310409
H	-2.112165	0.668473	0.224139
O	-1.023005	-0.962574	0.367987
O	1.023008	-0.962572	-0.367989
H	2.112166	0.668476	-0.224128
C	0.000000	1.179395	-0.000001
H	0.147271	1.818621	-0.869328
H	-0.147271	1.818627	0.869321
H	1.411728	0.132766	1.310413

TSIso

C	-1.195974	0.247054	-0.476508
C	0.985202	-0.042955	0.478133
H	0.264914	-0.984490	0.605943
H	1.494810	0.015321	1.450660
O	1.750459	-0.386398	-0.525518
O	-1.340734	-0.925804	0.268602
H	-2.169285	0.751609	-0.439707
C	-0.088004	1.031334	0.201588
H	-0.435882	1.436545	1.151403
H	0.313491	1.835869	-0.411971
H	-0.953195	0.030166	-1.520276

TSD1

C	1.260460	0.427740	0.305619
C	-1.197326	0.142438	0.257572
H	0.069834	-1.167167	-0.244925
H	-1.786732	0.319501	1.158969
O	-1.025599	-1.085428	-0.087910
O	1.326598	-0.750191	-0.159820
H	1.779055	1.235367	-0.216527
C	-0.522851	1.176215	-0.352033
H	-0.199400	1.054597	-1.375385
H	-0.676076	2.183806	0.006677
H	1.163627	0.580492	1.386092

TSD2

C	-1.252979	0.058328	-0.437608
C	1.271957	-0.175083	0.471563
H	0.156701	-0.762974	0.494011
H	1.785873	-0.052719	1.448989
O	1.891039	-0.080765	-0.553235
O	-1.173822	-1.084309	0.186068
H	-2.180540	0.709718	-0.132184
C	-0.567867	1.134921	0.236137
H	-0.662969	1.173438	1.316352
H	-0.329350	2.061103	-0.278094

H	-1.214117	0.083026	-1.532299

P1 (CH_2CHOH + HCHO)

P2 (CH3CHO + HCHO)

CH_2CHOH

C	0.038279	0.441050	0.000027
H	-1.123331	-1.072267	0.000723
H	-0.023789	1.520990	0.000183
O	-1.199722	-0.113110	-0.000102
C	1.192651	-0.207604	-0.000036
H	1.240906	-1.289155	-0.000182
H	2.118405	0.344639	0.000148

CH_3CHO

C	-1.162477	-0.147723	0.000031
H	-1.697082	0.225552	-0.875309
H	-1.147245	-1.233919	-0.002116
O	1.224962	-0.277279	0.000174
C	0.233170	0.398164	-0.000705
H	0.314750	1.502164	0.001344
H	-1.694278	0.221790	0.878736

HCHO

C	-0.525608	0.000000	-0.000006
H	-1.104928	-0.938699	0.000012
H	-1.104925	0.938701	0.000012
O	0.670438	0.000000	0.000001

P3

C	0.100239	0.865819	0.361355
H	0.070414	0.573335	1.412672
H	0.159736	1.953237	0.289206
O	1.321368	0.426875	-0.217101
O	1.465110	-0.952131	0.080783
C	-1.086295	0.336584	-0.383212
C	-1.955670	-0.514386	0.138558
H	0.973713	-1.376771	-0.635040
H	-1.194595	0.671464	-1.410055
H	-1.850700	-0.861298	1.159940
H	-2.800035	-0.886021	-0.426377

C_2H_2 + CH_2OO reaction

C_2H_2

C	0.000000	0.000000	-0.596949
H	0.000000	0.000000	-1.659754
C	0.000000	0.000000	0.596948
H	0.000000	0.000000	1.659759

Com

O	-1.384565	0.210863	-0.400102

C	-0.819552	1.114084	0.229318
H	-0.414298	0.901049	1.211773
H	-0.781423	2.077892	-0.261628
O	-1.422773	-1.022709	0.164826
C	1.556286	-0.575637	-0.016372
H	0.664984	-1.176149	0.018973
C	2.527373	0.123066	-0.047705
H	3.404794	0.722902	-0.078348

TSA

O	-1.141944	0.064524	-0.393517
C	-0.685280	1.055034	0.239935
H	-0.451241	0.943579	1.289116
H	-0.850371	2.014257	-0.234076
O	-0.825468	-1.115947	0.167826
C	1.433893	-0.660610	-0.008686
H	1.481697	-1.721292	0.031807
C	1.525635	0.545929	-0.081594
H	1.913729	1.532722	-0.179246

TSInsW

C	-0.333933	0.980908	0.249274
H	-0.275993	0.842353	1.322006
H	-0.012887	1.908825	-0.207440
O	-1.248493	0.356741	-0.397689
O	-1.392150	-0.907083	0.131932
C	1.086375	-0.410774	0.020470
C	2.260315	-0.139972	-0.086375
H	0.042257	-1.021106	0.095528
H	3.295221	0.091690	-0.184256

TSInsO

C	-2.102935	0.726714	0.030753
H	-1.316915	1.478553	0.148396
H	-3.156202	1.027591	-0.001531
O	-1.817590	-0.439357	-0.063876
O	-0.047987	-0.572995	0.012373
H	1.196531	-1.218271	0.154169
C	1.829479	-0.295807	0.044780
C	2.721508	0.502862	-0.038051
H	3.512885	1.208336	-0.113898

TSIso

O	2.262843	-0.084946	-0.038266
C	0.987132	-0.334028	-0.027696
H	0.746133	-0.403441	1.109106
H	0.633196	-1.295070	-0.419663
O	-1.867785	-0.705615	0.011199

C	-1.430385	0.428416	-0.028748
H	-2.109588	1.293469	-0.085082
C	-0.015843	0.734825	-0.025482
H	0.324369	1.754252	0.103731

P1

O	2.165612	-0.171201	-0.221515
C	1.032990	-0.358681	0.115845
H	-0.102832	0.914538	1.358119
H	0.646266	-1.369476	0.328786
O	-1.857425	-0.676513	0.052149
C	-1.325261	0.351507	-0.261952
H	-1.803818	1.040652	-0.978855
C	0.023868	0.760674	0.281519
H	0.405304	1.674993	-0.165599

P2

O	1.180398	-0.105720	-0.000171
H	1.580104	0.770988	-0.000136
C	-0.123727	-0.010717	0.000275
C	-1.317271	0.016159	-0.000122
H	-2.377304	0.042125	0.000585

P3

C	-0.095049	0.942723	0.209628
H	-0.329492	1.073786	1.267586
H	-0.007414	1.921398	-0.262841
O	-1.179290	0.322544	-0.451168
O	-1.458678	-0.886098	0.232630
C	1.151760	0.186475	0.056035
C	2.152271	-0.455893	-0.075956
H	-0.861744	-1.511224	-0.202105
H	3.048503	-1.015351	-0.192573

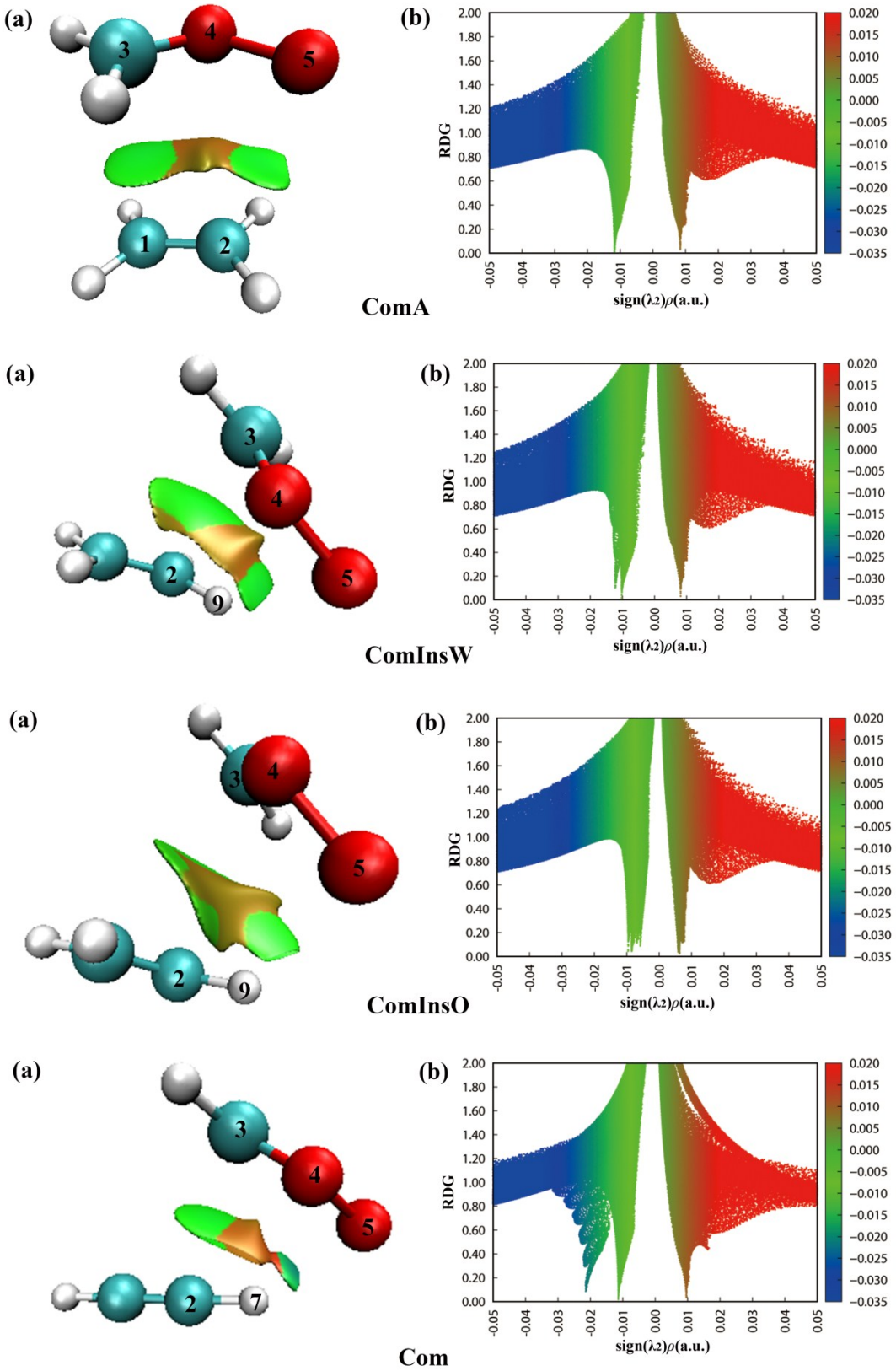

Figure S1. (a) Selected low-gradient (s = 0.5 a.u.) isosurface maps; (b) Plots of the RDG versus the electron density ρ_b multiplied by the sign of the second Hessian eigenvalue (λ_2) for the complexes.

RDG graphical analysis reveals the spatial location and the strength of the weak interactions. The blue, green, and red colors mean the strong attractive, poor attractive interactions, and steric effects, respectively. From Figure S1 we can see that the green regions are found between the H and O atoms or between the C and C atoms, indicating the non-covalent interactions in the complexes. The steric effects are also obvious, shown by the notable yellow or red regions in the center of the ring. The results of RDG analysis are in accordance with the AIM investigation.

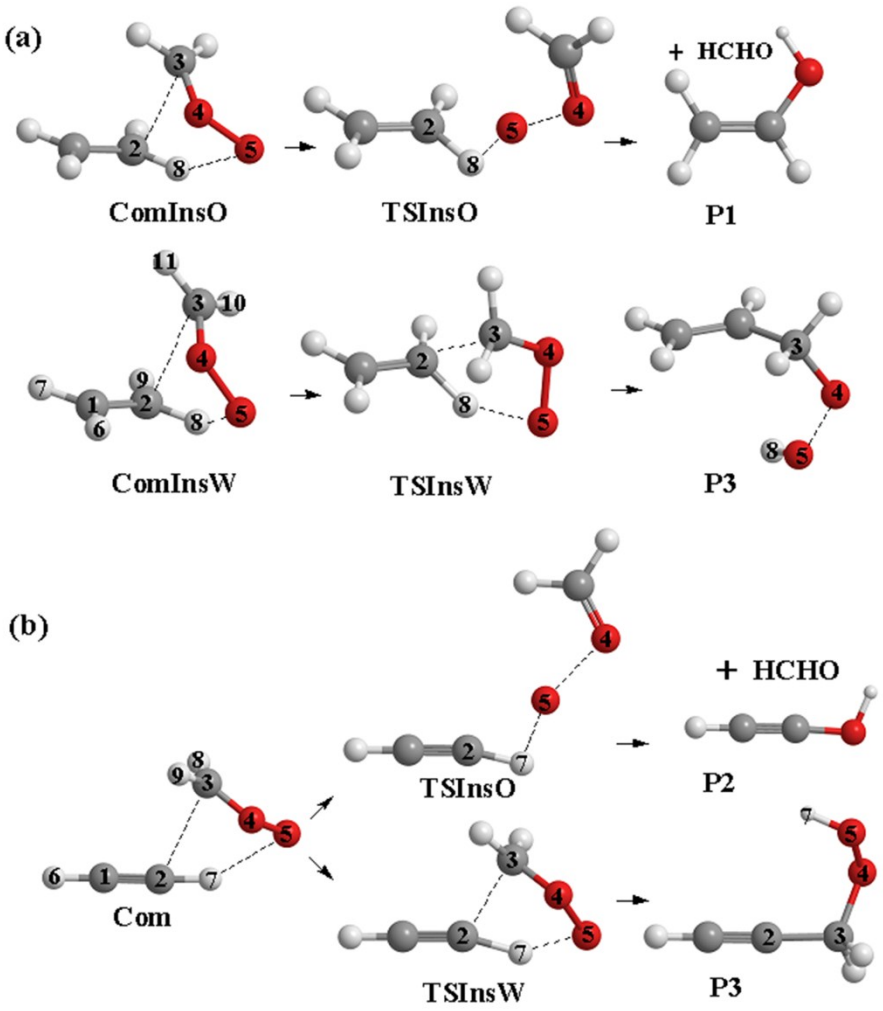

Figure S2. Optimized geometries of the transition states and products for the insertion reactions at the M06-2X/aug-cc-pVTZ level of theory. (a) CH_2OO + C_2H_4 reaction, (b) CH_2OO + C_2H_2 reaction