

Supporting Information:

Finding Minimum Structures on Seam of Crossing in Reactions of Type $A + B \rightarrow X$: Exploration of Nonadiabatic Ignition Pathways of Unsaturated Hydrocarbons

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S1. MSX1 and MSX3 at the CASPT2/aug-cc-pVDZ level.

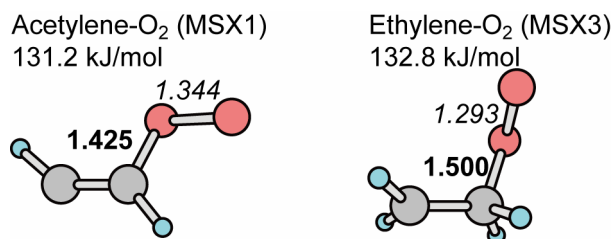


Figure S1. Optimized MSX structures at the CASPT2/aug-cc-pVDZ level. All π/π^* orbitals in the hydrocarbons and all p orbitals in oxygen atoms are included in the active spaces, i.e., 12 electrons and 10 orbitals (12e, 10o) for MSX1 and 10 electrons and 8 orbitals (10e, 8o) for MSX3.

MSX1 at the CAS(12e, 10o)-PT2/aug-cc-pVDZ level:

C	0.747347670797	0.402126396240	0.093703398508
C	1.819665738073	-0.337157753679	-0.190990740596
H	0.666467215885	1.487077377339	0.147094124824
H	2.095102259860	-1.386319724674	-0.251641325043
O	-0.483477521840	-0.276633172451	0.331004177200
O	-1.490704221527	0.408571796839	-0.237601274826

MSX3 at the CAS(10e, 8o)-PT2/aug-cc-pVDZ level:

C	0.818290367684	0.572201664166	0.165585312537
C	1.562640928388	-0.683037687291	-0.101383050458
H	0.602825456819	0.734935849642	1.229277871227
H	1.287882497317	1.459013066128	-0.292575838977
H	1.278430907296	-1.608875698101	0.414330106678
H	2.302266423802	-0.733046998931	-0.899334060719
O	-1.355880508446	-0.174824469592	0.226310855143
O	-0.529312692604	0.513990611884	-0.491168522859

S2. Cartesian Coordinates (in Å) for MSXs in Fig. 3.

MSX1:

C	0.755976886948	0.408399834372	0.103042413499
C	1.786409121040	-0.337830541966	-0.206405657412
H	0.690114431996	1.494554755031	0.162156031786
H	2.081873434543	-1.380079971545	-0.253978578730
O	-0.482297344957	-0.253309430078	0.349732042083
O	-1.477675388322	0.365930273802	-0.262977891159

MSX2:

C	0.745867272762	-0.366345466890	0.036644652609
C	1.189473721321	0.872725348863	0.108454013009
H	1.398208889960	-1.232431879260	-0.115984426736
H	2.094889799938	1.332540549607	-0.283907470976
O	-0.563834454401	-0.763519172447	0.289958868008
O	-1.404757115334	0.135998031092	-0.229098725921

MSX3:

C	0.824825833690	0.553894537971	0.166225233159
C	1.580709398072	-0.681803392202	-0.101114687068

H	0.595779434541	0.713278400801	1.226306712821
H	1.278743503286	1.445755775798	-0.280690011868
H	1.325106594643	-1.599390896886	0.426449599728
H	2.304182167576	-0.731391311159	-0.912864835071
O	-1.414238871905	-0.118986846890	0.233353039669
O	-0.527964679648	0.499000070465	-0.506622378802

MSX4:

C	2.146376506727	-0.836777860244	-0.166558064286
C	1.287444483054	0.339530951858	-0.319253802677
C	0.140902040708	0.889831473307	-0.000692733593
H	1.615536024996	-1.646571984047	0.364368859950
H	3.039137681635	-0.581955339693	0.425049542242
H	2.483688829801	-1.217022003167	-1.141090989958
H	-0.221540693189	1.895495215200	-0.210174897908
O	-0.816051222602	0.058949703589	0.656794365782
O	-2.011152892846	0.166254100785	0.095946647891

MSX5:

C	2.366732251626	0.688551574758	-0.033719767600
C	1.657237563367	-0.583864804017	-0.003726308978
C	0.413763891403	-1.013883707647	0.010594280364
H	3.141580315702	0.723104539135	-0.811622435114
H	2.830761365587	0.901832184311	0.941114494042
H	1.617497536750	1.492036990231	-0.208600363371
H	0.048557826522	-2.032190203831	0.121007749374
O	-0.603358648750	1.046516551103	0.339081938044
O	-0.643705359109	-0.102856471057	-0.320238579021

MSX6:

C	-1.142446930954	1.372721174736	-0.182819377785
C	-0.980949519417	-0.105271369523	-0.055999102256
C	-1.884317374989	-1.047435353672	0.095402744363
H	-0.670544797278	1.730551777821	-1.109255229537
H	-0.666203264135	1.886895078042	0.661468656286
H	-2.209864361962	1.618431046321	-0.201170955591
H	-1.948257646572	-2.128731283373	0.140013225334
O	0.375948310312	-0.607086509633	-0.109451217269
O	1.217814706785	0.113725616543	0.606735460567

MSX7:

C	-0.593155626321	-1.479658824709	-0.173198774061
C	0.688527265228	-0.974611661041	0.099064239230
C	1.434825080043	0.003752465480	0.254686863694
H	-1.102089436070	-1.985909075325	0.654989694683
H	-0.718714061432	-1.996512755524	-1.131465075333
H	-1.119968117399	-0.402629147403	-0.292784039815
H	2.327788629552	0.567087913415	0.443445592020
O	-1.109064936304	1.069884786569	-0.296003402158
O	0.098351172491	1.434802510750	-0.039725376138

MSX8:

C	0.364790534174	1.531476351595	-0.111091598636
C	-0.116551755467	0.278361586038	-0.032633181628
C	-1.397796709737	-0.159282292434	0.274617830484
H	-2.150658443676	0.595354316601	0.489304839742
H	-1.649210613284	-1.210367410893	0.302066354341
H	1.409882989367	1.698893222174	-0.368152546668
H	-0.272386029939	2.394315144286	0.078359181388
O	0.972561714280	-0.645944063345	-0.337897108020
O	0.429466966539	-1.867952665537	-0.243222756219

MSX9:

C	2.054444267562	0.975139127872	0.135680380315
C	1.575745430111	-0.245201725269	0.125030902469
C	0.420953741506	-1.087814656330	-0.085397407879
H	0.088957677791	-1.593448664499	0.829543437488
H	0.571018717146	-1.816651403871	-0.892738218542
H	3.106097365171	1.185358180610	0.347020144664
H	1.411068428701	1.842882975686	-0.062659150971
O	-0.811238768267	-0.321771480626	-0.584668879741
O	-1.373363173422	0.361634618643	0.373910274951

MSX10:

C	-1.621745025552	-0.700242685041	-0.000770563402
C	-1.296209428947	0.602429722741	-0.167085864258
C	-0.453186532609	1.565184951747	-0.130010873736
H	0.599113044673	1.060263959459	-0.009218601774
H	-0.524883728017	2.646253025089	-0.166633061070
H	-1.963185623117	-1.048655895304	0.975249585859
H	-1.834469226678	-1.338609133437	-0.857589618522
O	0.363447607190	-1.162275826316	-0.031214864594
O	1.211279351930	-0.317513427474	0.410160737458

MSX11:

C	-1.184601221839	1.398517004337	-0.366331619686
C	-1.304283998234	0.092675443163	0.339094872794
C	-0.533038795081	-1.093196491914	-0.063391269553
H	-1.085483076721	1.264942522159	-1.454010720253
H	-0.280017762340	1.946103041975	-0.038899259577
H	-2.048499997657	2.046108919857	-0.163341235047
H	-0.340700033201	-1.149616991033	-1.141488312072
H	-1.835749574128	0.051974364483	1.291653774256
H	-0.950176991159	-2.032988364124	0.317027249039
O	1.659208501050	-0.246166674331	-0.007010620659
O	0.857579810604	-1.107767946726	0.565750930724

MSX12:

C	-2.154639617684	-0.031789644438	-0.261009165078
C	-0.909691330013	-0.187925104856	0.542218004314
C	0.268449926601	0.676121281010	0.350132346757
H	-2.350759006169	1.021734783415	-0.510538686839
H	-2.086217868902	-0.580319680192	-1.220662936703
H	-3.028062006652	-0.437005586854	0.269249430663
H	0.010829792365	1.687250293541	0.008635084475
H	-0.775391187243	-1.094480377038	1.135160048607
H	0.946423854750	0.703097004836	1.209527647523
O	2.029276034249	-0.693543554014	-0.377706830266
O	1.123311908596	0.158111314985	-0.791162721920

MSX13:

C	-1.958403490111	0.315853409661	-0.144698049619
C	-0.494752284009	0.101237237217	0.195862334972
C	-0.112538725150	-1.289143875513	0.506062975195
H	-2.265835793808	-0.337227339818	-0.972625049001
H	-2.143822704909	1.358825954441	-0.429283088775
H	-2.576736485375	0.077600097993	0.730969331774
H	-0.740701367655	-2.121274778252	0.190014613875
H	-0.135313626537	0.803569973190	0.958499785119
H	0.865128608103	-1.503962422495	0.933218056935
O	1.504217365182	0.869426794247	-0.795687427034
O	0.262697710381	0.553443343410	-1.056836126534

MSX14:

C	-0.317470906505	1.379381787212	0.207995205375
C	0.506194253810	0.255325735376	-0.396256969004
C	1.514544680324	-0.355411173272	0.494962190860
H	-0.795097296132	1.057029141449	1.139859537000
H	-1.092365728400	1.713091030681	-0.494106060177
H	0.346050616214	2.226996086233	0.426094109401
H	1.237414073899	-0.633456612635	1.511532905614
H	0.949261373381	0.551471544338	-1.355130781944
H	2.479366701267	-0.680555790078	0.110486797473
O	-1.346040386165	-1.184010063135	-0.011302156838
O	-0.420114331656	-0.863820245836	-0.877301841347

MSX15:

C	0.843927903250	-0.280171690962	1.265486136956
C	1.893637568311	-0.211263121171	0.355458969119
C	2.041616156541	0.774801898692	-0.615145293931
H	0.059972503513	0.479125953590	1.284283061723
H	0.796042125570	-1.072105717771	2.011366419668
H	-0.248949992734	-1.055418551293	-0.540725959178
H	1.313814997861	1.581024879199	-0.715465605807
H	2.657939831385	-0.992838606918	0.403224163636
H	2.888318519887	0.771186012816	-1.299425439787

O	-1.956047346638	-0.423502757610	-0.874469214349
O	-0.987985834120	-1.286926027295	-1.152507298301

MSX16:

C	-0.965794894269	-1.292014979339	-0.167900748475
C	-0.447238427344	-1.078528293888	1.104815284158
C	-0.059408228248	0.216379261037	1.432073002133
C	-0.436090747795	1.323133249266	0.602345854306
C	-1.195336563421	1.121551146759	-0.545193324305
C	-1.341609425106	-0.185379942033	-0.997970597944
H	-1.789347075990	-0.385203696565	-1.970564821281
H	-1.511175192836	1.962993669256	-1.159657255322
H	-0.158906562194	2.330303408781	0.910734537354
H	0.494353432150	0.410939967824	2.349590752442
H	-0.191600769556	-1.917124428924	1.750359950152
H	-1.137373290037	-2.304390387327	-0.531169088628
O	1.418863100430	0.318566581955	-0.339035821415
O	0.938867083581	-0.476978343999	-1.182860466940

MSX17:

C	-0.068943190150	-1.139351337821	0.275997534117
C	1.240193638076	-1.387616561786	-0.092506466645
C	2.147846661826	-0.331565994176	-0.278813966549
C	1.700327038452	1.026345723896	-0.142637692151
C	0.413083834921	1.321016405920	0.181287182974
C	-0.574833688552	0.240214623838	0.517888623068
H	-0.996061155184	0.385642182758	1.529859771682
H	0.073312174955	2.353717355407	0.263898954291
H	2.407864188822	1.836082195050	-0.327116019989
H	3.176095761440	-0.534472207936	-0.575696621321
H	1.563901584602	-2.414904241970	-0.265128256339
H	-0.797266323184	-1.945590900737	0.358763066579
O	-1.759601035466	0.351728888399	-0.374904631139
O	-2.857045475969	-0.012745750411	0.259900263825

MSX18:

C	0.807288880857	-1.337460647549	0.332670783358
C	-0.050669160647	-0.397543001918	0.938909709933
C	0.171701394269	0.979910748065	0.744712492728
C	1.221784222707	1.410392282084	-0.066442144836
C	2.058435510972	0.471271400604	-0.680029047938
C	1.850612071796	-0.902947514075	-0.479971536629
H	2.508925677210	-1.627672223545	-0.959934494528
H	2.877126926182	0.807528592268	-1.317559312058
H	1.388686017539	2.475968616240	-0.225680485859
H	-0.489562327542	1.702534329837	1.221651096127
H	-0.823726424470	-0.730226347577	1.628294982303
H	0.638776582812	-2.402561756349	0.491432268282
O	-2.985769763322	0.361641855410	0.221809920710
O	-1.758925046309	-0.575373279991	-0.639960771210

MSX19:

C	0.278225072793	-0.207058057867	0.777354621004
C	0.342790326213	0.799877775994	-0.226997722628
C	-1.016517396613	-0.597578087575	1.226078156262
C	-2.159159852087	0.200578196447	0.955158500601
C	-0.881825397390	1.446851345226	-0.635868735450
C	-2.066956076252	1.269325212079	0.061036337053
C	1.466796946512	-0.846858299777	1.201990856824
C	2.688245427369	-0.477953226009	0.665648952257
C	1.598942687464	1.146309309228	-0.776010718597
C	2.752601563877	0.524008031347	-0.329054374934
H	1.409105281892	-1.632049007513	1.956800347134
H	-1.105675829524	-1.442003795754	1.908228861517
H	-3.110018569298	-0.054487636897	1.419434655802
H	-2.952578163747	1.845413617887	-0.202108416670
H	-0.827840272898	2.180410113229	-1.440594852584
H	1.650720842742	1.912999546426	-1.549717942093
H	3.718894250809	0.803646067082	-0.749882180118
H	3.603436267896	-0.964748160842	1.002994657252
O	-1.179619333134	-0.754635598612	-1.575638777593
O	-1.715667706980	-1.389710527121	-0.627659311023

C	0.376889578272	1.890960050208	-0.218357551699
C	-0.949353873578	1.892788042197	0.032214124464
C	-0.822253415984	-0.544986647389	0.572216136541
C	-1.677038061172	0.650403183767	0.412638538124
H	0.877443322018	2.819609918055	-0.498648300517
H	3.037201580040	1.626035840954	-0.702369740950
H	4.386562552975	-0.452799187113	-0.512573816499
H	3.303833036809	-2.590667788090	0.184506656910
H	0.874335850030	-2.649236646269	0.686666283541
H	-1.311110601038	-1.473543039463	0.868382923742
H	-2.382894220864	0.797017131732	1.241436905542
H	-1.533125935952	2.809799061893	-0.048765843889
O	-2.650700864934	0.328923902469	-0.750790516615
O	-3.794583197263	-0.134731005108	-0.319322257545

MSX24:

C	0.171844673580	0.034278720824	-0.445314574868
C	0.239186221288	1.085592510709	0.528306202060
C	-1.165617399209	-0.228712054216	-1.088684748693
C	-2.328454603581	0.115458820881	-0.187119531345
C	-0.954034099255	1.720642843666	0.974497113463
C	-2.230523680402	1.168977828474	0.672260306867
C	1.346042796777	-0.640805649607	-0.800640763267
C	2.574017161141	-0.274231145642	-0.249570887867
C	1.506255204935	1.456910841164	1.054494678778
C	2.657400146408	0.796859130280	0.660319300415
H	1.301535372300	-1.442383127682	-1.535496183143
H	-1.254317475573	0.285431198428	-2.068835430016
H	-3.263206344060	-0.419044016956	-0.352379699545
H	-3.108034162501	1.530160991146	1.210253517307
H	-0.875775483409	2.552970454195	1.674381204934
H	1.553687599359	2.250328038124	1.801324536232
H	3.622882005731	1.083815817956	1.077603380908
H	3.475289615458	-0.817595528987	-0.533756757410
O	-1.356791427554	-1.661875435594	-1.364266375078
O	-0.637804093152	-1.998582337155	-2.427863352507

MSX25:

C	-0.533133488576	-0.678660840565	0.483494780887
C	-0.489595519502	0.720859968668	0.120408981296
C	0.652589844091	-1.300371668213	1.031262080204
C	1.824209190279	-0.634045272610	1.140749873651
C	0.718077678499	1.409080982035	0.170608855534
C	2.003082195427	0.707165147601	0.498271925595
C	-1.749398415418	-1.374487600122	0.372500572590
C	-2.905611026628	-0.734915514622	-0.065565642372
C	-1.705000734744	1.356799284177	-0.294373243826
C	-2.880189361508	0.642361381966	-0.395306481883
H	-1.782199073647	-2.429783867851	0.646971122109
H	0.569317712136	-2.325193366177	1.397070229825
H	2.705075361549	-1.101723034827	1.578797588988
H	2.721443853334	1.345097012011	1.026940644639
H	0.744450337372	2.482536574389	-0.015014626522
H	-1.677580044035	2.415575699020	-0.554421114017
H	-3.793598314609	1.135145788123	-0.728809125147
H	-3.838934470901	-1.292831597246	-0.143880755791
O	1.907044237203	0.216300655304	-1.785053631890
O	2.745257923212	0.361942866093	-0.775580661598