Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplemental Material

Theoretical Studies on Reaction Kinetics of Methyl Crotonate with Hydroxyl Radical

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Table S1. Cartesian coordinates (in Å) of species involved in R1 to R10 of MC + OH at the M062x/6-311G(d,p) level.

MC	C	-5.47715500	-0.50363400	-0.11918000
	H	-5.56810700	-1.58873600	-0.01820500
	H	-4.58837400	-0.27947600	-0.70984100
	H	-6.35946800	-0.16254200	-0.66760000
	C	-5.41995100	0.13988800	1.22679800
	H	-6.26242900	-0.01288800	1.89826800
	C	-4.41169000	0.88728700	1.66976400
	H	-3.53046900	1.09378300	1.07293000
	C	-4.46029200	1.47550800	3.02816400
	O	-5.36263800	1.36009700	3.81688000
	O	-3.34300800	2.17627900	3.28985900
	C	-3.29378300	2.78424100	4.57988800
	H	-3.38617700	2.02737300	5.35936000
	H	-2.32820300	3.27984200	4.63738700
	H	-4.10386000	3.50604100	4.68960200
OH	O	0.00000000	0.00000000	0.10801800
	H	0.00000000	0.00000000	-0.86414100
vdW	C	-3.30392500	-0.29940300	0.05119200
	H	-3.83275400	0.19554700	0.87030900
	H	-3.31008000	-1.37516200	0.22727300
	H	-3.86740800	-0.08753900	-0.86154800
	C	-1.91523800	0.23407000	-0.06370300
	H	-1.79618400	1.30078900	-0.24205300
	C	-0.80796700	-0.49906400	0.03570200
	H	-0.82630500	-1.56797300	0.21314600
	C	0.51875000	0.13655500	-0.09419900
	O	0.71156100	1.31559300	-0.29497500
	O	1.50403900	-0.75382100	0.03752900
	C	2.83671400	-0.24366400	-0.06958200
	H	3.02263500	0.50087300	0.7060110
	H	3.49097500	-1.10067400	0.06289900
	H	2.99332800	0.20656000	-1.05107000
	O	3.12464000	2.76697100	-0.58159500
	H	2.19770200	2.45710900	-0.51356200
H_2O	O	0.00000000	0.00000000	0.11674300
	H	0.00000000	0.76116000	-0.46697300
	H	0.00000000	-0.76116000	-0.46697300
MC+OH---->PC1+H_2O(R1)				
PC1	C	-5.42858500	-0.38078000	-0.29992500
	H	-5.67386100	-1.43138900	-0.12177100
	H	-4.44669700	-0.32442800	-0.77062600
	H	-6.17636000	0.00476200	-0.99828500
	C	-5.46961800	0.38481600	0.98052600

	H	-6.40639200	0.39795400	1.53369600
	C	-4.44075000	1.05406800	1.49882500
	H	-3.46976900	1.09777700	1.01911100
	C	-4.59369100	1.77332400	2.77679600
	O	-5.58160400	1.84433700	3.45408700
	O	-3.41908200	2.37964300	3.12101500
	C	-3.37888300	3.08243400	4.28110000
	H	-2.42654800	3.53648000	4.48907600
	H	-4.26808200	3.14410400	4.88541000
MC+OH---->PC2+H_2O(R2)				
PC2	C	-5.56029800	-0.02413000	-0.13658800
	H	-4.69306700	0.00289000	-0.78609100
	H	-6.44932800	-0.51618800	-0.50698600
	C	-5.52679200	0.54630400	1.10983400
	H	-6.40708900	0.50721700	1.74492000
	C	-4.40947400	1.19038900	1.62936600
	H	-3.48935100	1.27768100	1.06442600
	C	-4.44836800	1.77429000	2.97095500
	O	-5.39728900	1.74865900	3.71831100
	O	-3.27716900	2.35901900	3.28872300
	C	-3.22755900	2.95274800	4.58461000
	H	-3.39083400	2.19732900	5.35420200
	H	-2.23370700	3.38323900	4.67533000
	H	-3.99152300	3.72525700	4.67946000
MC+OH---->PC3+H_2O(R3)				
PC3	C	-5.24196000	0.15990900	-0.35201600
	H	-6.32444100	0.30498900	-0.37482100
	H	-5.02948800	-0.90547200	-0.50314700
	H	-4.81469700	0.72072700	-1.18664300
	C	-4.68549800	0.62987300	0.92056800
	C	-3.98902300	0.15913400	1.93007100
	H	-3.65445700	-0.87764800	1.96916000
	C	-3.58674700	0.97290900	3.10268700
	O	-2.93811800	0.54548900	4.02183800
	O	-4.02213800	2.23998900	3.03284300
	C	-3.66037600	3.06748300	4.13752500
	H	-2.57522700	3.13555000	4.22276400
	H	-4.09033700	4.04336000	3.92748300
	H	-4.06403100	2.66123100	5.06556700
MC+OH---->PC4+H_2O(R4)				
PC4	C	-5.63940400	-0.53501400	-0.00488500
	H	-5.67310400	-1.62611800	0.04940800
	H	-4.72737100	-0.23400800	-0.51863200
	H	-6.50240100	-0.21407500	-0.59368200
	C	-5.70585500	0.05180900	1.37188200

	H	-6.58658100	-0.17680500	1.97851000
	C	-4.78948000	0.82045400	1.91685200
	C	-4.73403200	1.44922900	3.24242700
	O	-5.61625000	1.37741000	4.05883900
	O	-3.58868300	2.10913900	3.43630300
	C	-3.46033100	2.74710300	4.70865200
	H	-3.53379900	2.01110100	5.50967500
	H	-2.47980500	3.21504600	4.70434100
	H	-4.24365900	3.49449600	4.83767600
MC+OH---->INT1----> $CH_3CHCHOH$ + CH_3OCO (R5)				
INT1	C	-2.36242900	-0.33090100	-1.00529000
	H	-2.52211200	-1.41320000	-0.97651300
	H	-1.59747000	-0.14949800	-1.77241600
	H	-3.28447400	0.14609300	-1.34160700
	C	-1.94850100	0.18277200	0.32711200
	H	-2.17050200	1.19816700	0.63311400
	C	-1.01058100	-0.57874200	1.20934100
	H	-1.18987300	-1.65622200	1.09016700
	C	0.43039900	-0.31710100	0.77286000
	O	1.22255300	0.29188100	1.44350200
	O	0.69218600	-0.81302100	-0.43460400
	C	2.01268300	-0.56471400	-0.93085600
	H	2.75393000	-0.98610300	-0.25207500
	H	2.05848600	-1.05044600	-1.90152700
	H	2.18129800	0.50795800	-1.02694100
	O	-1.15502100	-0.21920400	2.55832300
	H	-0.34180200	0.22606600	2.82894900
$CH_3CHCHOH$	C	-2.98045300	-0.50856000	-0.79180700
	H	-2.99244900	-1.59969800	-0.75907500
	H	-2.43446100	-0.20540300	-1.68906100
	H	-4.01152500	-0.16405500	-0.90592900
	C	-2.35030800	0.05523700	0.44770700
	H	-2.28678300	1.13863100	0.53502600
	C	-1.87208800	-0.69931600	1.43130600
	H	-1.90601900	-1.78298900	1.40286800
	O	-1.28885000	-0.26228200	2.58115500
	H	-1.27096400	0.69937200	2.58519600
CH_3OCO	C	0.94968400	-0.39484300	1.01499900
	O	0.06240200	-0.34180900	1.78246000
	O	0.87936000	-0.46376600	-0.30449800
	C	2.13985600	-0.52104300	-0.99020500
	H	2.67808100	-1.42653300	-0.71132900
	H	1.89534000	-0.53969400	-2.04849900
	H	2.73563800	0.36059200	-0.75562200
MC+OH---->INT1----> INT3----> INT4----> $CH_3OCOCHO$ + CH_3CH_2 (R6)				

	C	-3.10945800	-0.47209800	-0.29789700
	H	-3.60094100	0.06549700	-1.11384400
	H	-3.51563400	-0.11733200	0.64982800
	H	-3.36286700	-1.52895800	-0.41632000
	C	-1.63048700	-0.27937700	-0.37187100
	H	-1.12049300	-0.60446400	-1.27458900
	C	-0.88869700	0.23816700	0.60793900
	H	-1.31668100	0.61856300	1.52948200
INT3	C	0.61280600	0.40719900	0.48223300
	O	0.64794100	1.67741200	-0.01134000
	O	1.12774400	-0.55232500	-0.36573300
	C	2.48943500	-0.33731200	-0.71364700
	H	3.12851600	-0.40295200	0.16872400
	H	2.75016900	-1.12443300	-1.41775400
	H	2.61434000	0.63747200	-1.19423300
	O	1.28561000	0.32085200	1.71244700
	H	1.22978000	1.18267500	2.13624700
	C	-2.40798100	0.82300400	0.80147300
	H	-3.02915500	1.67351000	0.55720200
	H	-2.04553900	0.70740500	1.81499800
	C	-2.28144900	-0.28865100	-0.18602000
	C	-0.97526100	-1.07229300	0.00450200
	H	-0.93779700	-1.89477800	-0.71626200
	C	0.24371800	-0.21555700	-0.23468800
	O	0.26321100	0.79962000	-0.88589400
INT4	O	1.33445400	-0.72715100	0.34334400
	C	2.54786100	-0.00099100	0.12411900
	H	2.45695700	1.01048000	0.51994600
	H	3.32029400	-0.55326600	0.65198500
	H	2.76921700	0.05031600	-0.94199000
	H	-3.10474900	-1.00223400	-0.04355400
	O	-2.42318200	0.16309700	-1.51775000
	H	-1.68845300	0.76722000	-1.68354600
	H	-0.91309900	-1.50850100	1.00341300
	C	-0.95395400	-1.17434200	-0.67252700
	H	-1.53993000	-0.86011500	-1.55803700
	C	0.44840700	-0.54888100	-0.67680300
$CH_3OCOCHO$	O	0.80009300	0.18352600	-1.56786100
	O	1.17478800	-0.90740200	0.37899300
	C	2.50625600	-0.35392000	0.43828300
	H	2.46078400	0.73550500	0.46877900
	H	2.94230700	-0.74884400	1.35196200
	H	3.08308100	-0.66524300	-0.43361200
	O	-1.36798400	-1.90959800	0.17689600
CH_3CH_2	C	-3.33901400	0.32832400	0.48766100

	H	-3.49412500	-0.57296700	1.08343800
	H	-3.79252900	0.14377700	-0.49657800
	H	-3.90893100	1.14194400	0.94418300
	C	-1.89509200	0.66976700	0.37407400
	H	-1.13495500	-0.09651900	0.43726200
	H	-1.58579600	1.66105700	0.07209500
MC+OH---->INT1----> INT3----> INT4----> CH_3CH_2CHO + CH_3OCO (R7)				
CH_3CH_2CHO	C	-3.68946900	-0.15999000	0.50820700
	H	-3.78713100	-1.00799300	1.18709500
	H	-4.30252600	-0.37398300	-0.36813500
	H	-4.08306900	0.72925900	1.00143600
	C	-2.23578200	0.04193600	0.10852500
	H	-2.11110100	0.89949400	-0.56388900
	C	-1.63779000	-1.15219200	-0.58831900
	H	-0.57737700	-1.04429600	-0.89552400
	O	-2.23229300	-2.17007700	-0.81716600
	H	-1.59918300	0.26077600	0.97450800
MC+OH---->INT1----> INT5----> INT6----> CH_3CH_2COCO + CH_3OH (R8)				
INT5	C	-2.42423400	0.04718900	-0.84093700
	H	-2.21038000	0.57636200	-1.77080300
	H	-3.22982300	0.57197900	-0.32369700
	H	-2.77072300	-0.95755200	-1.08639200
	C	-1.16784100	-0.01747100	0.04108400
	H	-0.82843700	0.98492300	0.30075800
	C	-1.41040500	-0.77410000	1.29435300
	C	-1.45645600	-0.26310800	2.63741700
	O	-1.69739700	-0.98659600	3.59427100
	O	-1.21564700	1.05659300	2.73998600
	C	-1.24857100	1.57297200	4.06988700
	H	-0.49450800	1.08271700	4.68665700
	H	-1.03698400	2.63504800	3.97795200
	H	-2.23094400	1.41394300	4.51598300
	O	-1.65847000	-2.08166300	1.17175500
	H	-1.82322200	-2.42354600	2.06692000
	H	-0.36163000	-0.51449300	-0.50955500
INT6	C	-2.16778400	0.75180500	0.62077600
	H	-2.16000100	1.74401200	0.16530100
	H	-1.32714000	0.69610400	1.31540500
	H	-3.08770900	0.64747300	1.19797700
	C	-2.09826700	-0.34455900	-0.43768500
	H	-2.03153300	-1.33304800	0.02034600
	C	-0.85483500	-0.17248700	-1.36411000
	H	-0.94204800	0.79796700	-1.87219600
	C	0.40675500	-0.13188600	-0.50253700
	O	1.04067200	0.86943600	-0.30864900

	O	0.68508400	-1.31749000	0.03519500
	C	1.85148700	-1.35936500	0.86187600
	H	1.74536000	-0.66846500	1.69879100
	H	1.92703200	-2.38431500	1.21364800
	H	2.73231600	-1.08462700	0.28135900
	O	-0.89077400	-1.20951900	-2.23911700
	H	-2.97721400	-0.32575500	-1.08355600
CH_3CH_2COCO	C	-2.98731200	-1.43577600	-0.97580500
	H	-3.41298000	-1.32401700	-1.97378500
	H	-3.76102200	-1.82461100	-0.31094500
	H	-2.17756100	-2.16427400	-1.02004100
	C	-2.45528800	-0.09545600	-0.46629200
	H	-3.25842800	0.64310900	-0.38417600
	C	-1.76463800	-0.27242000	0.86930600
	C	-2.23307700	0.52404900	1.92055900
	O	-2.58987700	1.18306500	2.79254500
	O	-0.84126000	-1.07493100	1.08759100
	H	-1.71147400	0.30543400	-1.16151900
CH_3OH	O	-0.61119100	-0.07504200	3.41593200
	C	-1.25685400	-0.67183800	4.52486900
	H	-1.08664000	-0.01720100	5.37833200
	H	-2.33652500	-0.76465800	4.36899200
	H	-0.84284700	-1.65847600	4.75686500
	H	-0.74254900	-0.62968000	2.64527500
MC+OH---->INT2----> $CH_3OCOCHCHOH + CH_3$ (R9)				
$CH_3OCOCHCHOH$	C	-2.14672000	-0.31402100	-0.59834900
	C	-1.03011800	-0.86626300	-0.06509300
	H	-1.08507100	-1.77838200	0.50942900
	C	0.25095400	-0.21911400	-0.27265200
	O	0.40472200	0.82123700	-0.91225200
	O	1.27907100	-0.86409500	0.30340900
	C	2.57594800	-0.26592700	0.12866300
	H	2.59650600	0.73681900	0.55796500
	H	3.26823300	-0.92128400	0.65213100
	H	2.83041600	-0.20471700	-0.93042900
	H	-3.12444000	-0.76670000	-0.46635600
	O	-2.18860700	0.79973100	-1.31796500
	H	-1.25801900	1.12871600	-1.37862600
CH_3	C	0.00000000	0.00000000	0.00000000
	H	0.00000000	1.07880800	0.00000000
	H	0.93427500	-0.53940400	0.00000000
	H	-0.93427500	-0.53940400	0.00000000
MC+OH---->INT2---->INT7---->CH_3COHCH_2 + CH_3OCO (R10)				
INT7	C	-2.37914100	0.80182200	0.40151200
	H	-2.42723800	1.26227300	1.37933000

	H	-2.64100800	1.39455300	-0.46347800
	C	-2.17885400	-0.66913600	0.29167000
	H	-3.07729100	-1.21332100	0.61416200
	C	-1.03795100	-1.16236700	1.19331600
	H	-0.86479200	-2.22928000	1.00359000
	C	0.25372400	-0.43067800	0.86902400
	O	0.88505400	0.18690700	1.68701100
	O	0.60389500	-0.55862100	-0.40789600
	C	1.80490000	0.12116500	-0.78918000
	H	2.64890100	-0.25256200	-0.20937300
	H	1.93939000	-0.08969500	-1.84625300
	H	1.69645800	1.19229700	-0.61876600
	O	-1.36400100	-0.96256000	2.54280600
	H	-0.63982100	-0.46950700	2.94926400
	H	-1.97056800	-0.96325300	-0.73886200
CH_3COHCH_2	C	-2.90196800	-0.78100200	1.18065200
	H	-3.96233000	-0.68063100	0.93859500
	H	-2.77938100	-0.79811300	2.26195700
	H	-2.55552400	-1.72883700	0.76257300
	C	-2.13556600	0.34902200	0.57572200
	C	-1.39472700	1.22914400	1.24704100
	H	-0.86258300	2.02835500	0.74336000
	O	-2.29328400	0.36644700	-0.78018000
	H	-1.79423100	1.09989700	-1.15135400
	H	-1.30904600	1.16228200	2.32157200
MC+OH---->INT2---->INT7---->INT8----> $CH_3COCH_2COOH + CH_3$ (R11)				
INT8	C	-2.00885700	-0.01321000	-1.14264300
	H	-1.55968200	-0.12414400	-2.13079200
	H	-2.20057800	1.04738600	-0.96938900
	H	-2.96312500	-0.54194700	-1.13560400
	C	-1.07259900	-0.57471400	-0.06224600
	H	-0.12812300	-0.03034300	-0.04771500
	C	-1.67199800	-0.48595600	1.29116400
	C	-1.16379400	0.36508700	2.33112200
	O	-0.18961600	1.08553300	2.25395100
	O	-1.92844900	0.26615300	3.46034200
	C	-1.49576600	1.06616600	4.55882200
	H	-1.49033400	2.12029200	4.28035000
	H	-2.20917800	0.88547700	5.35895200
	H	-0.49129400	0.77407200	4.86669400
	O	-2.76612500	-1.22758700	1.51334800
	H	-3.07014400	-1.06218000	2.41690100
	H	-0.85601100	-1.62689000	-0.27761800
	C	-3.48206800	-0.13783400	1.40096500
	H	-3.27073300	0.28732500	2.38643900

	H	-3.43790800	-1.22488400	1.50334300
	H	-4.46835800	0.17651600	1.06733500
	C	-2.43494800	0.33558900	0.43405800
	C	-1.03006200	-0.20070900	0.63710500
CH_3COCH_2COOH	H	-0.85623500	-0.48801700	1.67354800
	C	0.13810400	0.68281300	0.19306000
	O	-0.08509400	1.50092400	-0.83273700
	O	1.20603000	0.59528300	0.72214300
	O	-2.69748500	1.08736900	-0.47902600
	H	-0.96677700	-1.12098100	0.04133400
	H	-1.03584400	1.50875700	-1.05117100

Table S2. Cartesian coordinates (in Å) of transition states for major consumption reactions of INT1 at the M062x/6-311G(d,p) level.

INT1--->TS8--->INT3--->TS9--->INT4--->TS10--->$CH_3OCOCHO+CH_3CH_2$				
TS8	C	-2.81015800	-0.54766400	-0.85227200
	H	-2.73137000	-1.63134600	-0.74556500
	H	-2.19064100	-0.24854000	-1.70365700
	H	-3.84636200	-0.30158100	-1.10144800
	C	-2.37069900	0.15144900	0.39047300
	H	-2.40740200	1.23552900	0.43473900
	C	-1.83812000	-0.50196200	1.45040900
	H	-1.90085300	-1.58660400	1.51860100
	C	0.31286100	-0.68432900	0.80245800
	O	1.07648800	-0.31766900	1.64241400
	O	0.53143800	-0.79054100	-0.49323700
	C	1.86344900	-0.43776200	-0.93077800
	H	2.59348900	-1.09453600	-0.45840000
	H	1.86241900	-0.57177200	-2.00847900
	H	2.07467600	0.59824500	-0.66677400
	O	-1.57236700	0.16727300	2.61152900
	H	-0.70038600	-0.09434900	2.93467800
TS9	C	-2.78607900	-0.32752000	-0.64901800
	H	-3.40020400	0.42810600	-1.14035500
	H	-3.41821400	-0.87040300	0.06190600
	H	-2.44862200	-1.04349700	-1.40399300
	C	-1.61587800	0.29139900	0.06900800
	H	-1.86156500	1.13998300	0.70969300
	C	-0.67463100	-0.67928800	0.74675700
	H	-0.42932500	-1.48044300	0.02936300
	C	0.64448900	0.01357900	1.08856800
	O	1.15366400	-0.08961200	2.16720400
	O	1.21314900	0.75962600	0.12596100
	C	0.59382000	0.84212900	-1.13462100
	H	0.80357400	1.81123600	-1.57517700
	H	0.82102400	-0.01000000	-1.77516500
	H	-0.73242400	0.75829200	-0.80995900
	O	-1.23435800	-1.23488700	1.90405500
	H	-0.56646800	-1.17995700	2.60151500
TS10	C	-2.12215300	-0.25687500	-1.15311700
	H	-1.67878600	0.32557700	-1.96110500
	H	-3.21349600	-0.19739100	-1.24962100
	H	-1.85452300	-1.30645700	-1.28769900
	C	-1.67577600	0.24840100	0.17944100
	H	-1.50480600	1.29613400	0.38248600

	C	-1.72165900	-0.63696500	1.35609600
	H	-0.62482600	-0.46159900	0.77738900
	C	-1.56264800	-0.19563600	2.73565100
	O	-1.78888000	-0.92806000	3.68085000
	O	-1.09968400	1.06114900	2.84558400
	C	-0.82589500	1.48971200	4.18069200
	H	-0.08084400	0.84027900	4.64150600
	H	-0.44773800	2.50469000	4.09192400
	H	-1.73656700	1.46910300	4.77937600
	O	-2.29031400	-1.86822600	1.19381200
	H	-2.24786400	-2.30540800	2.05633200
INT1--->TS8--->INT3--->TS9--->INT4--->TS11--->$CH_3CH_2CHO+CH_3OCO$				
	C	-3.14073900	-0.64047800	0.12340100
	H	-3.64810400	-0.18114600	-0.72669000
	H	-3.54622000	-0.21338000	1.04139400
	H	-3.37002300	-1.70897100	0.11642000
	C	-1.63508400	-0.40823400	0.04552400
	H	-1.41194200	0.66206000	-0.00855300
	C	-0.91949800	-0.97666000	1.27581100
	H	-1.12229700	-2.04982200	1.36052500
TS11	C	0.58093800	-0.85951800	1.09106400
	O	1.31147000	-1.26774000	0.26695700
	O	0.86529500	0.97333200	1.47298600
	C	1.92318500	1.42748900	1.00941200
	H	2.29843900	1.07294700	0.04473100
	H	2.51795600	2.13269700	1.59370500
	O	-1.33809700	-0.38487400	2.47554400
	H	-0.88115800	0.45980000	2.56082900
	H	-1.21327000	-0.87615800	-0.84872400
INT1--->TS12--->INT5-->TS13-->INT6-->$CH_3CH_2COCO+CH_3OH$				
	C	-2.55992700	-0.51837000	-0.61114300
	H	-3.18232700	0.08833100	-1.27032000
	H	-3.19048700	-0.92787400	0.17860000
	H	-2.15595300	-1.35127700	-1.19219800
	C	-1.43160700	0.31818600	-0.01242300
	H	-1.83894100	1.16748600	0.54643900
	C	-0.58327200	-0.49605200	0.94488700
TS12	H	0.04481700	-1.32742300	0.15530100
	C	0.71066300	0.16060300	1.36397400
	O	0.90773600	0.74191000	2.38715100
	O	1.67165900	-0.04812900	0.43147400
	C	1.33568600	-1.06869100	-0.47725200
	H	1.18581700	-0.70424300	-1.48962900
	H	1.98204700	-1.93515700	-0.36803500
	O	-1.32958600	-0.98766100	1.98929000

	H	-0.80008100	-0.98376400	2.79514800
	H	-0.78961800	0.72213800	-0.80037200
TS13	C	-2.18479000	-0.62786700	0.04230100
	H	-3.18648500	-0.56046200	-0.38368500
	H	-2.21997300	-1.37545500	0.84173200
	H	-1.51281000	-0.98466500	-0.74150700
	C	-1.72816200	0.72921700	0.57034600
	H	-2.39631400	1.08143300	1.36007800
	C	-0.30090400	0.69314500	1.13167800
	H	-0.04270600	1.66198300	1.57749100
	C	-0.29115600	-0.26112500	2.35653600
	O	-0.85508300	0.01479200	3.36547700
	O	0.36647000	-1.43951400	2.23123400
	C	0.85477300	-1.85925000	0.99520500
	H	1.87843000	-2.21192900	1.09512300
	H	0.17837400	-2.55981800	0.50532600
	O	0.65657100	0.40202900	0.17432600
	H	0.88902200	-0.83117200	0.29626500
	H	-1.73792300	1.47059100	-0.23206500

Table S3. Cartesian coordinates (in Å) of transition states for major consumption reactions of INT2 at the M062x/6-311G(d,p) level.

INT2--->TS14--->$CH_3OCOCHCHOH+CH_3$				
	C	-1.07599100	1.28000100	-1.11976000
	H	-1.54958100	2.25639400	-1.18371700
	H	-1.05626600	0.76111600	-2.07800000
	H	0.22531500	1.52043600	-0.90888500
	C	-1.47603600	0.41545400	0.05446600
	H	-2.30653000	-0.24516000	-0.21006400
	C	-0.34032500	-0.52250300	0.52519700
	H	0.21360100	-0.88101600	-0.35159900
TS14	C	0.60988600	0.22976800	1.46172200
	O	0.65685000	-0.03336600	2.62988400
	O	1.34590100	1.24500600	0.97914800
	C	1.47191900	1.44916900	-0.40433500
	H	1.97599800	0.62860900	-0.91611600
	H	1.93785000	2.41651100	-0.56223600
	O	-0.86010500	-1.62687100	1.20850600
	H	-0.60872500	-1.53661300	2.13767800
	H	-1.80849100	1.02181500	0.90144600
INT2--->TS15--->INT7--->TS16---> $CH_3COHCH_2+CH_3OCO$				
	C	-3.27365400	0.28547800	0.81546200
	H	-3.23644300	1.13201200	1.51337100
	H	-3.35674400	-0.63420000	1.39572600
	H	-4.16192400	0.39678700	0.19248100
	C	-2.04802400	0.27570400	-0.02892300
	C	-0.80565300	-0.38456400	0.44795900
	H	-0.83272000	-0.88459400	1.40579500
	C	0.45726900	-0.12339100	-0.19173100
TS15	O	0.59820700	0.57213300	-1.19571000
	O	1.49107000	-0.75145500	0.39764300
	C	2.76138000	-0.54196100	-0.21728100
	H	3.01918700	0.51765700	-0.20977200
	H	3.47079800	-1.11243600	0.37662100
	H	2.75054200	-0.89730300	-1.24816800
	H	-1.59290600	-0.98860000	-0.34860600
	O	-1.98632100	1.22962500	-0.97898600
	H	-1.06824300	1.27219700	-1.31566900
	C	-3.00411300	0.17390700	0.72018700
	H	-2.15926800	0.40621600	1.37281200
TS16	H	-3.43186200	-0.77380000	1.04788400
	H	-3.75148100	0.95883200	0.84282300
	C	-2.54837100	0.07928700	-0.72960900

	H	-3.40529100	-0.09758100	-1.39155300
	C	-1.60729900	-1.08520200	-0.97473600
	H	-1.09832300	-1.08181200	-1.96194300
	C	0.18022800	-0.25835800	-0.17414300
	O	0.27897000	0.90020700	0.03739300
	O	1.01771500	-1.23592600	0.00405200
	C	2.29527800	-0.86044200	0.57458800
	H	2.13680200	-0.41746700	1.55706400
	H	2.85813100	-1.78542400	0.64958400
	H	2.79347800	-0.14903900	-0.08308600
	O	-1.67836100	-2.13979300	-0.34349500
	H	-2.07421600	1.00389400	-1.06695100
INT2--->TS15--->INT7--->TS17--->INT8--->TS18---> $CH_3COCH_2COOH+CH_3$				
	C	-3.37982900	-0.13190900	-0.03207600
	H	-3.62649800	-0.86333700	0.73765700
	H	-3.43737800	-0.63076500	-1.00175700
	H	-4.12676600	0.66237000	-0.01156100
	C	-1.98806800	0.44632200	0.19995400
	H	-1.70247200	1.16769000	-0.56647500
	C	-0.94213300	-0.64227800	0.27279400
	H	-0.30910700	-0.65302300	-1.03219900
TS17	C	0.52339000	-0.13756100	-0.07866300
	O	0.76340700	1.04716600	-0.23501100
	O	1.43602700	-1.10044600	0.12228300
	C	2.79238900	-0.66212200	0.02083600
	H	3.00509500	0.09250100	0.77836300
	H	3.39600400	-1.55038500	0.18548900
	H	2.98479700	-0.24284000	-0.96830100
	O	-1.09576300	-1.76442800	0.70591700
	H	-1.93948900	0.97879100	1.15612400
	C	-2.88624300	0.18758100	1.27845300
	H	-3.96657900	0.23768200	1.38444800
	H	-2.39371400	1.15532100	1.35173700
	C	-2.31900900	-0.76394200	0.22712800
	H	-3.01677100	-1.58111500	0.04120400
	C	-1.09168500	-1.32061300	0.97567700
	H	-0.80350700	-2.32190000	0.64462300
TS18	C	0.08515800	-0.37481100	0.77695900
	O	0.32523600	0.58886800	1.44797400
	O	0.79457900	-0.72893900	-0.30551100
	C	1.88404500	0.13604900	-0.63526300
	H	2.59345800	0.17850200	0.19127300
	H	2.34751900	-0.29452900	-1.51872000
	H	1.51848300	1.14229400	-0.84278200
	O	-1.49572800	-1.37306200	2.31648600

	H	-2.40945700	-0.45474100	2.25783300
	H	-2.07661200	-0.29072300	-0.72688800

Table S4. T1 diagnostics of transition states and products for the reactions of MC + OH.

Species	T1 Diagnostics	Species	T1 Diagnostics	Species	T1 Diagnostics
TS1	0.0194	TS11	0.0252	INT3	0.0143
TS2	0.0219	TS12	0.0174	INT4	0.0189
TS3	0.0229	TS13	0.0203	INT5	0.0173
TS4	0.0255	TS14	0.0222	INT6	0.0175
TS5	0.0262	TS15	0.0183	INT7	0.0162
TS6	0.0260	TS16	0.0239	INT8	0.0161
TS7	0.0247	TS17	0.0188	PC1	0.0200
TS8	0.0165	TS18	0.0244	PC2	0.0244
TS9	0.0210	INT1	0.0148	PC3	0.0263
TS10	0.0242	INT2	0.0160	PC4	0.0296

Table S5. (1) The calculated rate constants of H-atom abstraction reactions of MC via OH radical in this work, units are s^{-1}, cm^3 and cal mol^{-1}. **(2)** The calculated thermodynamic data of PC1 (MB2DMJ) and PC2 (MB2D4J).

(1) The rate constants of H-atom abstraction reactions of MC			
Reactions	A	n	E_a
MB2D+OH=MB2D4J+H_2O	1.10E+22	-2.39	10360
DUP			
MB2D+OH=MB2D4J+H_2O	7.66E+14	-0.57	2858
DUP			
MB2D+OH=MB2DMJ+H_2O	1.38E+20	-2.02	10204
DUP			
MB2D+OH=MB2DMJ+H_2O	4.40E+11	0.10	819
DUP			

(2) The calculated thermodynamic data of MB2DMJ and MB2D4J								
MB2DMJ	C	5H	7O	20	0G	300.00	5000.00	1300.00 1
1.32241018E+01	2.15290960E-02	-8.16848309E-06	1.43407198E-09	-9.54123853E-14				2
-2.34464352E+04	-3.98071655E+01	4.23977381E+00	4.30469091E-02	-2.59279524E-05				3
6.91647854E-09	-4.52603336E-13	-2.05928398E+04	7.88522896E+00					4
MB2D4J	C	5H	7O	20	0G	300.00	5000.00	1300.00 1
1.39393132E+01	2.38524664E-02	-9.11438065E-06	1.60768000E-09	-1.07303796E-13				2
-3.03568646E+04	-4.59747822E+01	7.45040869E-01	5.48779412E-02	-3.38680597E-05				3
8.63779961E-09	-3.70004733E-13	-2.61174956E+04	2.42526536E+01					4

Fig. S1. H-abstraction reactions and hydroxyl addition reactions. The red lines represent the dominant channels which are included in the main text. Energies were calculated at the QCISD(T)/CBS//M062x/6-311++G(d,p) level (outside brackets) and CBS-QB3 level (in brackets), respectively. All energies are relative to that of MC + OH with the unit of kcal mol^{-1}.

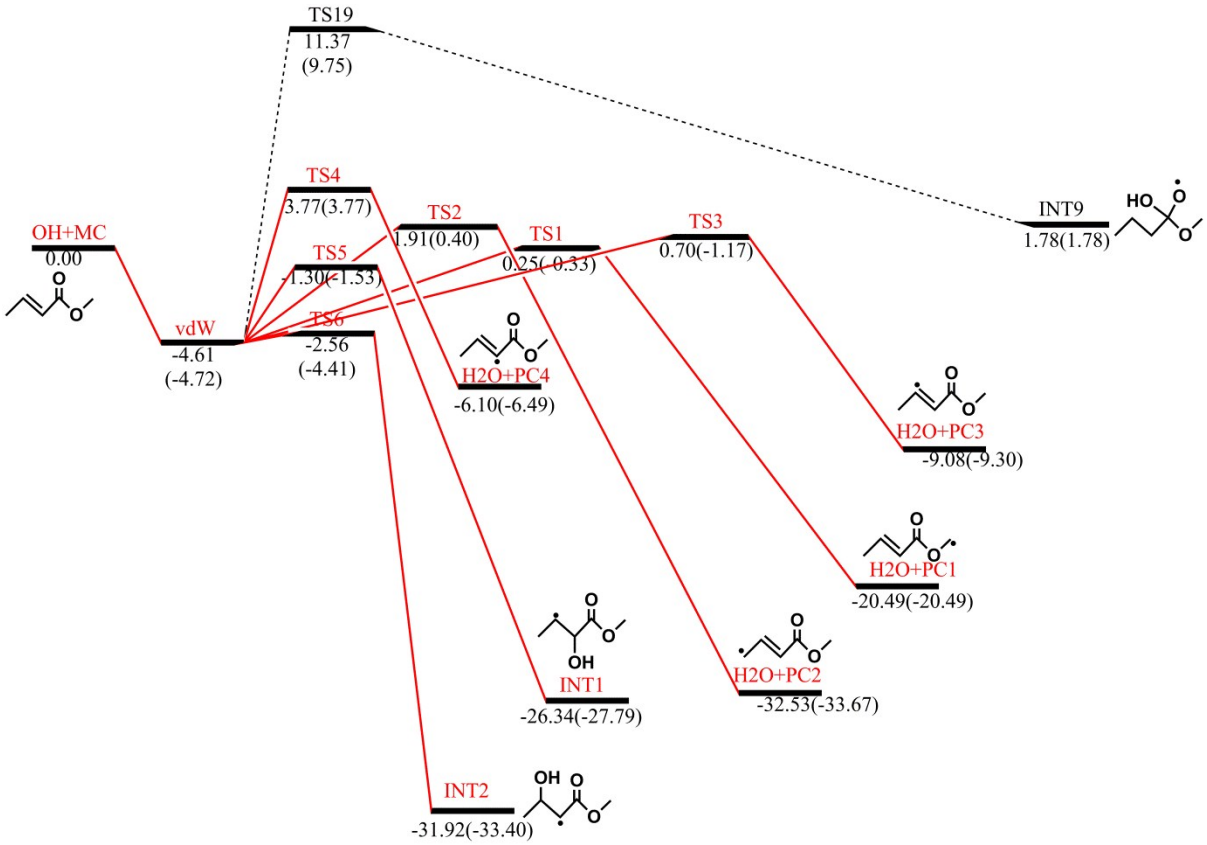


Fig. S2. Potential energy surface of detailed dissociation channels for INT1. The red lines represent the dominant channels which are included in the main text. Energies were calculated at the QCISD(T)/CBS//M062x/6-311++G(d,p) level (outside brackets) and CBS-QB3 level (in brackets), respectively. All energies are relative to that of MC + OH with the unit of kcal mol^{-1}.

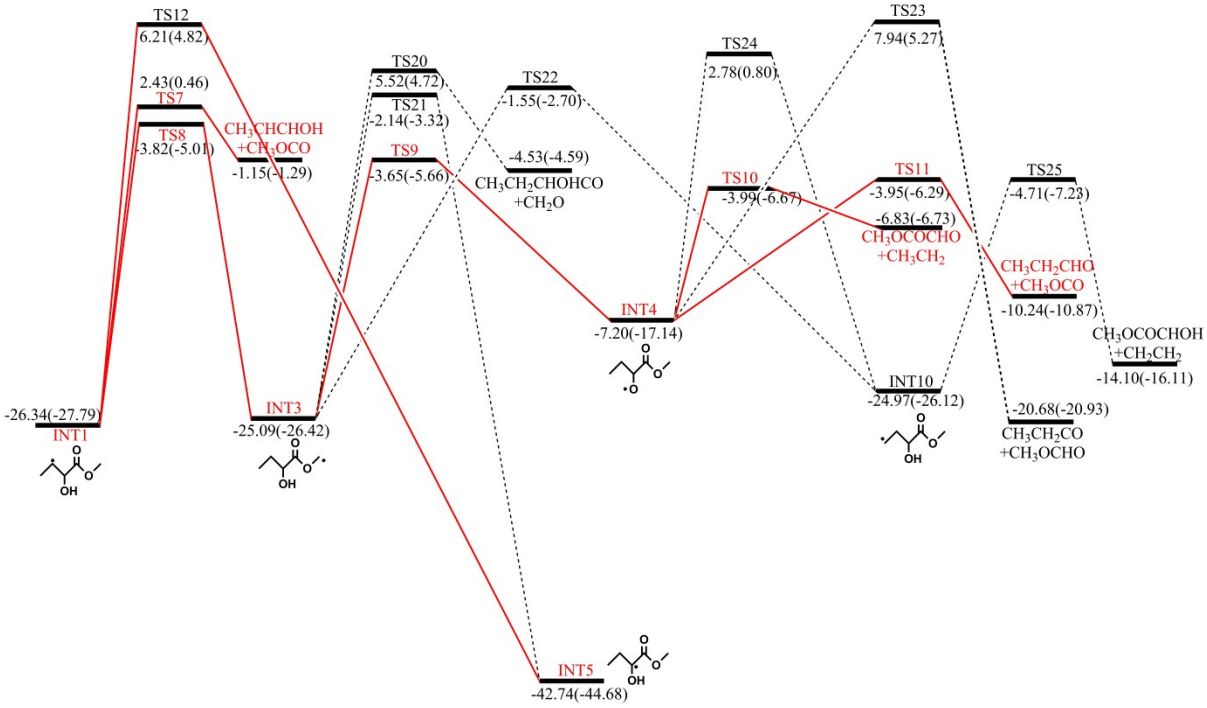


Fig. S3. Potential energy surface of detailed dissociation channels for INT2. The red lines represent the dominant channels which are included in the main text. Energies were calculated at QCISD(T)/CBS//M062x/6-311++G(d,p) level (outside brackets) and CBS-QB3 level (in brackets), respectively. All energies are relative to that of MC + OH with the unit of kcal mol^{-1}.

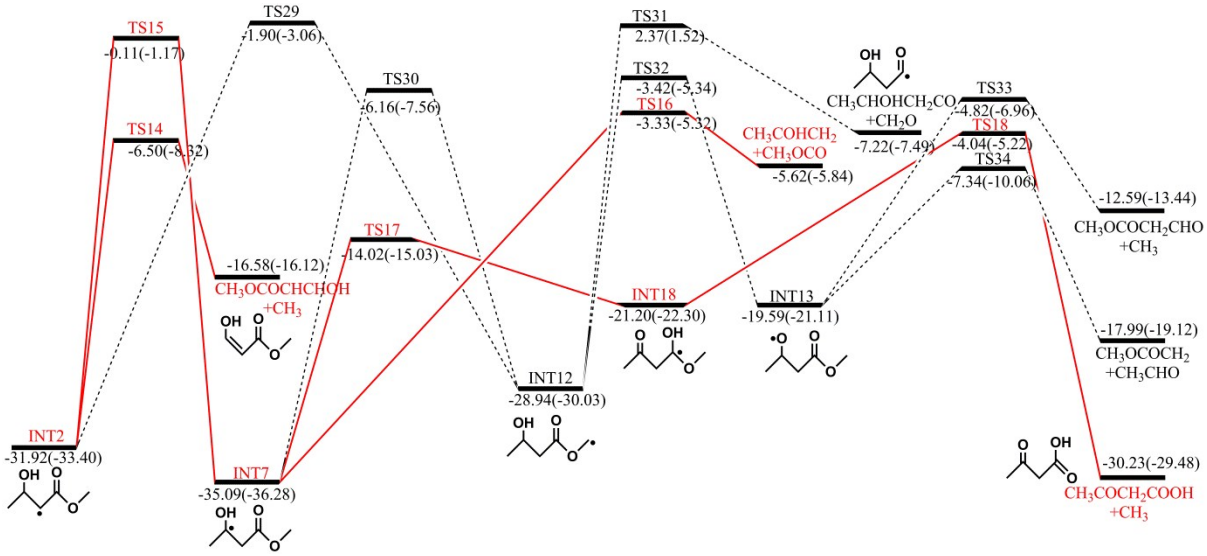


Fig. S4. Potential energy surface of detailed dissociation channels for INT5. The red lines represent the dominant channels which are included in the main text. Energies were calculated at QCISD(T)/CBS//M062x/6-311++G(d,p) level (outside brackets) and CBS-QB3 level (in brackets) respectively. All energies are relative to that of MC + OH with the unit of kcal mol^{-1}.

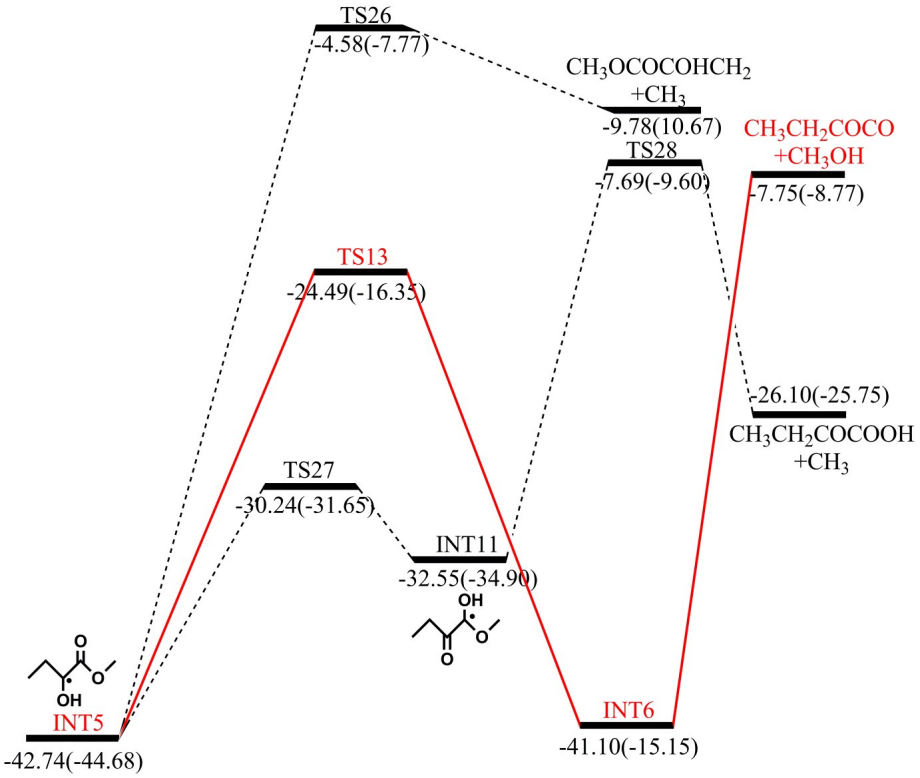


Fig. S5. Optimized geometries of transition states (TS5 – TS18) calculated at M062x/6-311++ G(d,p) level. The unit of bond length is Angstrom.

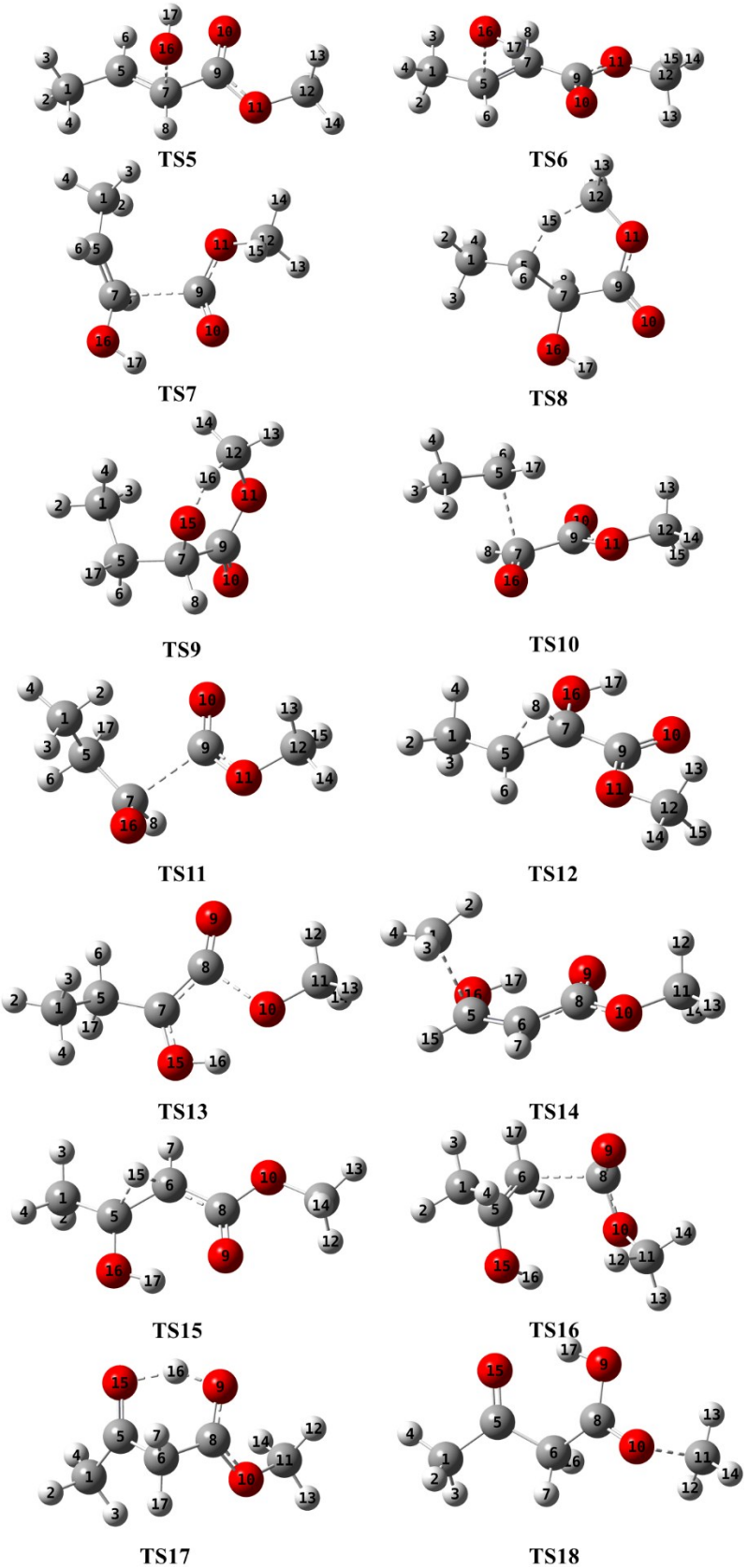


Fig. S6. Minimum energy path along the C-O reaction coordinate for the reaction of INT6 to CH_3CH_2COCO + CH_3OH. The values of relative energies were calculated at the QCISD(T)/CBS//M062x/6-311++G(d,p) level. Dash line in the plot indicates the relative dissociation energy of CH_3CH_2COCO + CH_3OH.

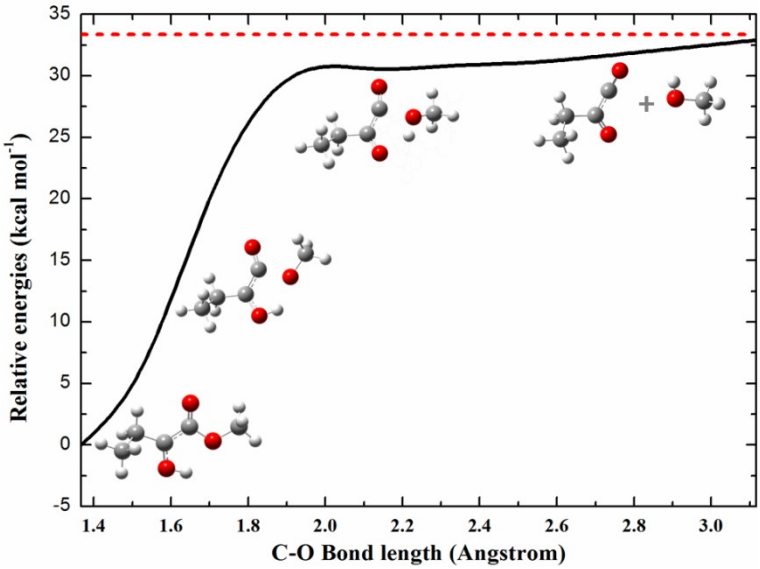


Fig. S7. Mole fraction profiles of CH_3CHO, CH_3OH, acrolein (C_3H_4O) and MePropenoate ($C_4H_6O_2$) from the experimental measurements (symbols) and modeling simulations by the Gaïl model[1] (dash lines) and by the resent revised model (symbols with solid lines). The experiment was conducted in a JSR with 750 ppm of MC, ϕ=0.375, P=1 atm, τ=0.07s.

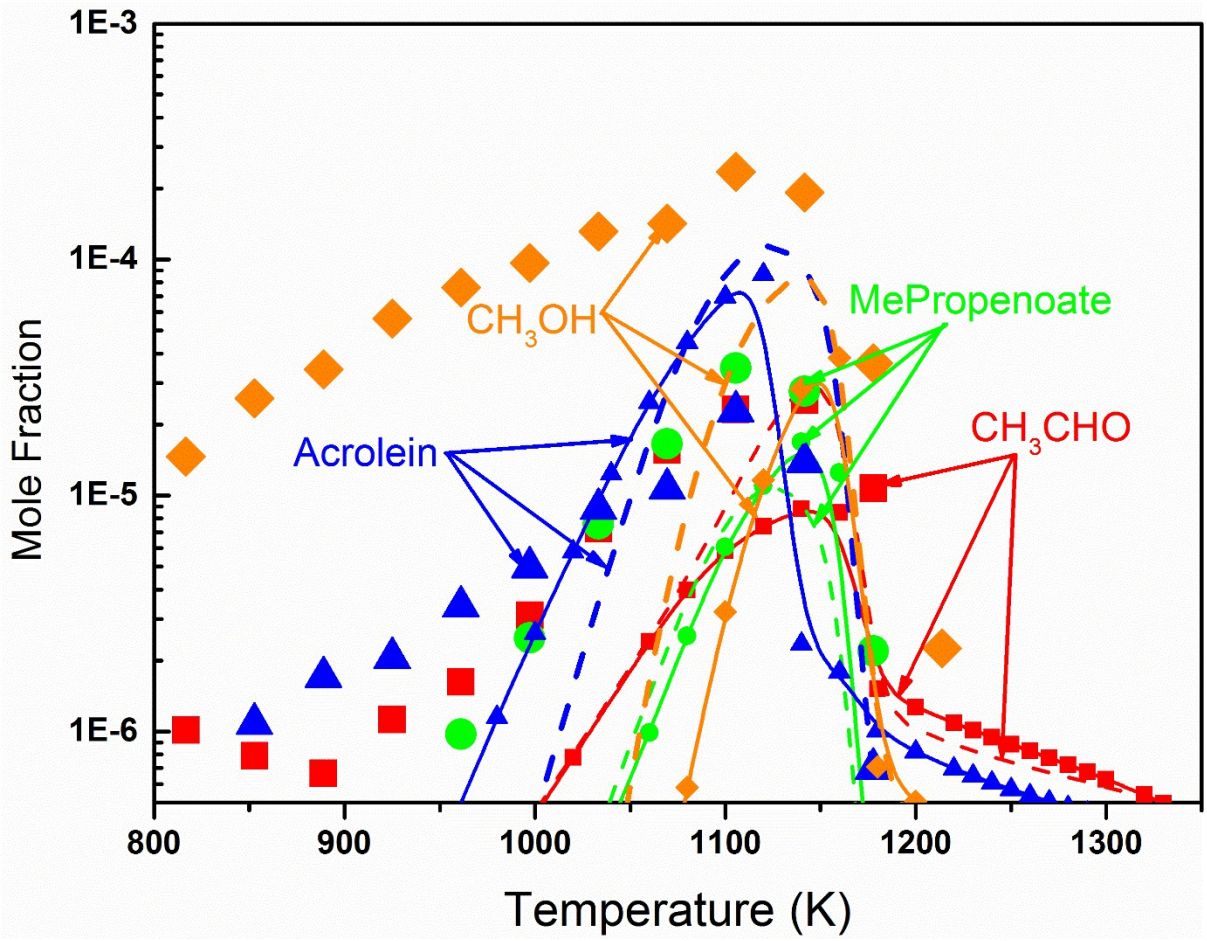
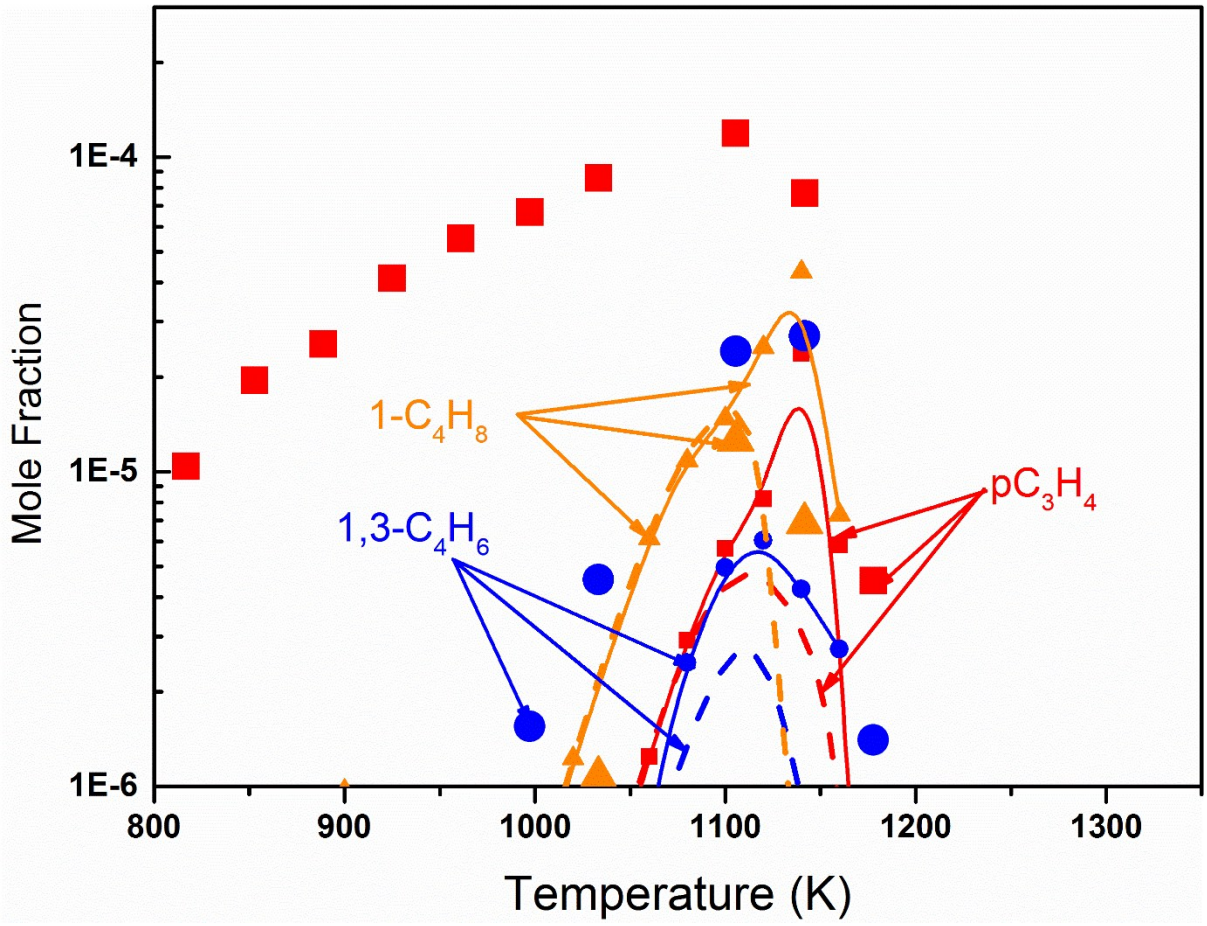


Fig. S8. Mole fraction profiles of 1-$C4H_8$, pC_3H_4 and 1,3-C_4H_6 from the experimental measurements (symbols) and modeling simulations by the Gaïl model[1] (dash lines) and by the present revised model (symbols with solid lines). The experiment was conducted in a JSR with 750 ppm of MC, ϕ=0.375, P=1 atm, τ=0.07s.



Reference

1. S. Gaïl, S. M. Sarathy, M. J. Thomson, P. Diévart and P. Dagaut, *Combust. Flame*, 2008, **155**, 635-650.