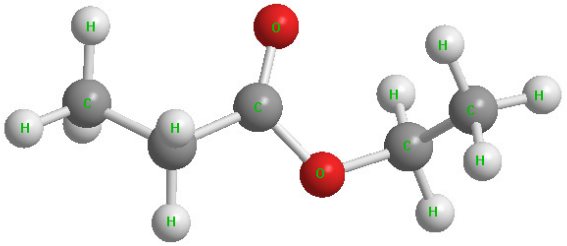
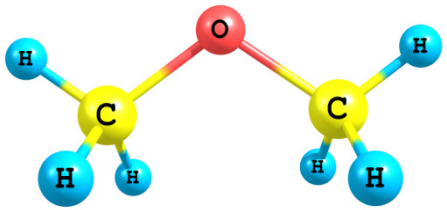
Thermochemistry and Kinetics of Bioalcohols and Bioesters as Fossil Fuel Alternatives. Ab Initio and DFT Studies

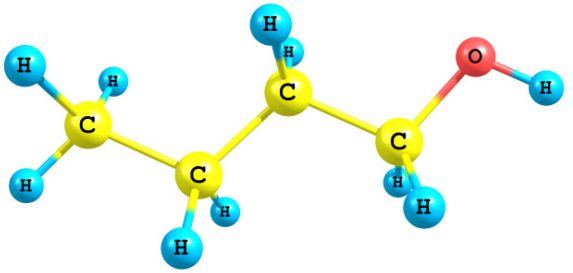
Ahmed M. El-Nahas,

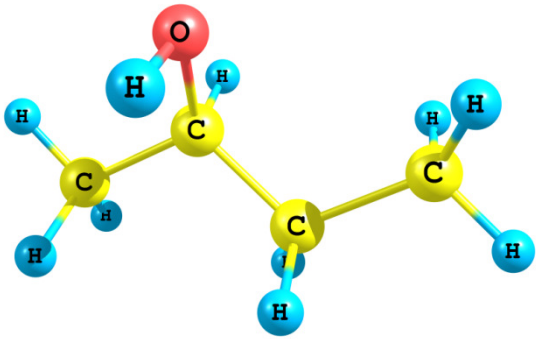
Professor of Physical Chemistry(Computational Chemistry)

Chemistry Department, Faculty of Science, El-Menoufia University, Shebin El-Kom, Egypt









Current Situation Regarding Energy

Increasing population



Increasing demand for energy

Increasing cost

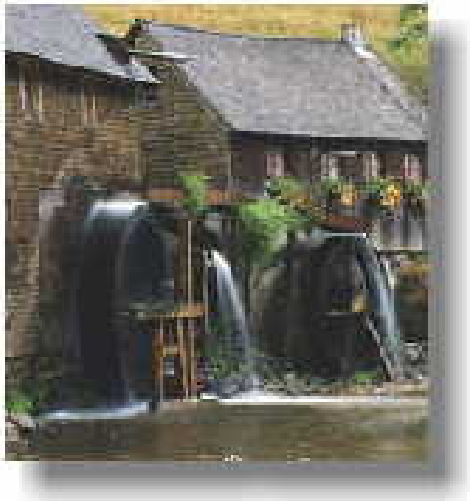
Depletion of Oil reserves

Pollution

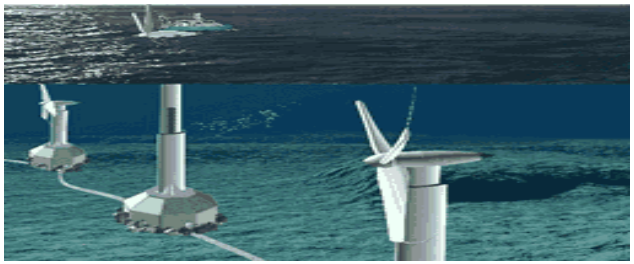
Political conflict

Global warming

Renewable Energy







Hydropower Solar Energy Wind Power

Biomass



Biofuel





1. Energy independence
2. Environmentally friendly.
3. Domestic.
4. Rural development.

- **Over 600 million tons Rice husk are produced per year.**
- **In Egypt, 16 million tons of crops residues per year.**
- **Jåpan has plan to 1.8 million KL biofuel by 2020.**



Biofuel Generations



First Generation

Food crops (cereal, oil, suga

Sugar beets





Rapeseed

Soybeans – Tofu, or Diesel?



corn



camelina

Second Generation

Non-food crops & residue of food part of food crops); Switch grass, jatropha

Third Generation

Algae

- The algae oil can then be converted to **biodiesel**; the algae's carbohydrate content can be fermented into **bioethanc and biobutanol**
- Algae can produce up to 300 times more oil per acre than conventional crops, such as rapeseed, palms, soybeans, or jatropha



Switch grass



jatropha



Algae

Biofuel

•**Biofuel** is any fuel that is derived from biomass.

Biogasoline

Biodiesel

Alcohols,
ethanol, Ethanol, Propanol, Butanol, and Pentanol

Monoesters of fatty acids,
Methyl, ethyl,
propyl, isopropyl

Ethers;
DME, MTBE

Gasoline varies from 4 to 12 hydrocarbons long

Diesel fuel is 10 to 20 carbons long, which is close to the same size as plant oils (14 to 18 carbons in length).

Ethanol is currently the most used biofuel as an alternative to gasoline in the transportation sector, with 83.1 billion liters produced in 2012 in Brazil and North America [1].

1 Energy Policy Network for the 21st Centry. Renewables 2013, Global Status Report.

Various Production Types of Bioethanol



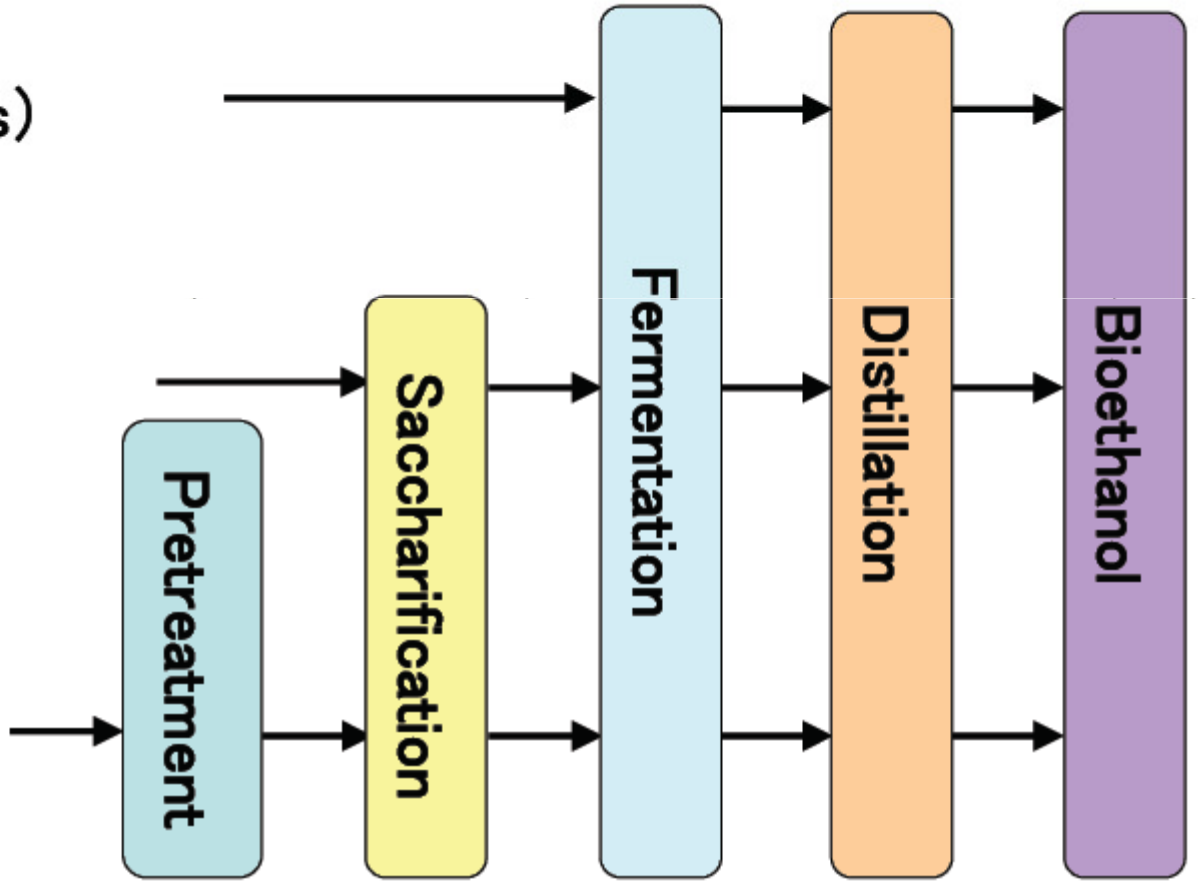
Sugarcane（Molasses）



Wheat, Corn（Starch）



Wood（Cellulose,
Hemicellulose）



Bioethanol vs. Biobutanol

Lower alcohols (biomethanol and bioethanol) are:

1. **hygroscopic**
2. **have low energy content but still in use .**

Higher alcohols offer some advantages as gasoline substitutes because of

1. **low toxicity,**
2. **higher energy density,**
3. **lower hygroscopicity**

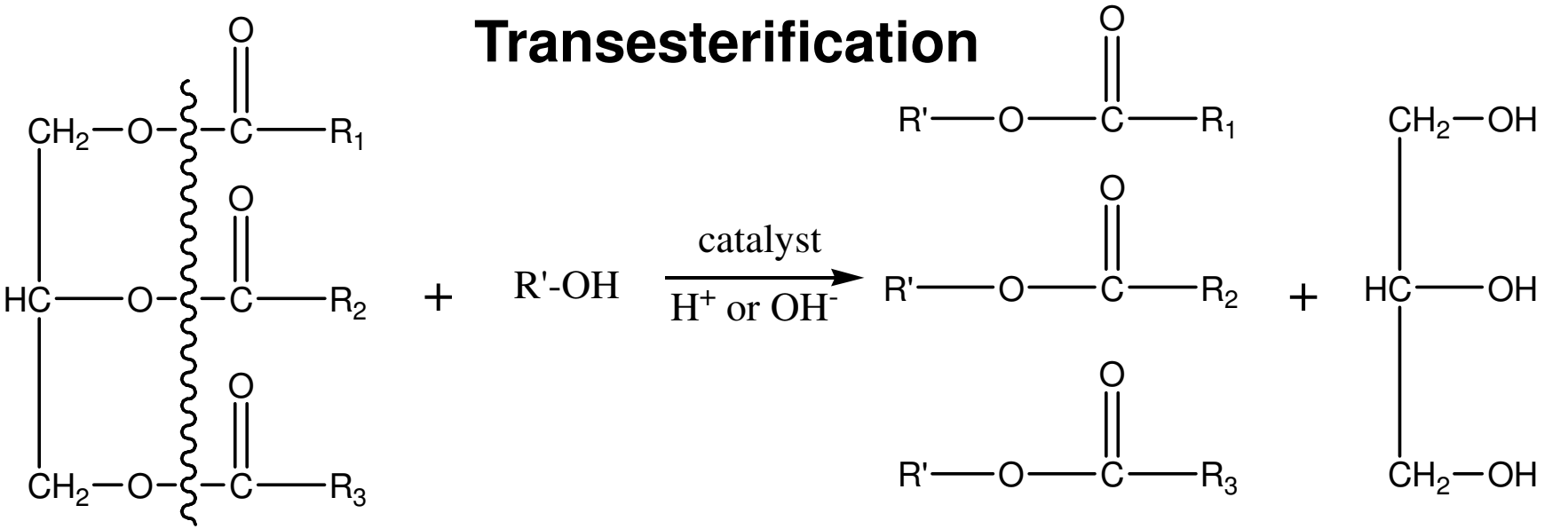
1-butanol vs. 2-butanol and isobutanol

1-butanol is produced with low yield; the fermentation process is poisoned by 1-buatnol. Yield 14 g/L increased to 18 g/L by different strains.

2-buatnol is formed with high yield.

Biodiesel Fuel

Transesterification



Triglyceride (Oil/fact)

R'=CH_3 or C_2H_5, $(CH_3)_2CH$, or others, but small alcohol is easier

Ester/Biodiesel

Glycerol

- **Acid catalysis is slower than base by 4000 times but good for low cost feedstock of high FFA**
- **It helps in esterification and transesterification**
- **Enzyme are expensive**

QUEST FOR COMPUTATIONAL QUANTUM CHEMISTRY

What would we like to get from Computational Chemistry ?

What would we like to get from Computational Chemistry ?

- Determination of accurate thermochemical properties of free radicals is of great importance in many branches of chemistry, in particular atmospheric and combustion modeling.

- Detailed chemical kinetic mechanisms are used to describe transformation of reactants to products (via Chemkin or other codes) needs thermochemical data such as enthalpies of formation, bond dissociation energies, entropies, and heat capacities.

What would we like to get from Computational Chemistry ?

- For kinetic studies and reaction mechanism, higher accuracy is needed: CCSD(T), Gn, and CBS methods.
- How about DFT??

$$k = \left(\frac{\mathrm{k}T}{h}\right) e^{\Delta S^{\ddagger}/R} \cdot e^{-\Delta H^{\ddagger}/RT}$$

Computational Methods:

CBS-QB3

All systems

- **Geometry optimization and frequencies**: B3LYP/6-311G(d,p)
- **Energy and CBS extrapolation**:
- MP2/6-311++G(2df,2p)
- MP4(SDQ)/6-31+G(d,p)
- CCSD(T)/6-31+G(d)
- Extrapolation to CBS

EP.MB

IPB

BMK/6-31+G(d,p) (L1)

BMK/6-311++G(2d,2p)// BMK/6-31+G(d,p) (L2)

BMK/6-311+G(2d,2p)// BMK/6-31+G(d,p) (L3)

isobutanol

CBS-QB3, BMK, BB1K/6-311++G(2d,2p)

B3LYP/6-31+G(d,p)

BMK/6-31+G(d,p); BMK/6-311++G(2d,2p)

2-butanol

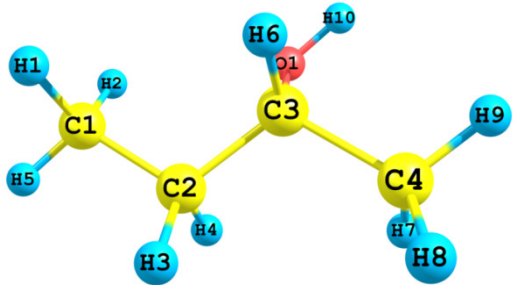
CBS-QB3,MP2/6-311++G(2d,2p); CCSD(T)/MP2/6-311++G(2d,2p)/MP2/6-311++G(2d,2p)

B3LYP, BHandHLYP, BMK, MPW1K,MPWB1K, MPW1B95,LC-ωPBE/6-311++G(2d,2p)

Procedures (for alcohols & esters):

Geom. Opt & freq. calcn.

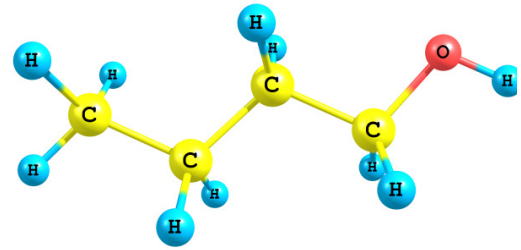
IRC, SP



Enthalpies of formation:

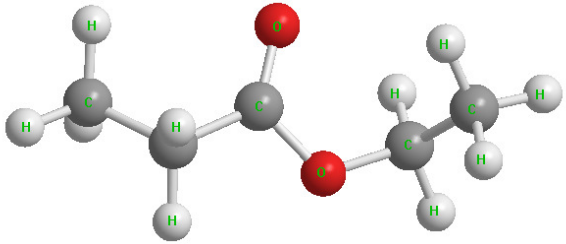
From atomization energies

From isodesmic reactions



$$EtC(O)O\dot{C}HCH_3 + CH_3OCH_3 \rightarrow EtC(O)OCH_2CH_3 + CH_3O\dot{C}H_2 \quad (7)$$

$$EtC(O)O\dot{C}HCH_3 + CH_3CH_3 \rightarrow EtC(O)OCH_2CH_3 + CH_3\dot{C}H_2 \quad (8)$$



Pyrolysis (uni-) and H-abstraction and bimolecular Reactions

Rate constant calculations

TABLE I. Changes in electronic energies, standard enthalpies, and free energies for the successive reactions $H^+(H_2O)_n+H_2O\rightarrow H^+(H_2O)_{n+1}$ using model chemistries.

	Present work				Literature Computational			
n	CBS-QB3	CBS-APNO	G2	G3	CCSD-TZ2P[a]	CCSD-pVTZ[b]	CCSD-DZP[c]	CCSD-TZ2P
					ΔE_e			
1	−33.7	−34.4	−33.6	−33.8	−34.42	−34.96	−36.3	−33.0
2	−23.7	−23.8	−23.4	−23.6	−23.95	−23.96		
3	−19.5	−19.9	−19.8	−20.1	−20.28	−20.26		

			Computational		Experimental	
n			CCSD-TZ2P[a]	CCSD-pVTZ[b]	Ref. 17	Ref. 15
			ΔH°			
1	−33.9	−34.2	−33.2	−33.4	−35.06	−35.30	−31.8	−31.6
2	−21.4	−21.3	−21.3	−21.4	−20.57	−21.72	−19.0	−19.5
3	−17.2	−17.9	−17.9	−18.1	−17.67	−18.24	−17.6	−17.5

			Computational		Experimental	
			MP2[d]	SCF/DZ+p[e]	Ref. 17	Ref. 15
			ΔG°			
1	−25.1	−25.8	−25.7	−25.9	−26.1	−26.9	−24.6	−24.3
2	−14.5	−13.4	−13.7	−13.8			−12.8	−13.0
3	−8.5	−10.7	−10.2	−10.5			−9.5	−9.3

[a]MCCM-UT-CCSD//MP2/TZ2P (Ref. 36).
[b]MCCM-UT-CCSD//MP2/cc-pVTZ (Ref. 36).
[c]Reference 27.
[d]MP2/6-311++G(d,p) (Ref. 29).
[e]SCF/DZ+p with SAC correction (Ref. 80).

TABLE 1. Reaction Energies, Barrier Heights, and Bond Energies (in kcal/mol).

Method	V_f^a	V_r^b	ΔE	D_e(C–H)	D_e(H–H)	Ref.
***N*⁷ methods**						
W1	9.6	15.7	-6.1	103.5[c]	109.6[c]	18
G3SX//B3LYP/6-31G(2df,p)	9.8	15.9	-6.1	103.7	109.8	p.w.[d]
G3SX(MP3)//B3LYP/6-31G(2df,p)	10.0	16.2	-6.3	103.6	109.9	p.w.
G3X//B3LYP/6-31G(2df,p)	9.7	16.4	-6.7	103.3	110.0	p.w.
Ext-CCSD(T)aug-cc-pV*X*Z (*X*=3, 4)	9.6	15.8	-6.1	103.5	109.6	p.w.
CCSD(T)/aug-cc-pVQZ//QCISD/MG3	9.6	15.6	-6.0	103.1	109.2	p.w.
G3S//MP2(full)/6-31(d)	9.9	15.7	-5.8	103.8	109.6	p.w.
CCSD(T)/aug-cc-pVTZ//QCISD/MG3	9.6	15.4	-5.9	102.7	108.5	p.w.
CBS-QB3//QCISD/MG3	9.5	16.2	-6.7	104.0	110.7	p.w.
CBS-QB3//B3LYP/6-31G(d′)	9.4	16.1	-6.7	104.0	110.7	p.w.
CBS-Q//QCISD/MG3	9.4	16.2	-6.8	103.8	110.6	p.w.
CBS-Q//MP2/6-31G(d′)	9.0	15.7	-6.7	103.9	110.5	p.w.
MCG2/3//QCISD/MG3	9.7	16.5	-6.8	104.2	111.0	p.w.
MCG3/3	10.0	16.9	-6.9	104.0	110.9	p.w.

The MG3 Basis set is equivalent to a 6-311++G(3d2f,2df,2p) basis for H–Si, and an improved 6-311+G(3d2f) basis for P–Ar.

N^4 methods						
BB1K/MG3S	8.7	14.5	-5.7	101.6	107.3	p.w.
BB1K/6-31+G(d,p)	8.4	14.2	-5.8	102.8	108.6	p.w.
MPWB1K/MG3S	8.7	13.9	-5.2	102.0	107.1	p.w.
MPW1K/MG3S	7.9	13.5	-5.6	99.4	104.9	p.w.
MPW1K/6-31+G(d,p)	7.7	13.4	-5.6	100.6	106.2	p.w.
B1B95/MG3S	7.0	13.5	-6.5	101.0	107.6	p.w.
MPW1B95/MG3S	7.1	12.9	-5.8	101.5	107.3	p.w.
B3LYP/cc-pVDZ	2.0	10.6	-8.6	98.8	107.4	26
B3LYP/6-31+G(d,p)	3.2	12.9	-9.7	102.0	111.7	p.w.
B3LYP/6-31G(d)	3.6	11.7	-8.1	101.7	109.8	26
B3PW91/6-31G(d)	5.0	11.2	-6.2	100.7	106.8	26

Table 2. Barriers heights (kcal/mol) calculated for the decomposition of 2-butanol to different products at CBS-QB3, CCSD(T)/6-311++G(2d,2p)//MP2/6-311++G(2d,2p), and MP2/6-311++G(2d,2p).

1-Butene	Trans-2-butene	Cis-2-butene	MeEth Carbene	MeEth ketone	Acetladehyde	Me-cyclopropane	VinylOH	Ethanol
CBS-QB3								
65.97	67.16	67.90	77.98	81.40	85.00	94.89	109.55	111.91
CCSD(T)								
64.97	66.31	67.04	76.00	83.27	86.38	93.69	109.97	112.50
MP2								
63.60	64.89	65.58	79.04	82.45	85.06	94.06	107.90	111.13

Exp. 65-67 for different alcohols.

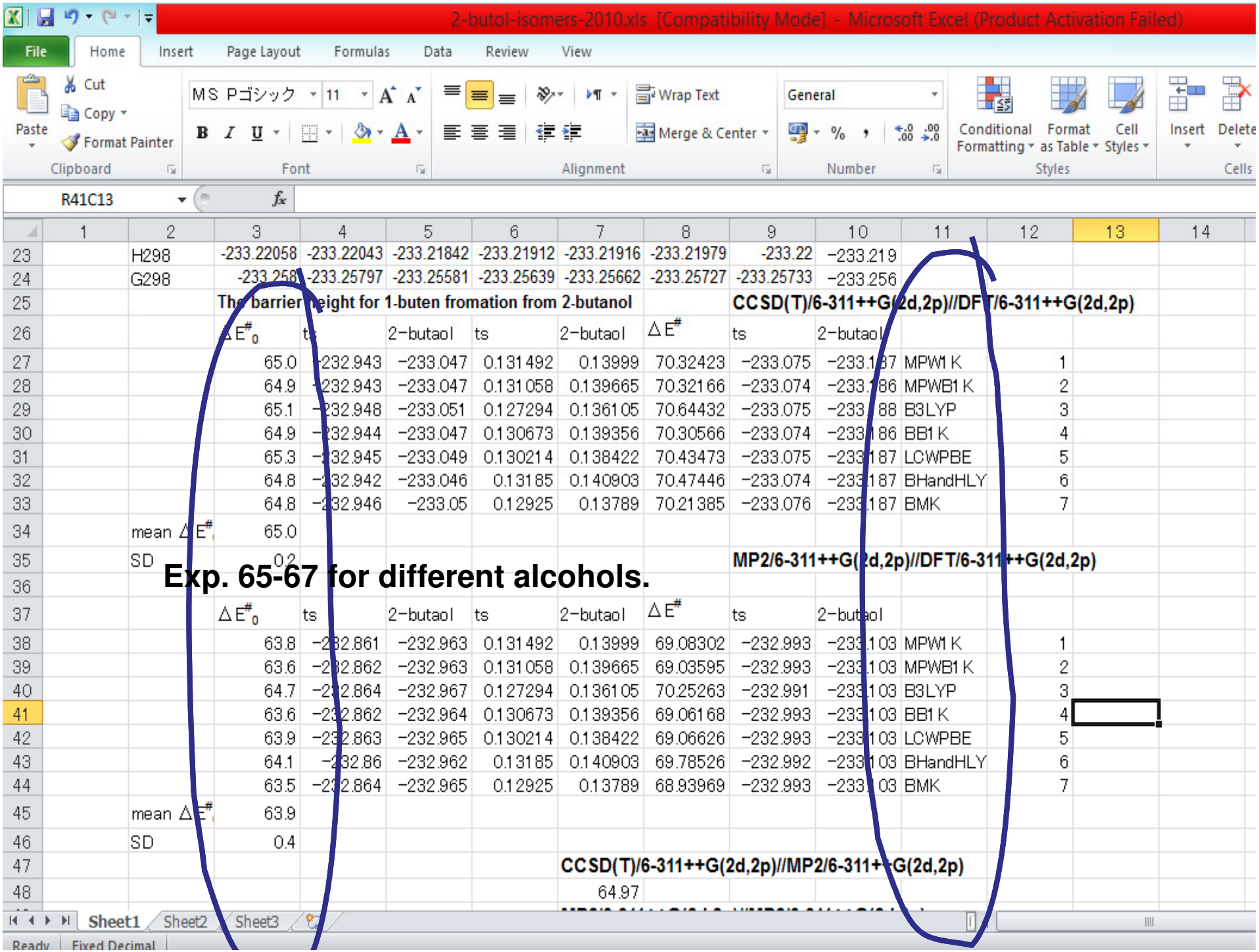
Table 2. Barrier heights ($\Delta E^{\#}_0$, kcal/mol) calculated at the MP2 and DFT methods with the 6-311++G(2d,2p) basis sets for the decomposition of 2-butanol to 1-butene and water.

MP2	B3LYP	BMK	BB1K	LC-ωPBE	MPW1B95	MPWB1K	MPW1K	BHandHLYP
63.60	59.25	66.11	65.93	67.03	62.49	66.47	67.47	68.30

Table 3. Calculated barrier heights (kcal/mol) for formation of 1-butene from 2-butanol at DFT/6-311++G(2d,2p)

Exp. 65-67 for different alcohols.

B3LYP	BMK	BB1K	LC-ωPBE	MPWB1K	MPW1K
59.25	66.11	65.93	67.03	66.47	67.47



2-butol-isomers-2010.xls [Compatibility Mode] - Microsoft Excel (Product Activation Failed)

File Home Insert Page Layout Formulas Data Review View

Cut Copy Format Painter Paste Clipboard

MS Pゴシック 11 Font

Wrap Text Merge & Center Alignment

General Number

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	1	2	3	4	5	6	7	8	9	10	11	12	13	14
23		H298	-233.22058	-233.22043	-233.21842	-233.21912	-233.21916	-233.21979	-233.22	-233.219				
24		G298	-233.258	-233.25797	-233.25581	-233.25639	-233.25662	-233.25727	-233.25733	-233.256				
25			The barrier height for 1-buten fromation from 2-butanol						CCSD(T)/6-311++G(2d,2p)//DFT/6-311++G(2d,2p)					
26			$\Delta E^{\#}_0$	ts	2-butaol	ts	2-butaol	$\Delta E^{\#}$	ts	2-butaol				
27			65.0	-232.943	-233.047	0.131492	0.13999	70.32423	-233.075	-233.187	MPW1K	1		
28			64.9	-232.943	-233.047	0.131058	0.139665	70.32166	-233.074	-233.186	MPWB1K	2		
29			65.1	-232.948	-233.051	0.127294	0.136105	70.64432	-233.075	-233.188	B3LYP	3		
30			64.9	-232.944	-233.047	0.130673	0.139356	70.30566	-233.074	-233.186	BB1K	4		
31			65.3	-232.945	-233.049	0.130214	0.138422	70.43473	-233.075	-233.187	LCWPBE	5		
32			64.8	-232.942	-233.046	0.13185	0.140903	70.47446	-233.074	-233.187	BHandHLY	6		
33			64.8	-232.946	-233.05	0.12925	0.13789	70.21385	-233.076	-233.187	BMK	7		
34		mean $\Delta E^{\#}$	65.0											
35		SD	0.2						MP2/6-311++G(2d,2p)//DFT/6-311++G(2d,2p)					
36														
37			$\Delta E^{\#}_0$	ts	2-butaol	ts	2-butaol	$\Delta E^{\#}$	ts	2-butaol				
38			63.8	-232.861	-232.963	0.131492	0.13999	69.08302	-232.993	-233.103	MPW1K	1		
39			63.6	-232.862	-232.963	0.131058	0.139665	69.03595	-232.993	-233.103	MPWB1K	2		
40			64.7	-232.864	-232.967	0.127294	0.136105	70.25263	-232.991	-233.103	B3LYP	3		
41			63.6	-232.862	-232.964	0.130673	0.139356	69.06168	-232.993	-233.103	BB1K	4		
42			63.9	-232.863	-232.965	0.130214	0.138422	69.06626	-232.993	-233.103	LCWPBE	5		
43			64.1	-232.86	-232.962	0.13185	0.140903	69.78526	-232.992	-233.103	BHandHLY	6		
44			63.5	-232.864	-232.965	0.12925	0.13789	68.93969	-232.993	-233.103	BMK	7		
45		mean $\Delta E^{\#}$	63.9											
46		SD	0.4											
47							CCSD(T)/6-311++G(2d,2p)//MP2/6-311++G(2d,2p)							
48							64.97							

Exp. 65-67 for different alcohols.

Sheet1 Sheet2 Sheet3

Ready Fixed Decimal

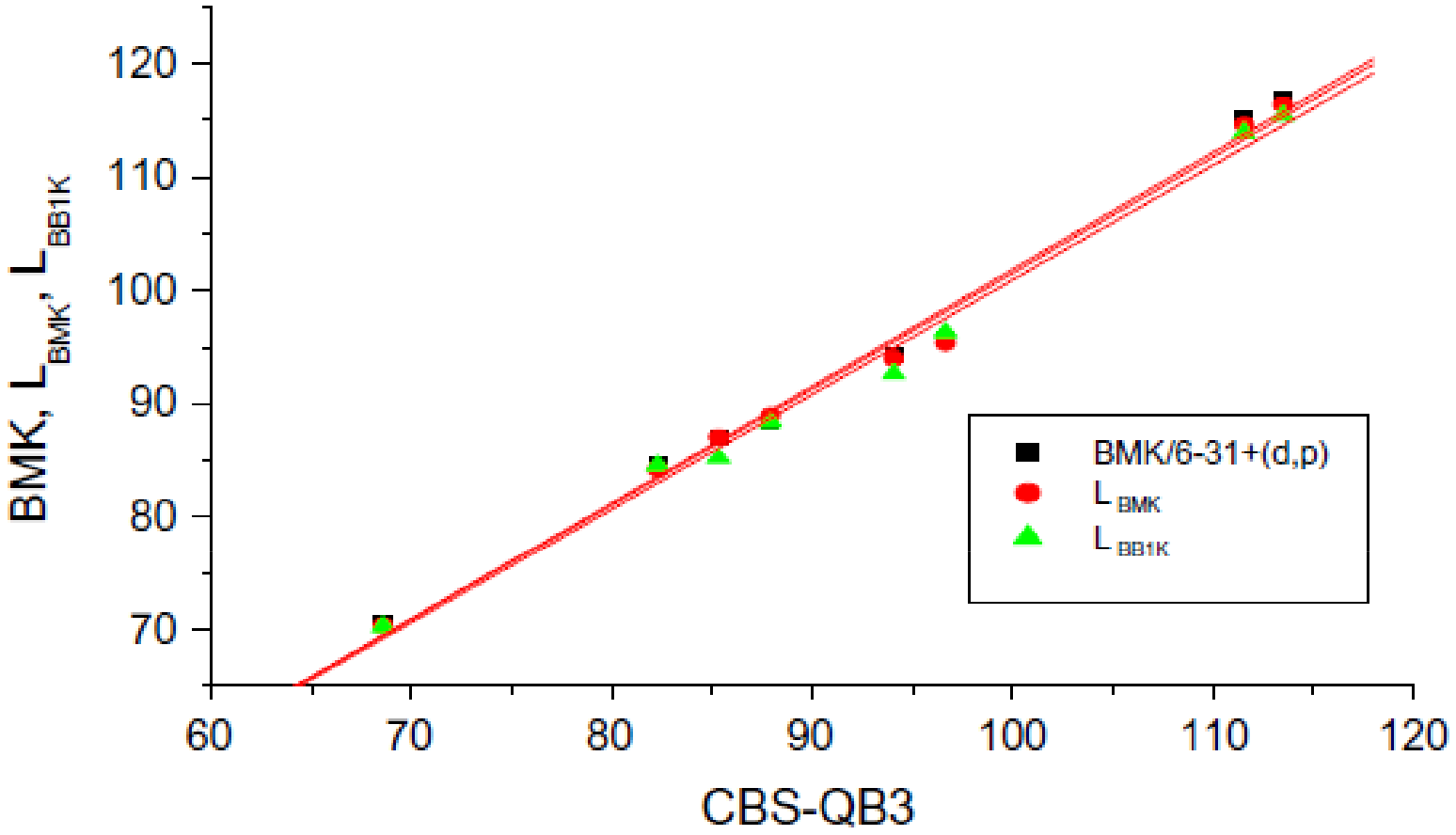


Fig. 1. Correlation between energy barriers (kcal/mol) for complex decomposition of isobutanol at CBS-QB3 against BMK/6-31+G(d,p), BMK and BB1K.

Table 1. Enthalpies of formation (kcal/mol) for alcohols and their radicals at CBS-QB3 (AE).

Species	Theory	Exp.	Species	Theory	Exp.
CH_3OH	-48.87	-48.2[a]	$(CH_3)_2CHOH$	-65.27	-65.2[a]
CH_3CH_2OH	-56.64	-56.1[a]	$CH_3CH_2CH_2CH_2OH$	-65.73	-65.7[a]
$CH_3CH_2CH_2OH$	-61.10	-60.9[a]	$CH_3CH_2CH(OH)CH_3$	-70.10	-70.5[a]
$C{\cdot}H_2CH_2CH_2OH$	-11.24		$CH_3CH_2CH_2O{\cdot}$	-8.05	-9.9[f]
$C{\cdot}H_2CH_2OH$	-5.53	-5.9[b]	$CH_3C{\cdot}HCH_2OH$	-12.94	
$C{\cdot}H_2OH$	-4.11	-3.97±0.22[c]	$(CH_3)_2CHO{\cdot}$	-11.10	-11.0±1.2[g]
$CH_3CH_2CH_2CH_2O{\cdot}$	-13.29	-14.7[d]	$(CH_3)_2C{\cdot}OH$	-23.24	
$CH_3CH_2CH_2C{\cdot}HOH$	-22.42		$CH_3CH_2O{\cdot}$	-3.38	-3.7±0.8[h]
$CH_3CH_2C{\cdot}HCH_2OH$	-17.39		$CH_3O{\cdot}$	4.53	4.1±1[i]
$CH_3C{\cdot}HCH_2CH_2OH$	-18.73		$C{\cdot}H_3$	35.482	34.82[j]
$C{\cdot}H_2CH_2CH_2CH_2OH$	-15.36		$CH_3C{\cdot}H_2$	29.833	28.8±0.5[k]
$C{\cdot}H_2CHOHCH_3$	-14.61		$CH_3CH_2C{\cdot}H_2$	25.910	23.9[j]

Table 1. Enthalpies of formation (kcal/mol) for alcohols and their radicals at CBS-QB3 (AE).

$CH_3CH_2C{\cdot}HOH$	-17.22		$(CH_3)_2C{\cdot}H$	22.4	21.5[l]
$CH_3C{\cdot}HOH$	-13.01	-14.5±3[e]	$CH_3CH_2CH_2C{\cdot}H_2$	20.68	20.1[m]
$CH_3CH_2CHOCH_3$	-16.07		$CH_3CH_2C{\cdot}HCH_3$	17.91	16[j]
$CH_3CH_2C{\cdot}OHCH_3$	-27.73				
$CH_3CH_2CHOHC{\cdot}H_2$	-19.52				
$CH_3C{\cdot}HCHOHCH_3$	-22.58				
$C{\cdot}H_2CH_2CHOHCH_3$	-20.27				

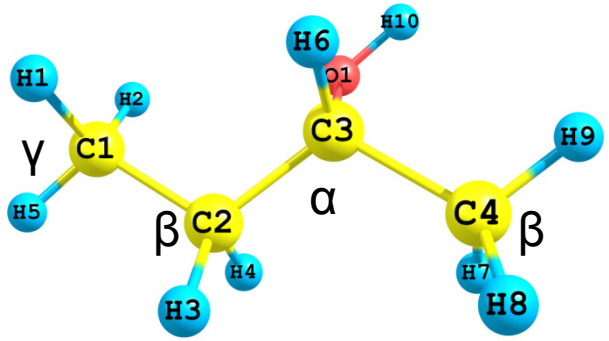
Enthalpies of Formation, AE/CBS-QB3, Isodesmic at BMK/6-311++G(2d,2p)//BMK/6-31+G(d,p)

Species	AE	Isodesmic	Exp.
$(CH_3)_2CHCH_2OH$	-67.89	-69.14	-67.83 ± 0.2 -67.61, -67.88 ± 0.4
$C^{\bullet}H_2OH$	-4.12	-5.09	-3.97±0.22
$C^{\bullet}H_3$	35.47	35.26	34.82
$(CH_3)_2C^{\bullet}H$	22.41	22.29	21.50
$(CH_3)_2C=CH_2$	-2.67	-4.32	-4.30± 1.1
$(CH_3)_2CHCHO$	-50.56	-49.77	-51.72
$CH_3CH_2CH_3$	-24.42	-25.39816	-25.02 ± 1.2
CH_2O	-27.33	-25.46	-26.05 ± 0.43
CH_3OH	-48.89	-47.81	-48.99 ±2.39l
$CH_3CH=CH_2$	5.83	4.69	4.88
H_2O	-58.21		-57.80 ± 0.01

Enthalpies of Formation, AE/CBS-QB3, Isodesmic at BMK/6-311++G(2d,2p)//BMK/6-31+G(d,p)

Species	AE	Isodesmic
$CH_3C^{\bullet}HCH_2OH$	-14.25	-12.84
$(CH_3)_2CHC^{\bullet}H_2$	19.09	16.15
$(CH_3)_2CHC^{\bullet}HOH$ cis	-24.24	-24.39
$(CH_3)_2CHC^{\bullet}HOH$ trans	-23.79	-23.93
$(CH_3)_2C^{\bullet}CH_2OH$	-22.56	-22.78
$^{\bullet}CH_2(CH_3)CHCH_2OH$	-17.76	-18.42
$(CH_3)_2CH\ CH_2O^{\bullet}$	-14.94	-16.10

Decomposition pathways



1. Simple bond fission followed by by β-scission

2. Complex decomposition

1-Butene formation

2-Butene formation

Carbene formation

Methy ethyl ketone formation

Ethene formation

Acetaldehyde formation

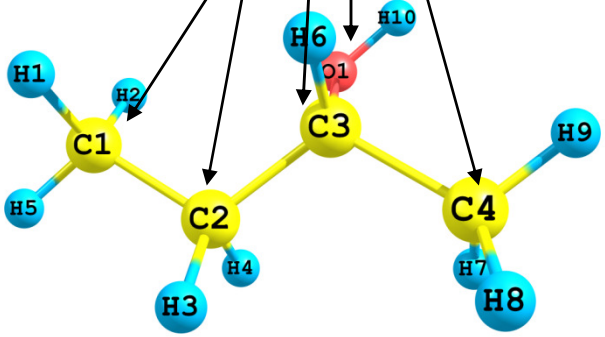
Methyl cyclopropane formation

Vinyl alcohol formation

Stability of free radicals

Table 1. the relative energies of radicals derived from 2-butanol at CBS-QB3.

Radical	ΔE_0 (kcal/mol)
$CH_3CH_2CHO{\bullet}CH_3$	0
$CH_3C{\bullet}HCHOHCH_3$	-6.90
$CH_3CH_2CHOHC{\bullet}H_2$	-3.76
$CH_3CH_2C{\bullet}OHCH_3$	-11.91
$C{\bullet}H_2CH_2CHOHCH_3$	-4.48



How many sigma_X-Y can resonate with the radical centers?

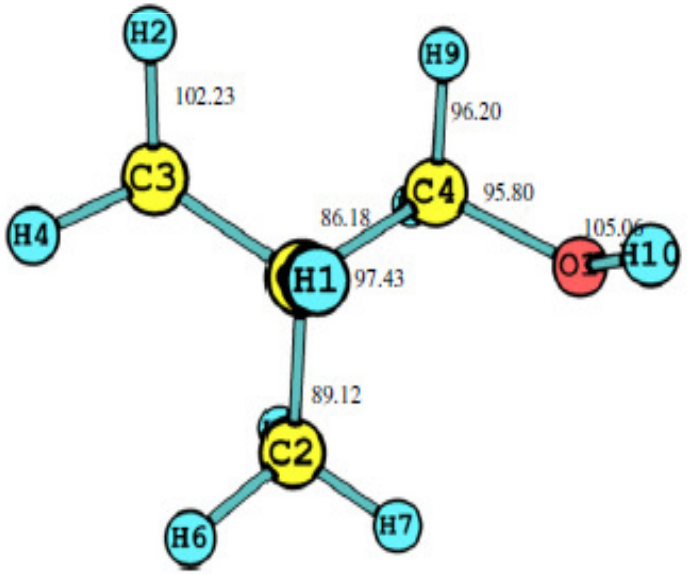


Fig. 2. Bond dissociation energies of isobutanol (kcal/mol) at CBS-QB3 level.

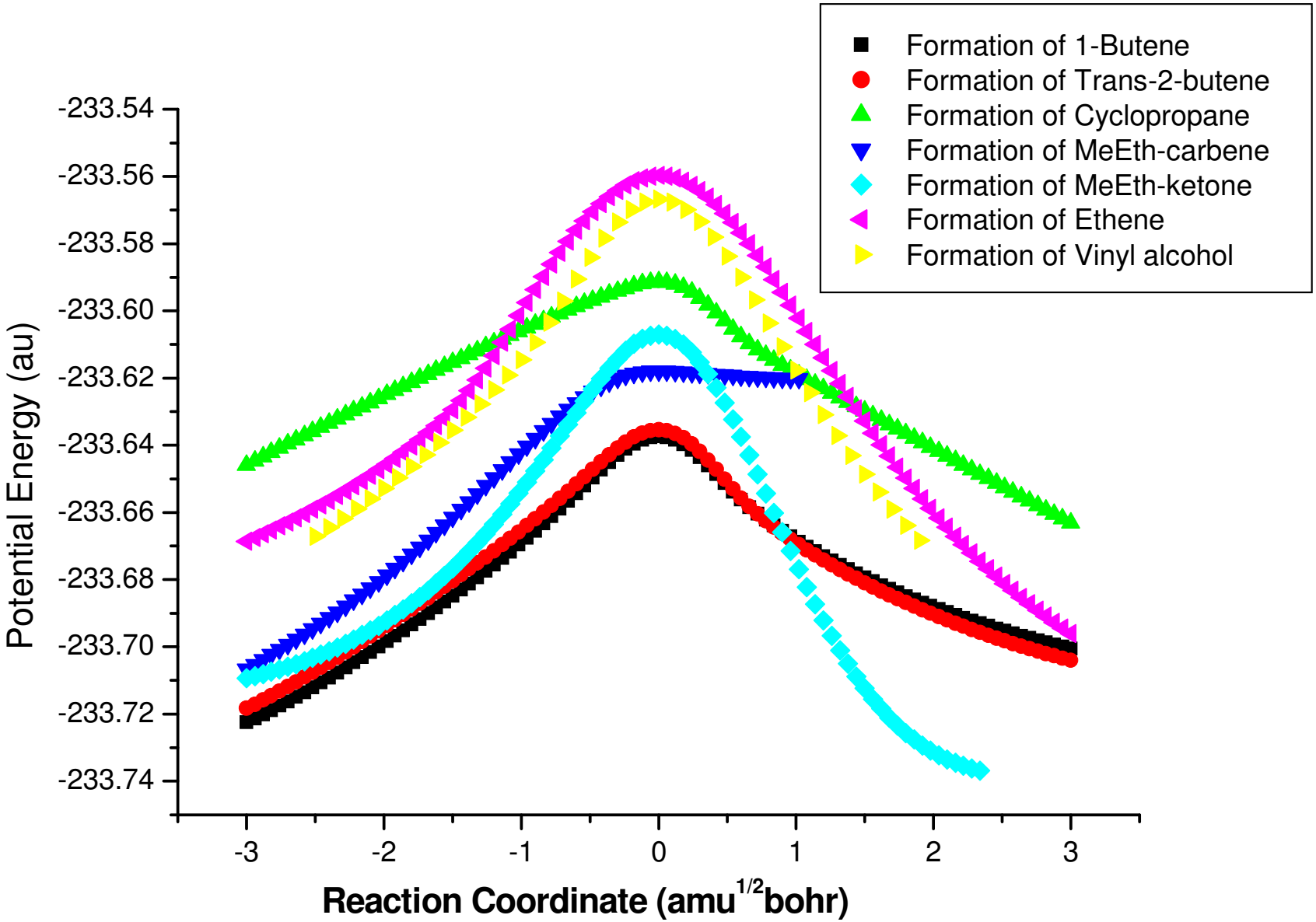
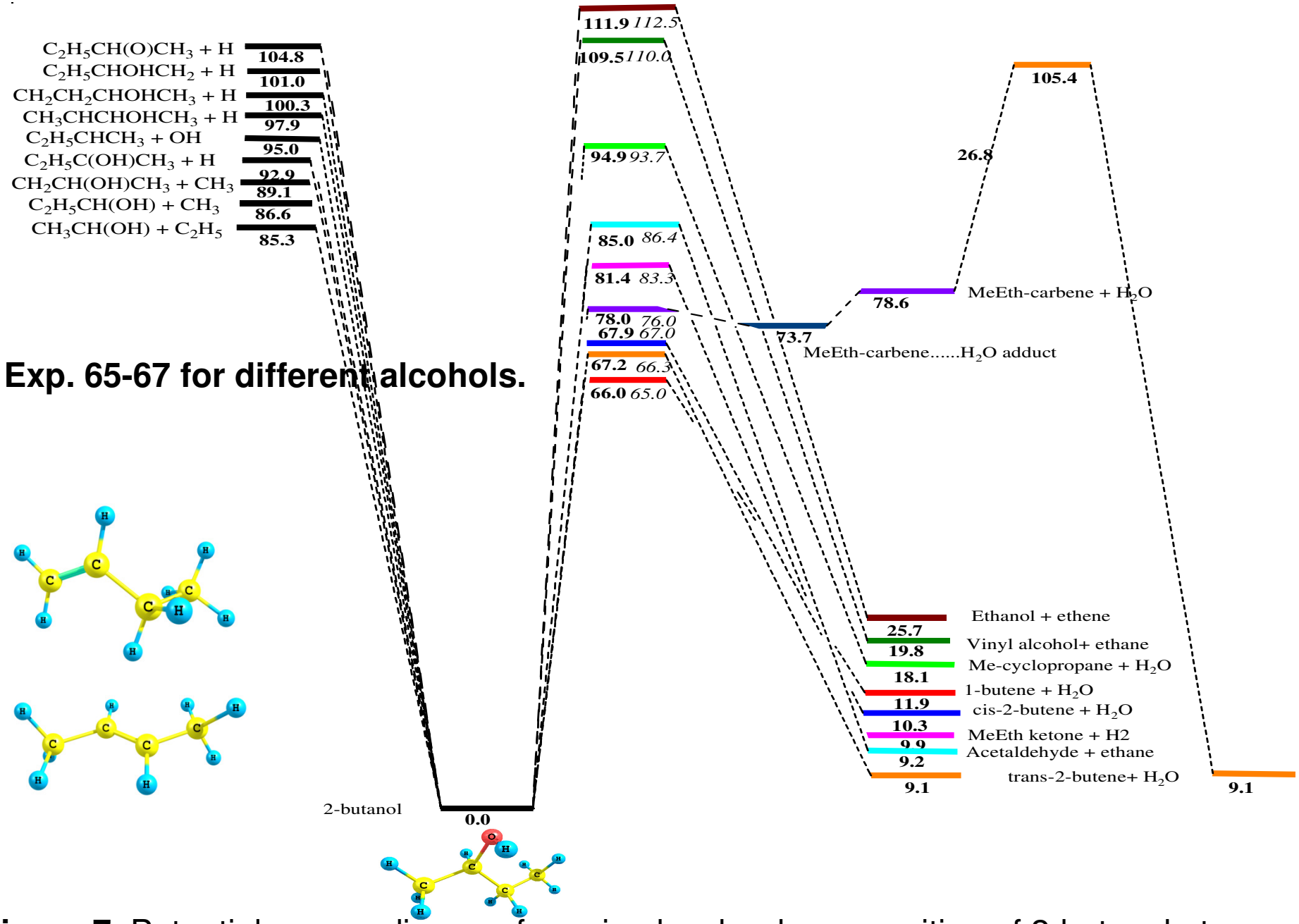


Figure xx: Potential energy profile along MEP from the IRC calculation of 2-butanol

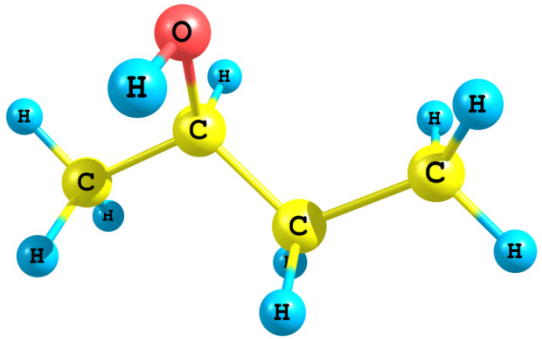
Decomposition pathways



Exp. 65-67 for different alcohols.

Figure 7. Potential energy diagram for unimolecular decomposition of 2-butanol at CBS-QB3

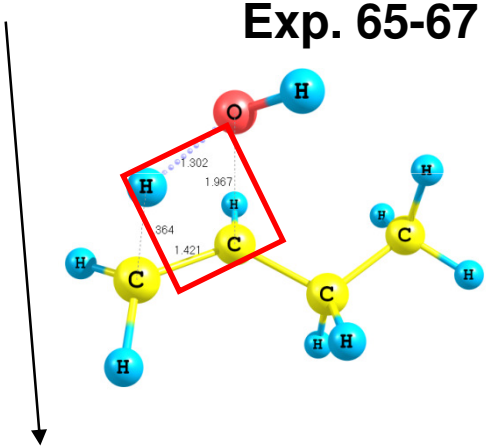
1-Butene formation

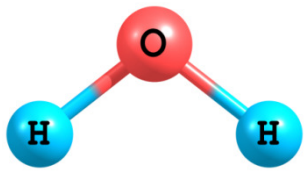


CBS-QB3 values

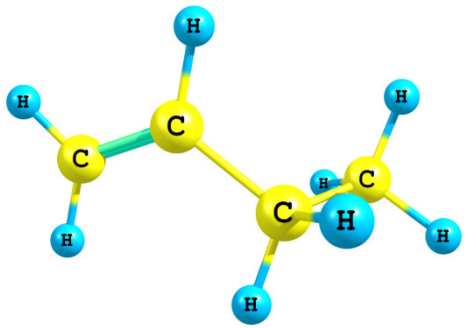
$\Delta H^{\#}$= 66.0 kcal/mol

Exp. 65-67 for different alcohols.





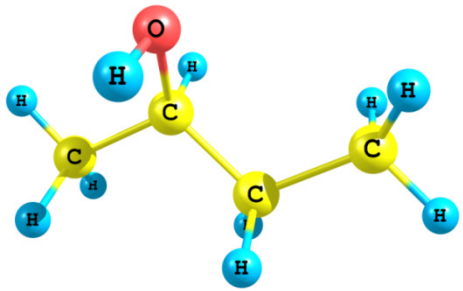
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ΔH_r= 11.9 kcal/mo

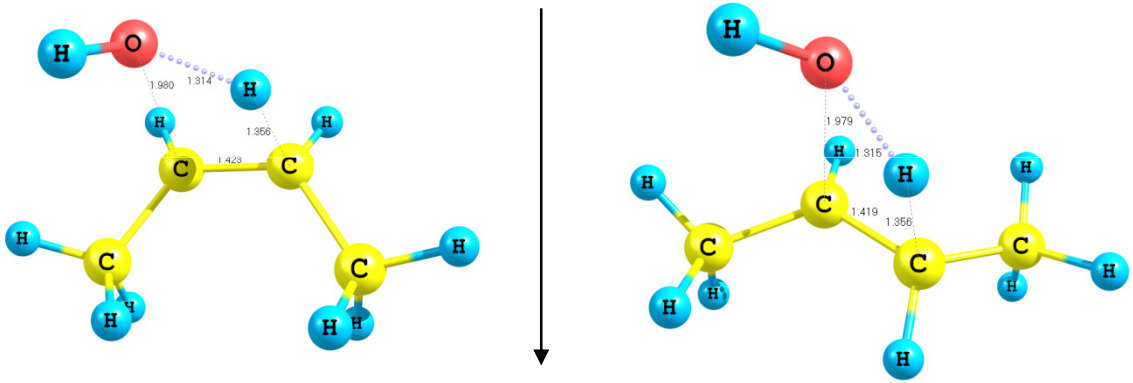
2-Butene formation

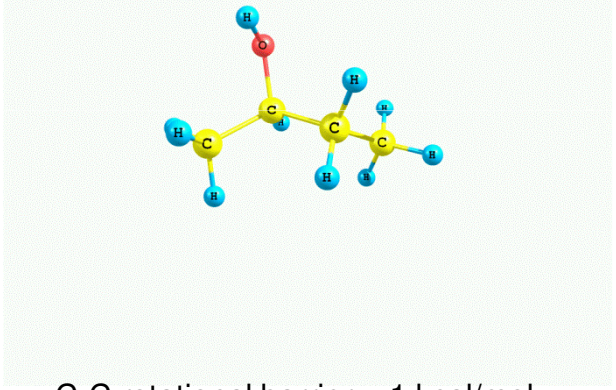
$\Delta H^{\#}$= 67.9 kcal/mol



$\Delta H^{\#}$= 67.2 kcal/mol

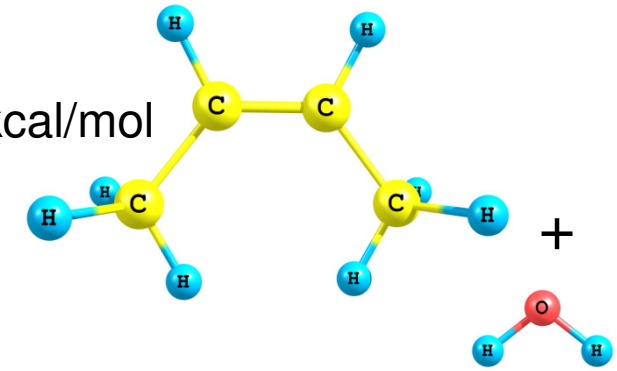
Exp. 65-67 for different alcohols.



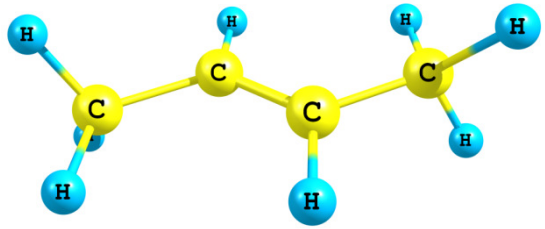


C-C rotational barrier < 1 kcal/mol

ΔH_r= 10.3 kcal/mol

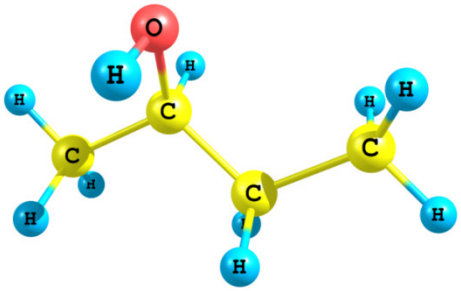


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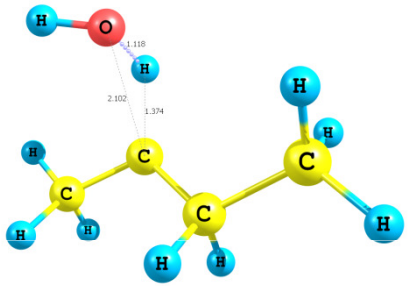


ΔH_r= 9.1 kcal/mol

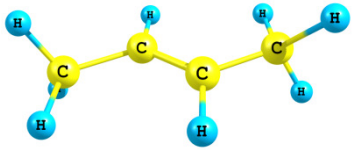
Carbene formation



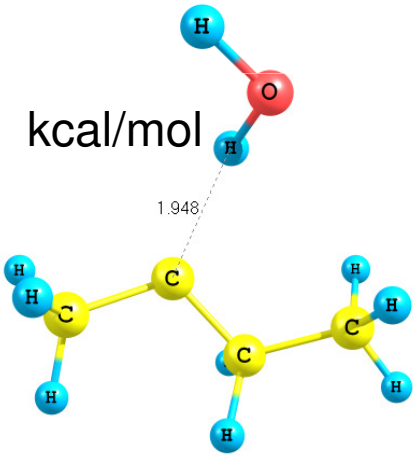
$\Delta H^{\#}$= 78.0 kcal/mol

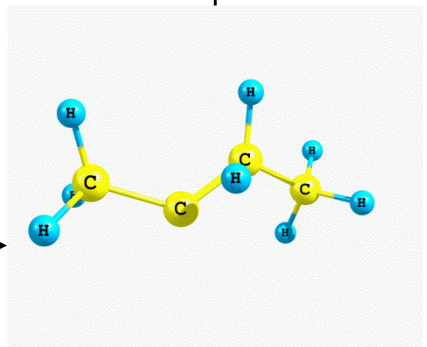


ΔH_r= 9.1 kcal/mol



ΔH_r= 73.7 kcal/mol

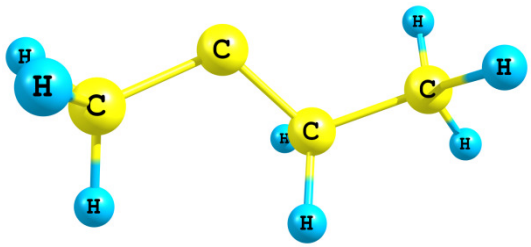




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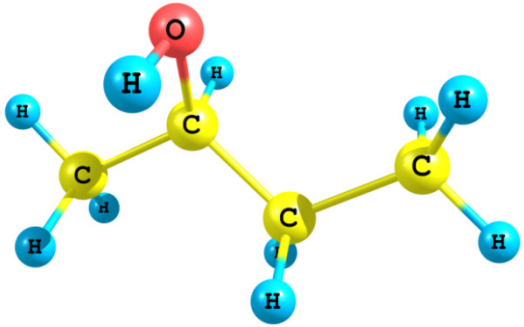


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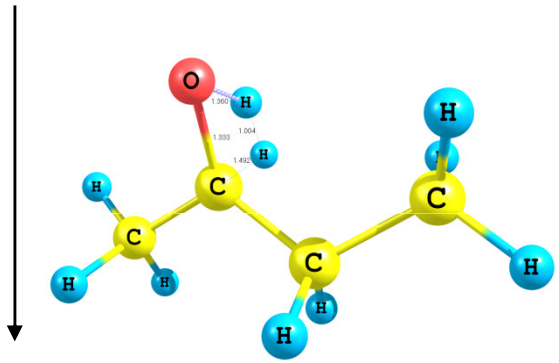


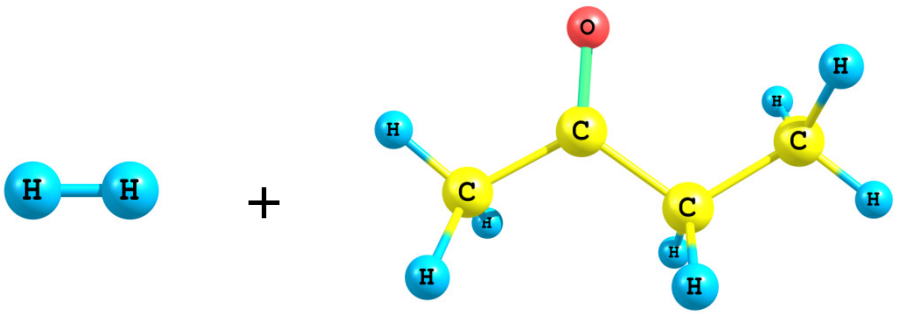
ΔH_r= 78.6 kcal/mol

Methy ethyl ketone formation



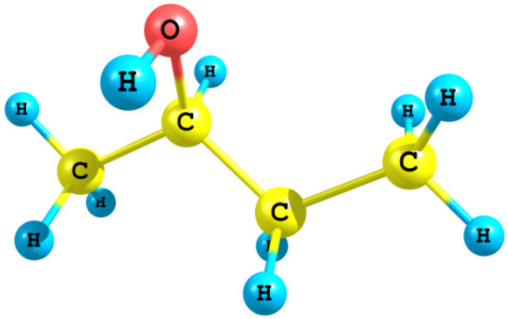
$\Delta H^{\#}$= 81.4 kcal/mol



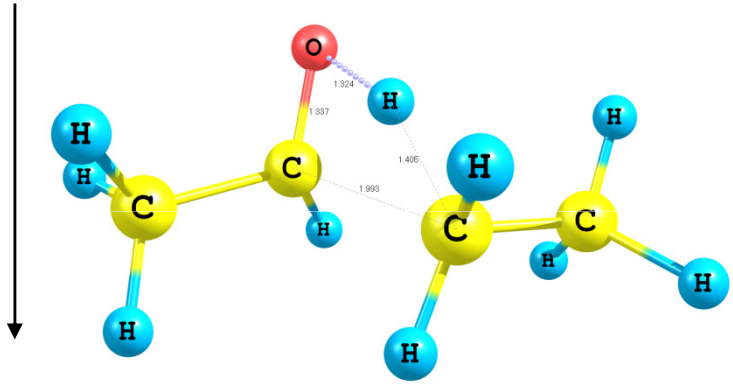


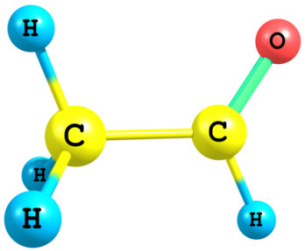
ΔH_r= 9.9 kJ/mol

Acetaldehyde formation

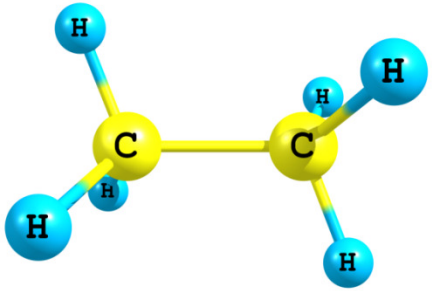


$\Delta H^{\#}$= 85.0 kcal/mol



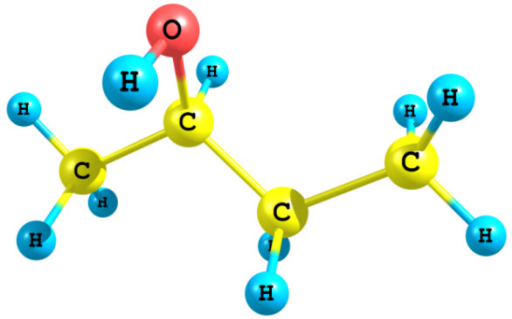


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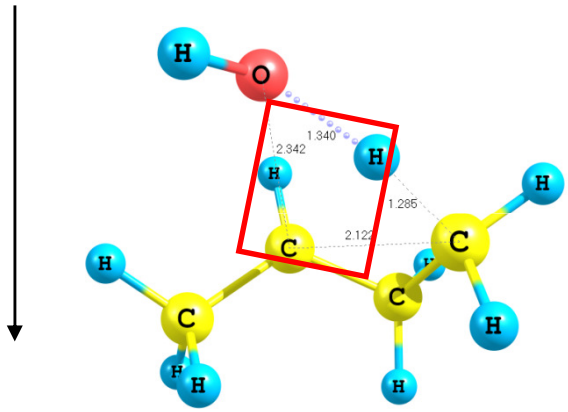


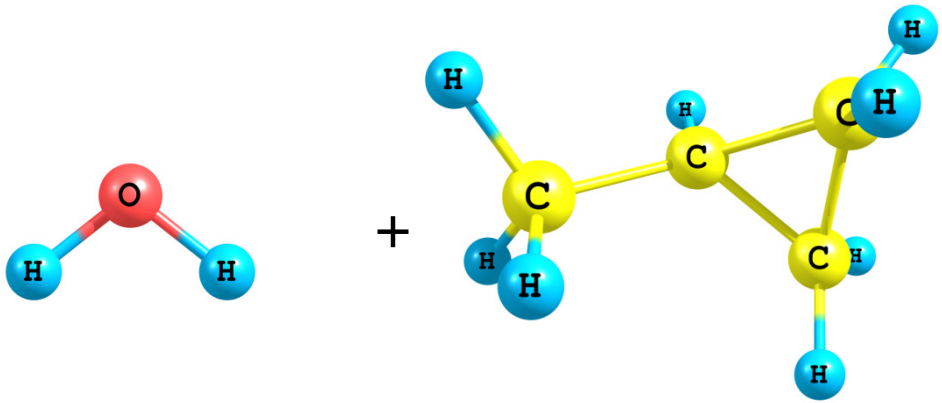
ΔH_r= 9.2 kcal/mol

Methyl cyclopropane formation



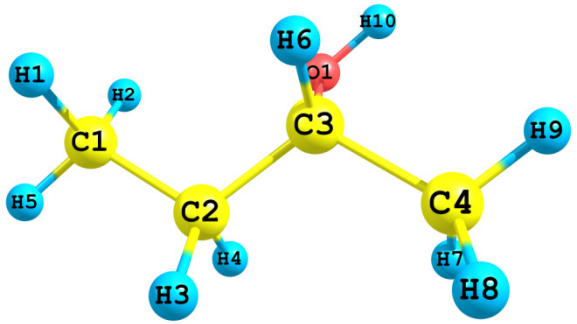
$\Delta H^{\#}$= 94.9 kJ/mol



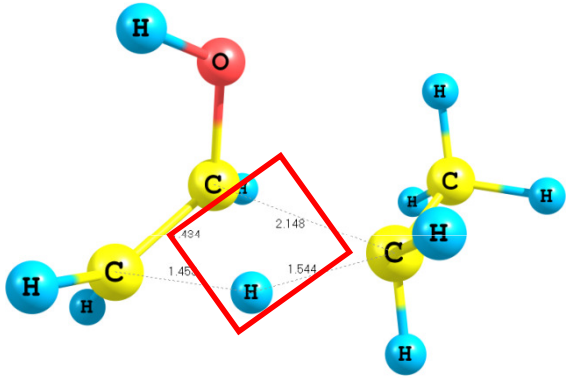


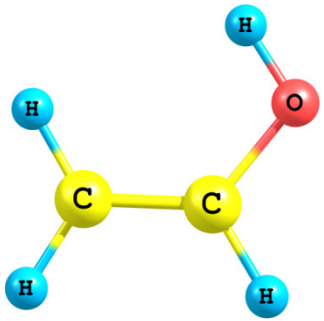
ΔH_r= 18.1 kcal/mol

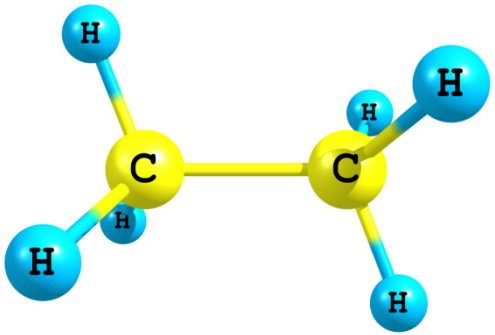
Vinyl alcohol formation



$\Delta H^{\#}$= 109.5 kcal/mol

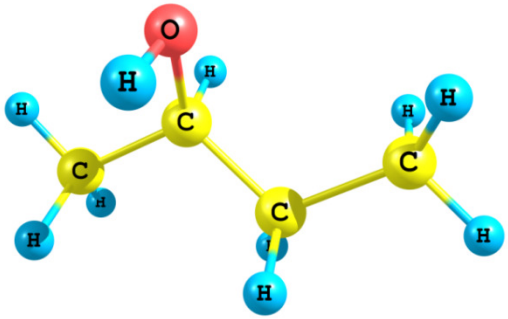




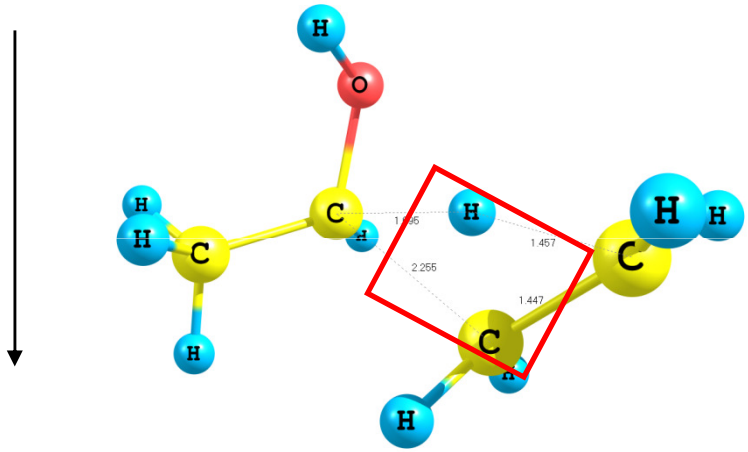


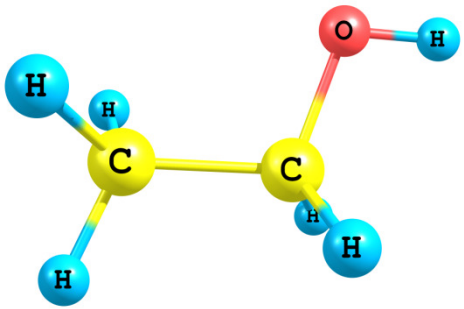
ΔH_r= 19.8 kcal/mol

Ethene formation

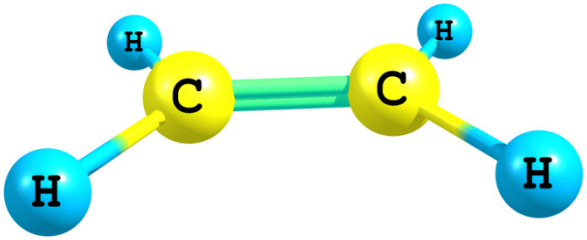


$\Delta H^{\#}$= 111.9 kcal/mol





+



ΔH_r= 25.7 kcal/mol

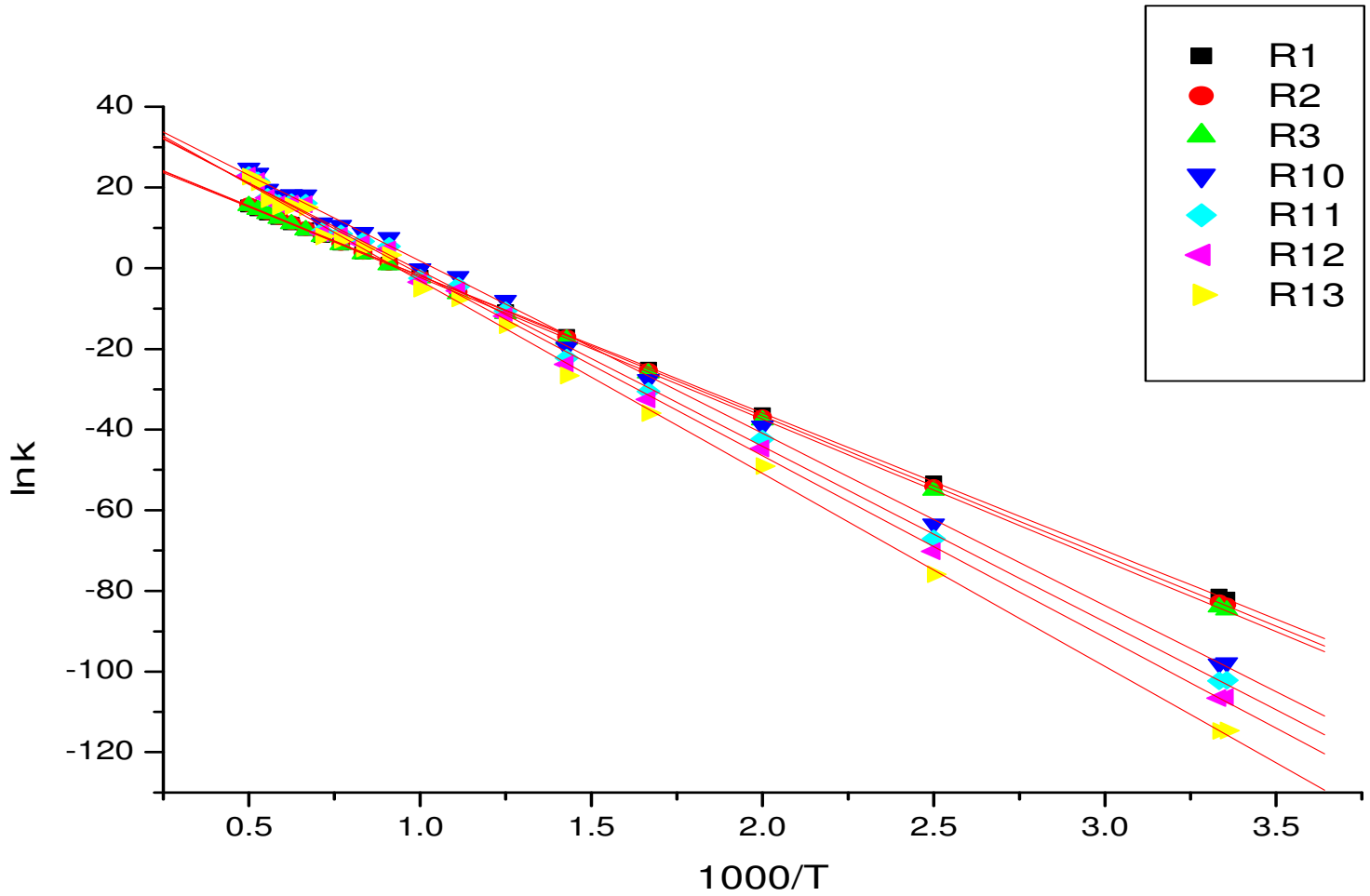
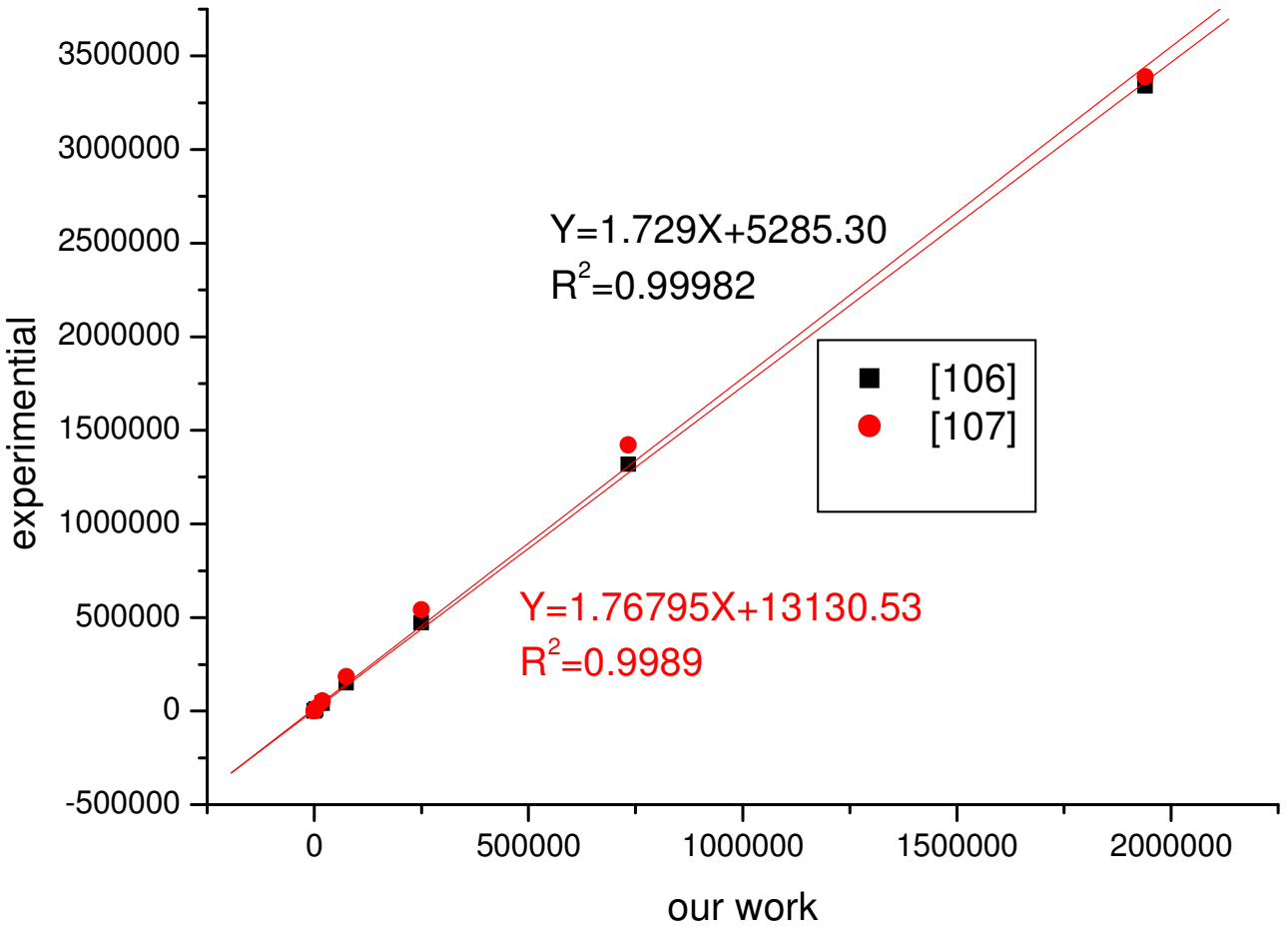


Figure 8. Arrhenius plots for the unimolecular thermal decomposition of 2-butanol to 1-butene (R1), trans-2-butene (R2), cis-2-butene (R3), 1-ethyl alcohol radical (R10), 1-propyl alcohol radical (R11), 2-isopropyl alcohol (R12), and 2-butyl radical (R13) over the temperature range 298-2000 K.

Table 5. Rate expressions for the predominant reactions (R1, R2, R3 R10, R11, R12, and R13) over the temperature range 298-2000 K.

Reaction	E_a (kcal/mol)	A (s^{-1})
Exp. 65-67 for different alcohols.		
R1	67.69	9.80E+13
R2	69.05	1.03E+14
R3	69.79	1.78E+14
R10	84.25	2.06E+19
R11	86.51	4.36E+18
R12	89.47	8.21E+18
R13	95.01	2.67E+19



Correlation between experimental and present calculation of rate constant.

Branching ratios

Table 6. Percent Contribution of Each Channel in the Overall Reaction of the Thermal Decomposition of 2-Butanol

T/K	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R14	R11	R12	R18	R13	R15	R16	R17
298	80.25	15.51	4.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
300	79.98	15.69	4.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
400	67.80	23.42	8.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
500	56.69	27.63	12.46	0.00	0.00	0.00	0.00	0.00	0.00	3.09	0.00	0.12	0.01	0.00	0.00	0.00	0.00	0.00
600	50.14	30.77	15.70	0.01	0.00	0.00	0.00	0.00	0.00	3.20	0.00	0.16	0.02	0.00	0.00	0.00	0.00	0.00
700	45.59	32.98	18.37	0.03	0.00	0.00	0.00	0.00	0.00	2.82	0.00	0.17	0.04	0.00	0.00	0.00	0.00	0.00
800	5.64	4.61	2.75	0.01	0.00	0.00	0.00	0.00	0.00	79.55	0.00	5.71	1.57	0.00	0.16	0.00	0.00	0.00
900	1.90	1.71	1.07	0.01	0.00	0.00	0.00	0.00	0.00	85.59	0.00	6.97	2.39	0.00	0.35	0.00	0.00	0.00
1000	10.01	9.72	6.35	0.09	0.00	0.00	0.00	0.00	0.00	65.06	0.00	5.87	2.41	0.00	0.48	0.00	0.00	0.00
1100	0.12	0.13	0.09	0.00	0.00	0.00	0.00	0.00	0.00	86.15	0.00	8.46	4.02	0.00	1.03	0.00	0.00	0.00
1200	0.47	0.52	0.36	0.01	0.00	0.00	0.00	0.00	0.00	83.59	0.00	8.81	4.75	0.00	1.49	0.00	0.00	0.00
1300	0.75	0.85	0.61	0.03	0.00	0.00	0.00	0.00	0.00	81.18	0.00	9.09	5.45	0.00	2.04	0.00	0.00	0.00
1400	2.67	3.15	2.28	0.14	0.00	0.01	0.00	0.00	0.00	74.63	0.00	8.80	5.79	0.00	2.53	0.00	0.00	0.00
1500	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	79.64	0.00	9.82	7.00	0.00	3.50	0.00	0.00	0.00
1600	0.06	0.07	0.05	0.01	0.00	0.00	0.00	0.00	0.00	77.88	0.00	9.98	7.64	0.00	4.31	0.00	0.00	0.00
1700	0.25	0.32	0.24	0.03	0.00	0.00	0.00	0.00	0.00	75.76	0.00	10.05	8.19	0.00	5.15	0.00	0.00	0.00
1800	0.16	0.21	0.16	0.02	0.00	0.00	0.00	0.00	0.00	74.39	0.00	10.18	8.78	0.00	6.08	0.00	0.00	0.00
1900	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	73.18	0.00	10.33	9.40	0.00	7.07	0.00	0.00	0.00
2000	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	71.41	0.00	10.45	10.08	0.00	8.03	0.00	0.00	0.00

K, k_forwd,k_bac(ass.)

Pyrolysis of Isobutanol

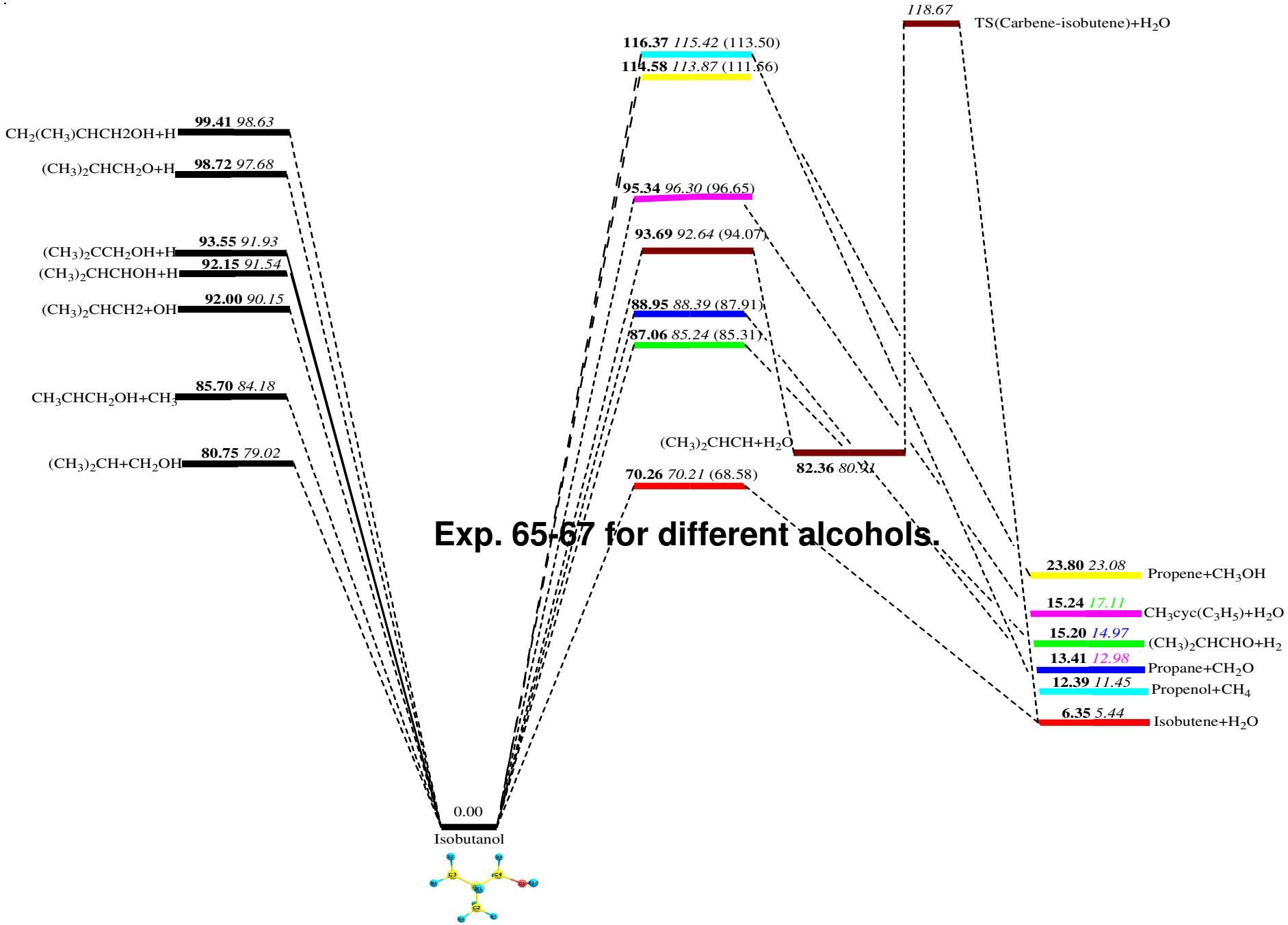
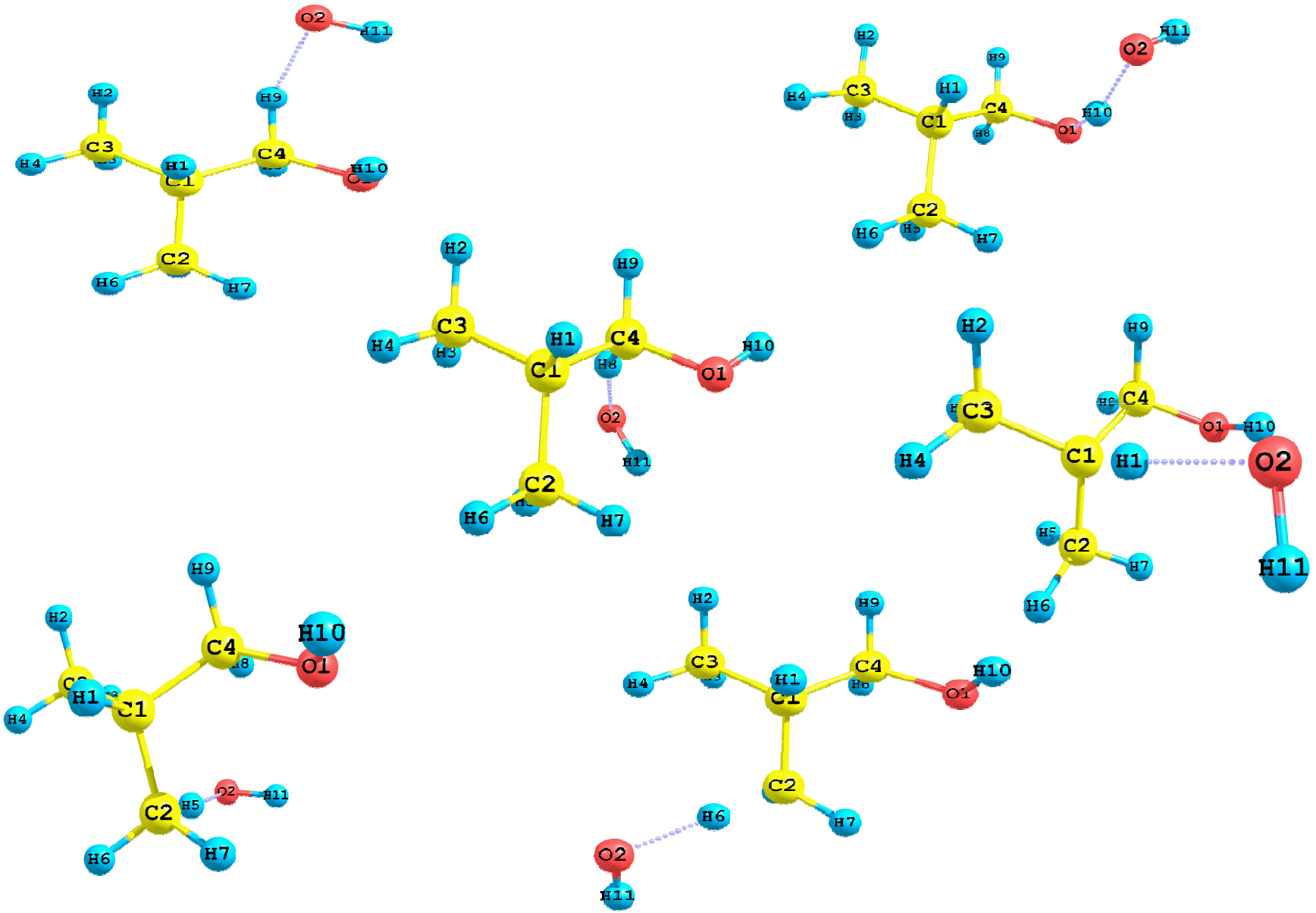


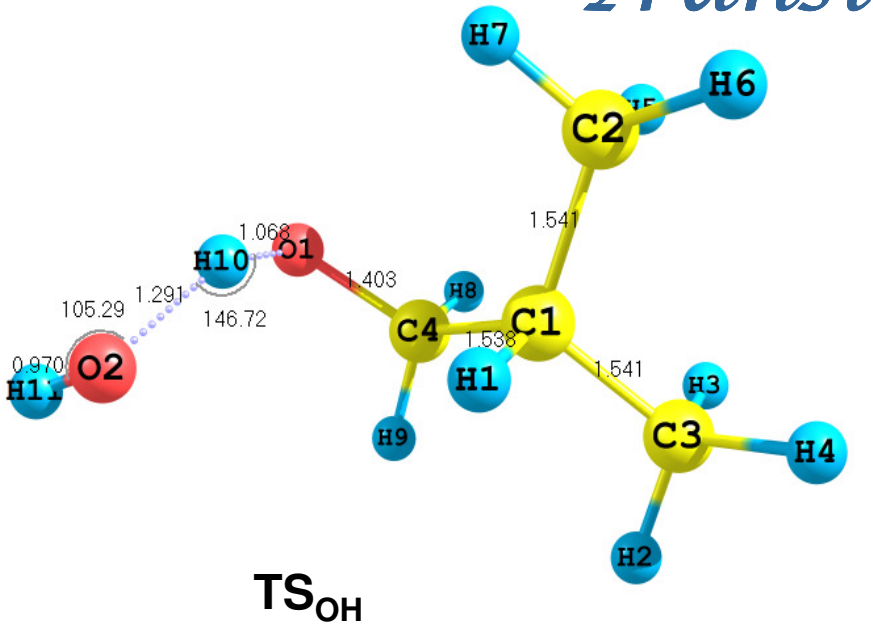
Fig. 12 Potential energy diagram for unimolecular thermal decomposition of isobutanol at **BMK**(bold), BB1K (Italic)and **CBS-CBS** in parentheses. For clarification, products and relevant transition states have the same color.

Oxidation of Isobutanol by OH

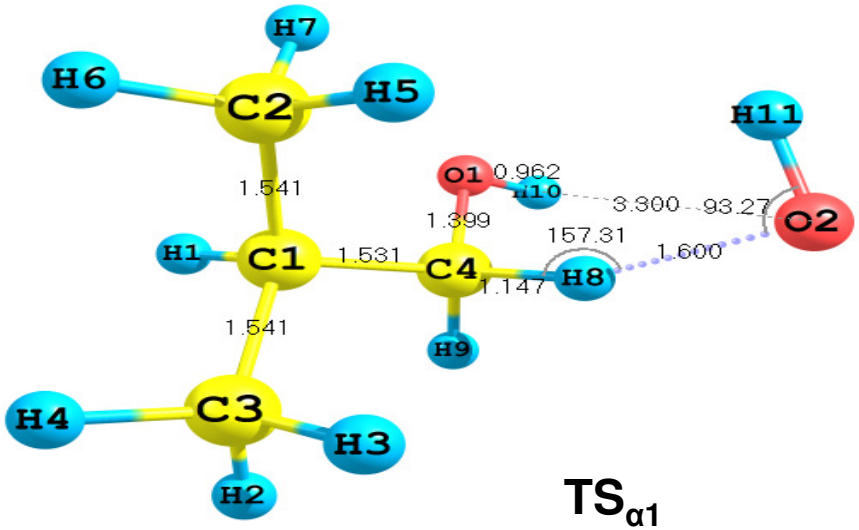
H-atom abstraction using HO·



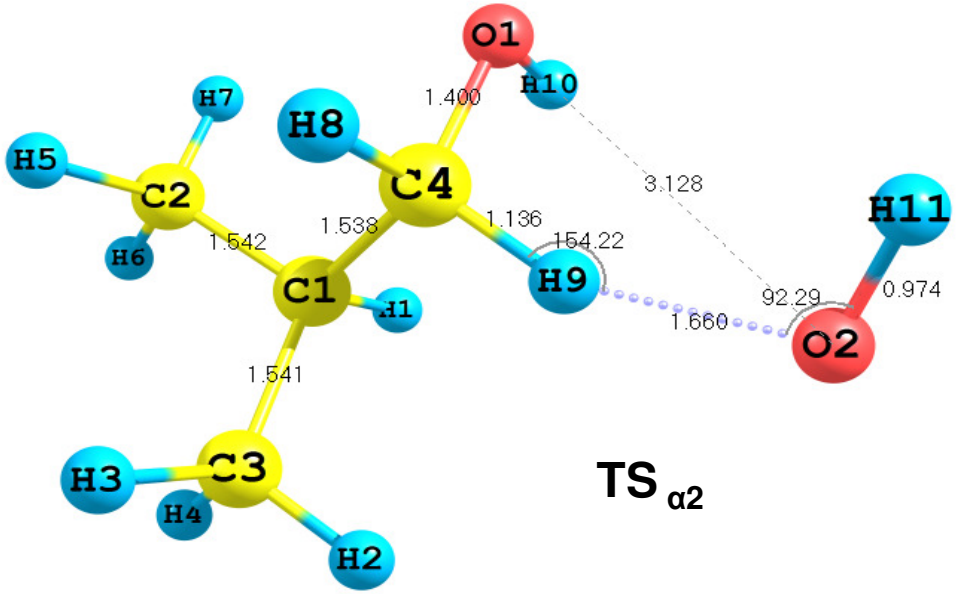
Transition states



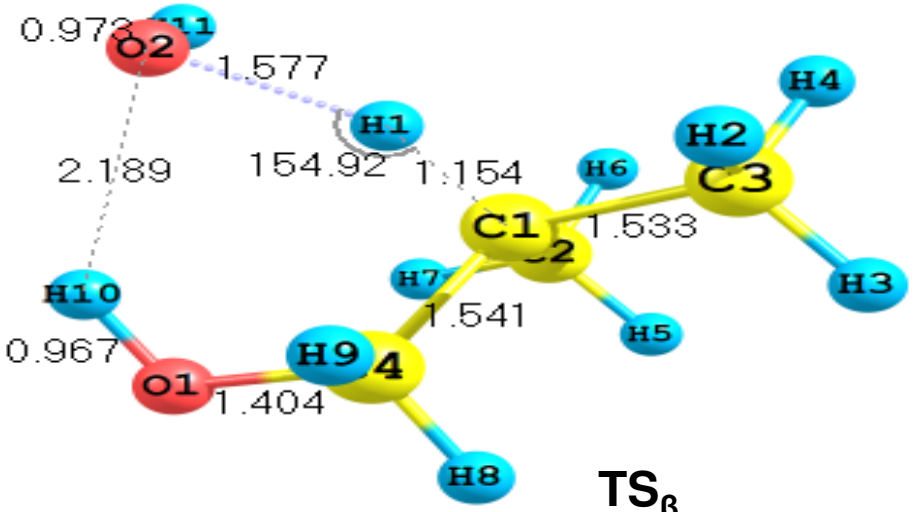
TS_{OH}



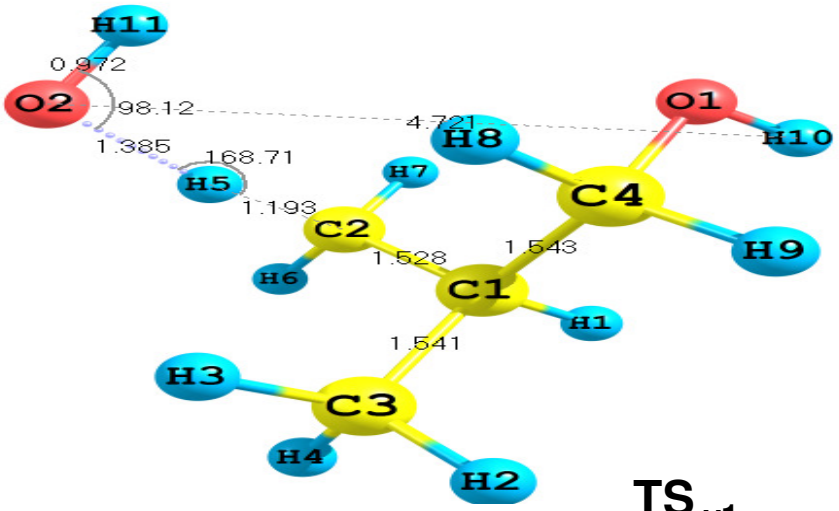
$TS_{\alpha 1}$



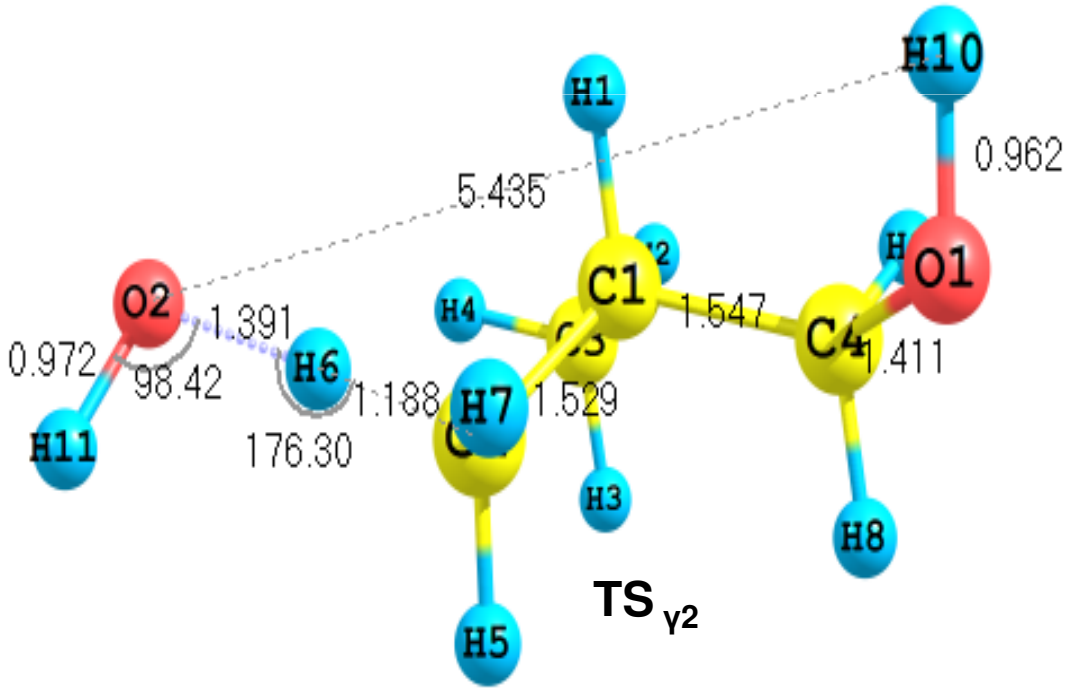
$TS_{\alpha 2}$



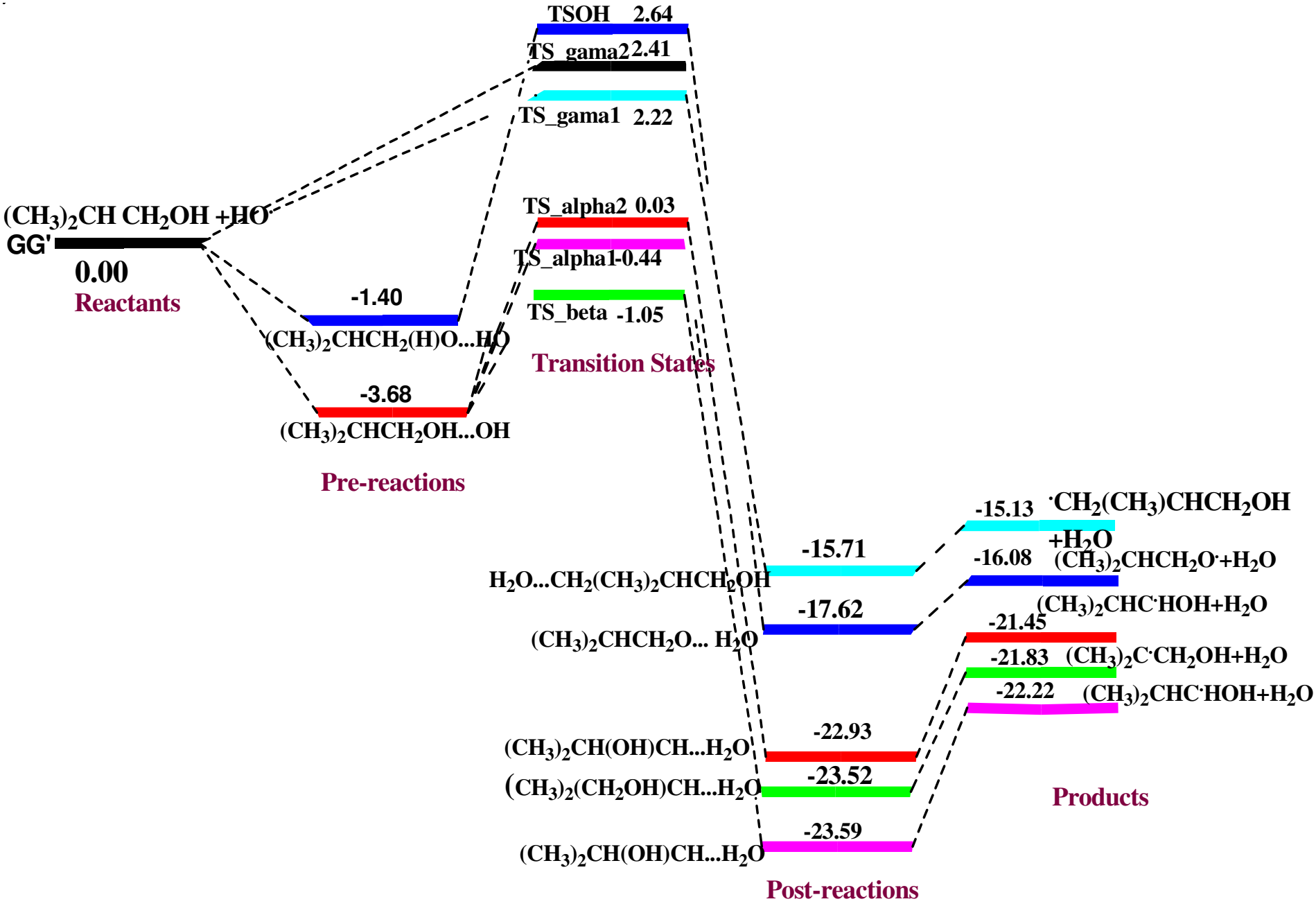
TS_{β}



$TS_{\gamma 1}$



$TS_{\gamma 2}$



Potential energy diagram (ΔE_o,$\Delta E_o^{\#}$, kcal/mol) for oxidation of isobutanol using HO· at BB1K/6-311++G(2d,2p)/BMK/6-31+G(d,p).

Conclusions

- **Enthalpies of formations from atomization energies for C_1-C_4 alcohols and their derived radicals were calculated with higher accuracy.**
- **For all butanols, butene via four-center transition states represents the most favorable channel.**
- **2-butanol releases acetaldehyde and ketone while n- and isobutanol produces only aldehydes, agree with experiment.**
- **Production of unsaturated alcohols or cyclopropane cost a lot of energy and unlikely occur except at higher temperatures.**
- **Higher amount of propene is expected from isobutanol in agree with experiment.**
- **Accurate energies could be achieved at CBS-QB3.**
- **BB1K, BMK, MPW1K,MPWB1K, LC-ωPBE all give good energy barrier for different reactions.**

Biodiesel model (esters)

Calculated properties

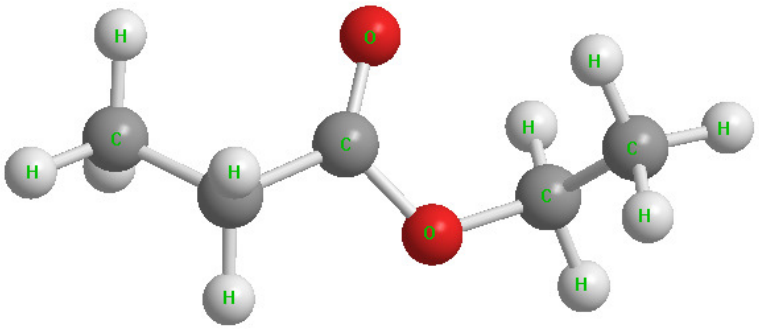
Enthalpies of formation

Atomization energy

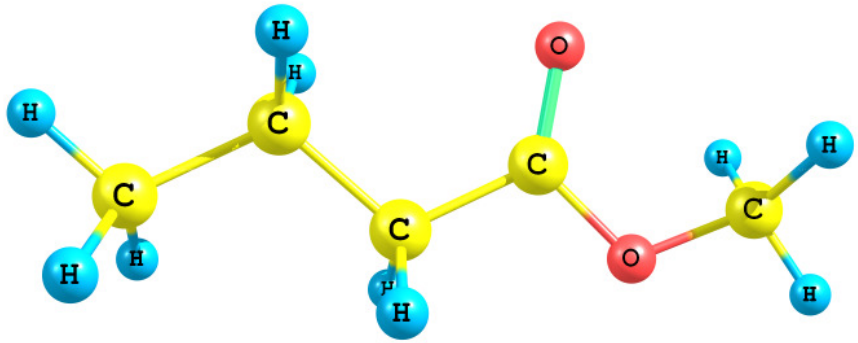
Isodesmic reactions

Bond Dissociation Enthalpies (BDE)

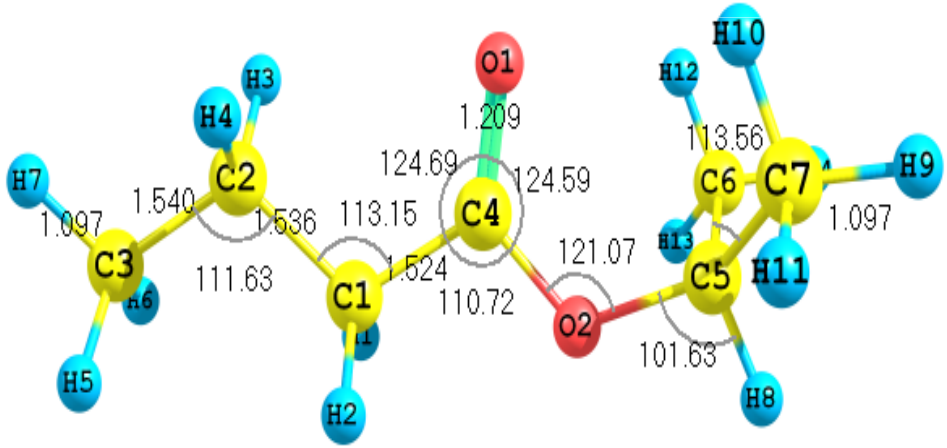
Potential energy surface for unimlecular decomposition of EP MB



EP



MB


O1
1.209
H10
H12
113.56
H3
H4
C2
124.69
124.59
C6
C7
H9
H7
1.540
1.097
1.536
113.15
C4
1.097
121.07
C3
111.63
1.524
C1
110.72
C5
H11
H13
O2
101.63
H5
H2
H8

IPB

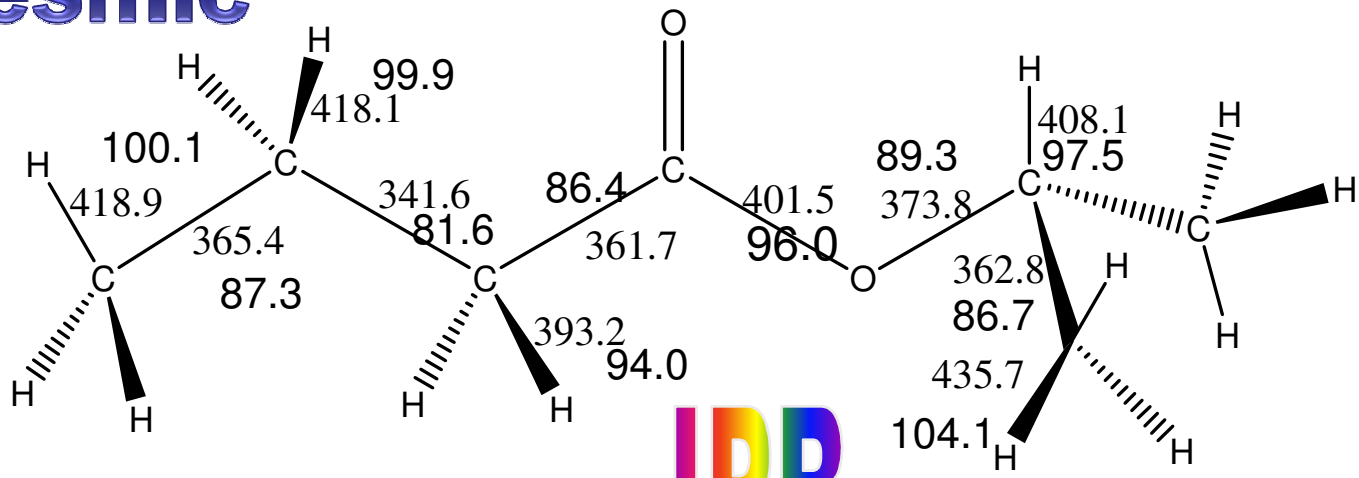
Enthalpies of formation (AE, kcal/mol) for EP and MB and their fragments at CBS-QB3.

Species	CBS-QB3	Exp.	Species	CBS-QB3	Exp.
$C_2H_5CO_2C_2H_5$	-111.3	-111.5	$C_3H_7CO_2CH_3$	-108.3	
$C_2H_5CO_2H$	-107.6	108.3	$C_3H_7CO_2H$	-113.8	-112.7
$CH_3CH=C=O$	-15.2		$C_2H_5CO_2CH_3$	-103.4	
$C_2H_5CO_2\bullet$	-49.5		$C_2H_5CH=C=O$	-20.7	
$C\bullet H_2CO_2C_2H_5$	-59.3		$C_3H_7CO_2\bullet$	-56.6	
$C\bullet H_2CO_2C_2H_5$	-59.3		$C\bullet H_2CH_2CO_2CH_3$	-53.8	
$C\bullet H_2CO_2C_2H_5$	-60.2		$\bullet C=OOCH_3$	-37.2	
$C\bullet H_2CO_2C_2H_5$	-60.1		$C_3H_7CO_2CH_2\bullet$	-61.2	
$C_2H_5C\bullet O$	-9.0		$CH_3CH_2C\bullet HCO_2CH_3$	-65.7	
$\bullet C=OOC_2H_5$	-48.2		$CH_3C\bullet HCH_2CO_2CH_3$	-61.4	
$\bullet C=OOC_2H_5$	-48.2		$\bullet CH_2CH_2CH_2CO_2CH_3$	-59.0	

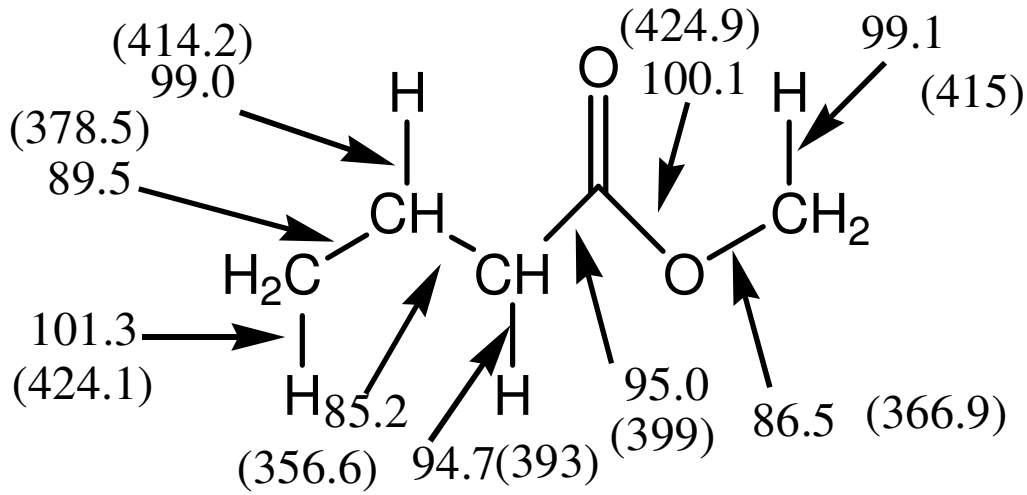
Enthalpies of formation (AE, kcal/mol) for EP and MB and their fragments at CBS-QB3.

Species	CBS-QB3	Exp.	Species	CBS-QB3	Exp.
$C_2H_5CO_2CH_2\bullet$	-56.3		$C\bullet H_2CO_2CH_3$	-51.9	
$CH_3C\bullet HCO_2C_2H_5$	-69.1		$C_3H_7C\bullet O$	-12.3	
$C\bullet H_{2C}H_2CO_2C_2H_5$	-61.5		$C_3H_7\bullet$	23.9	
$C_2H_5CO_2C\bullet HCH_3$	-63.1		$HCO_2\bullet$	-27.3	-30±3
$C_2H_5CO_2CH_2C\bullet H_2$	-60.6		$HCO_2\bullet$	-29.8	-30±3
			$CH_3CO_2\bullet$	-44.2	-43±3
			$CH_3CO_2\bullet$	-46.9	-43±3

BDEs, isodesmic

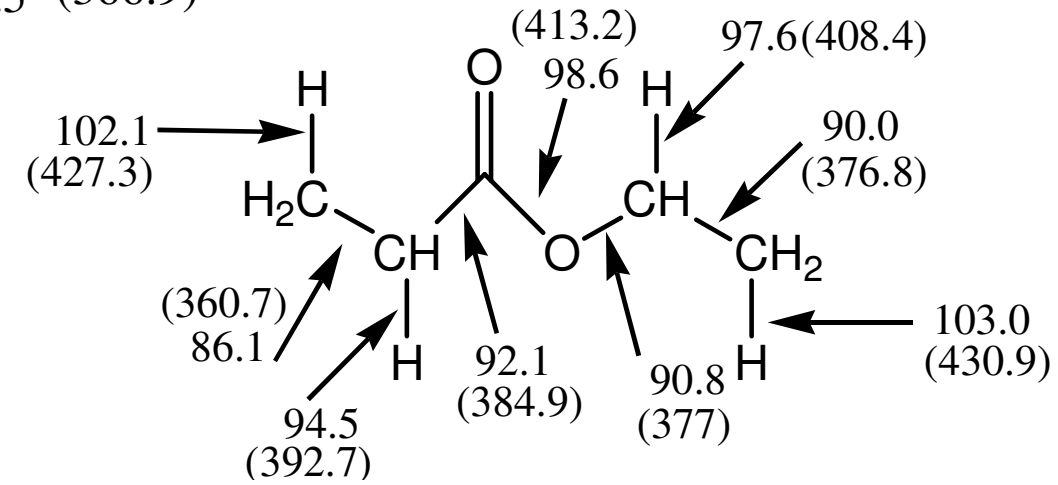


IPB



EP

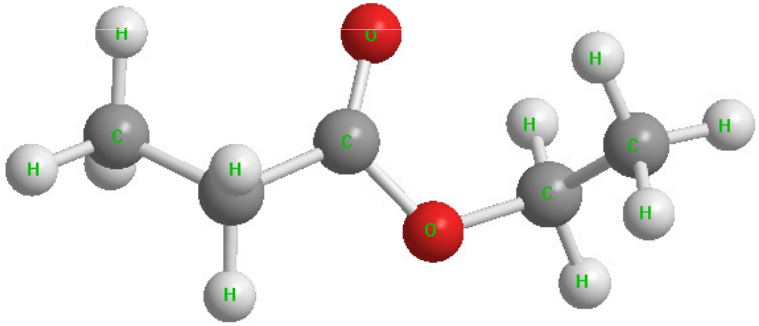
MB



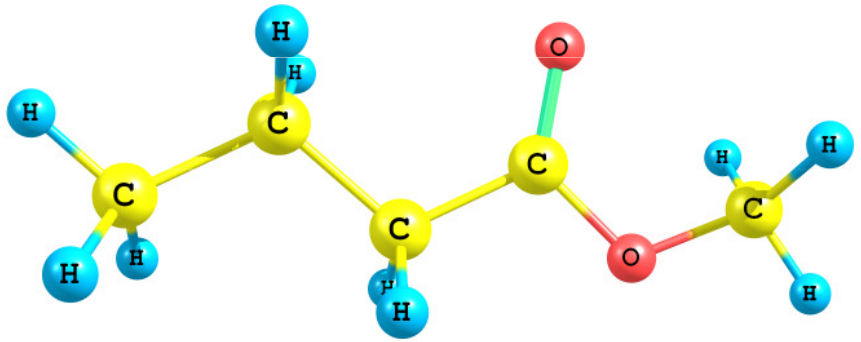
It has been shown[1] that unimolecular of EP gives

Ethylene and propanoic acid, whereas

MB dissociation forms **methyl radical**



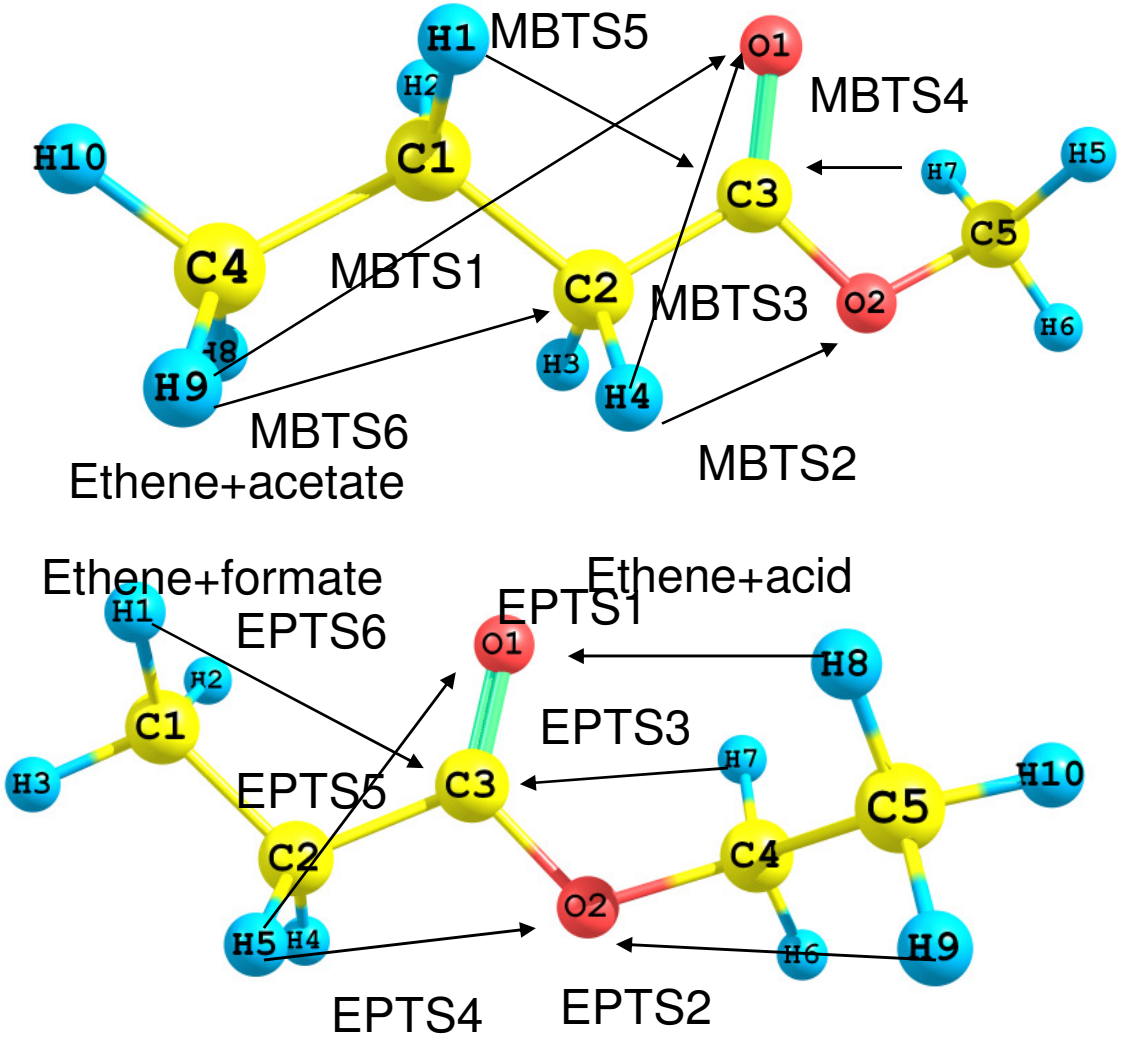
EP



MB

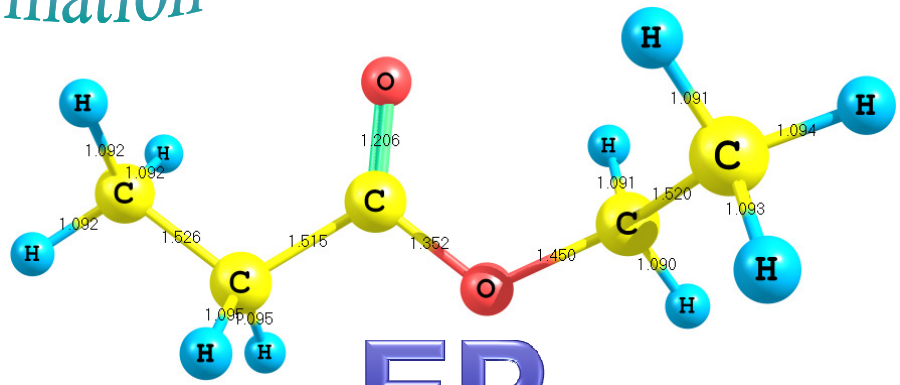
[1]Schwartz et al, JPCA 110 (2006) 6643-48

Unimolecular Decomposition of EP & MB



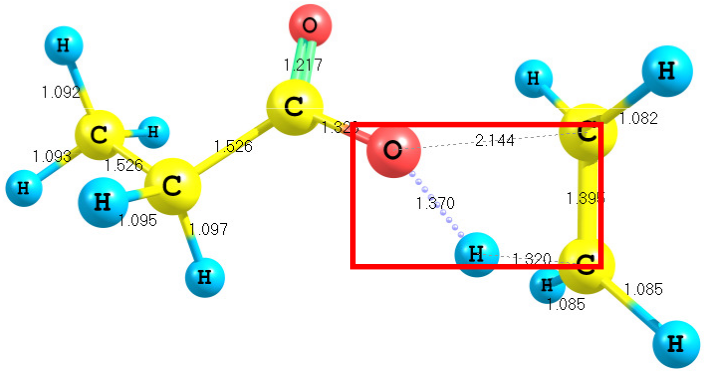
Ethylene formation

UNIMOLECULAR DISSOCIATION

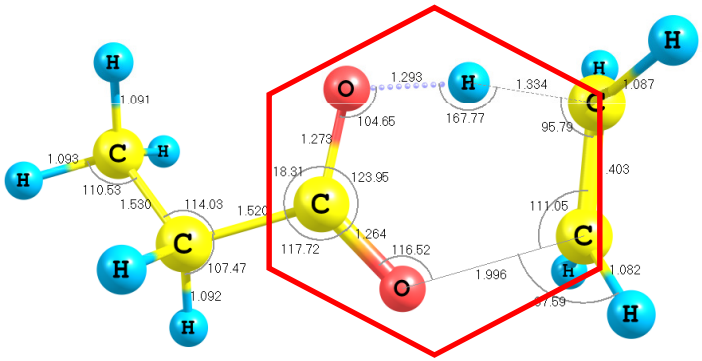


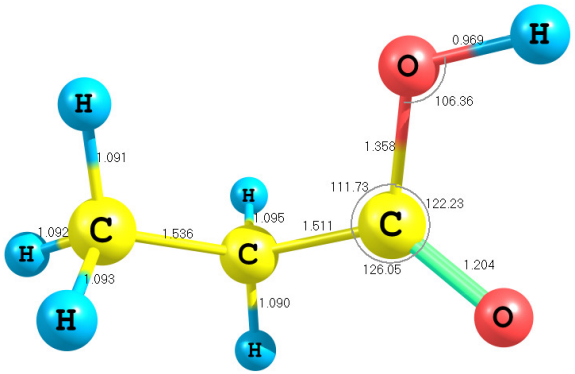
EP

$\Delta H^{\#}$=66.7 kcal/mol

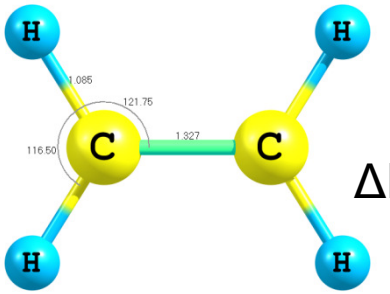


$\Delta H^{\#}$= 50.7 kcal/mol





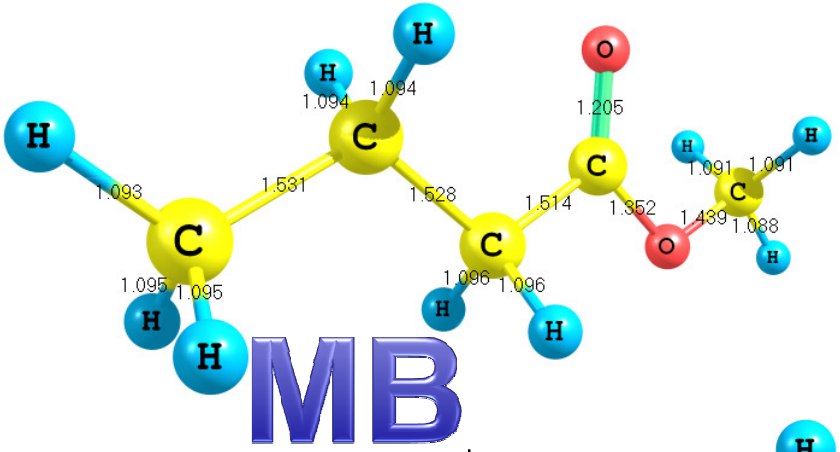
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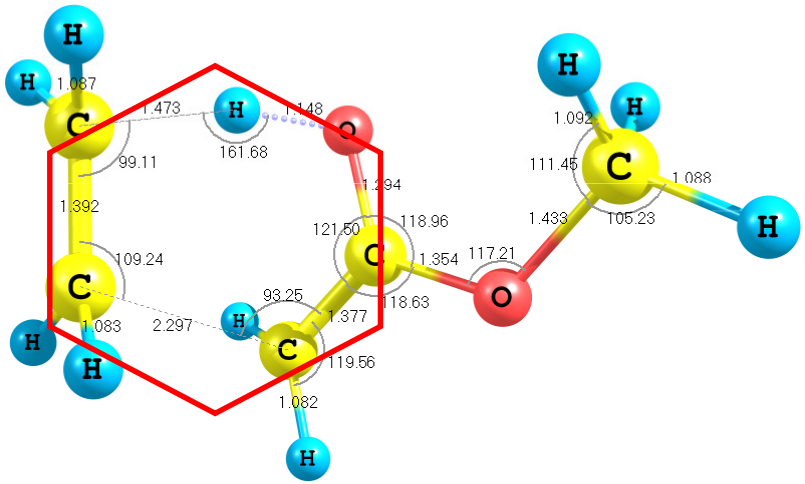
ΔH_r= +16.2 kcal/mol

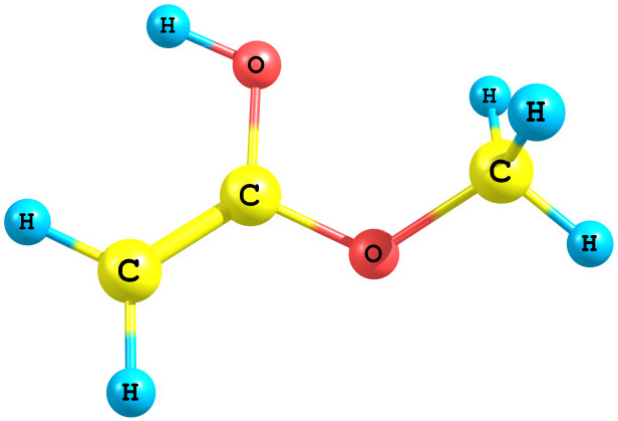
Ethylene formation

UNIMOLECULAR DISSOCIATION

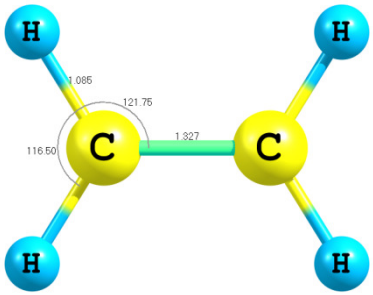


$\Delta H^{\#}$=67.6 kcal/mol

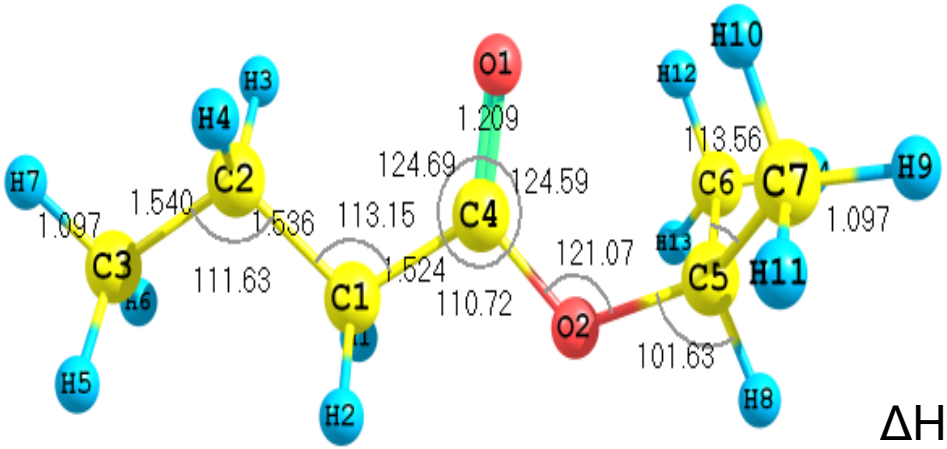




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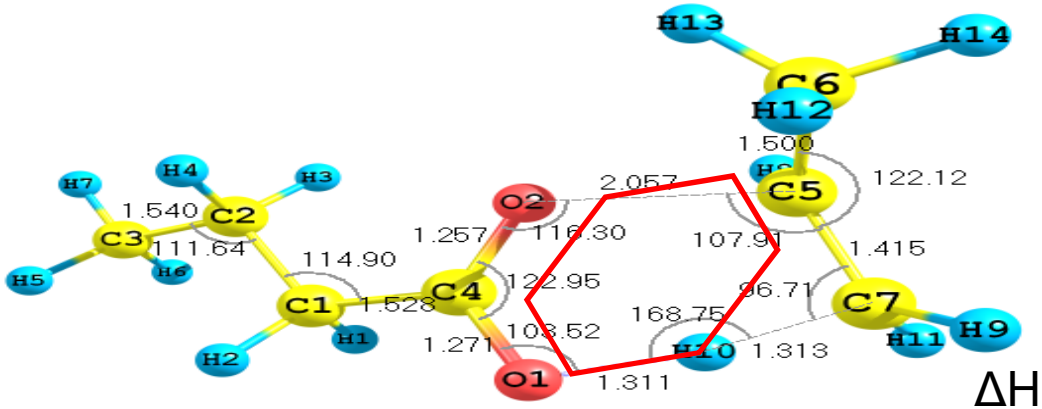


ΔH_r= +52.3 kcal/mol



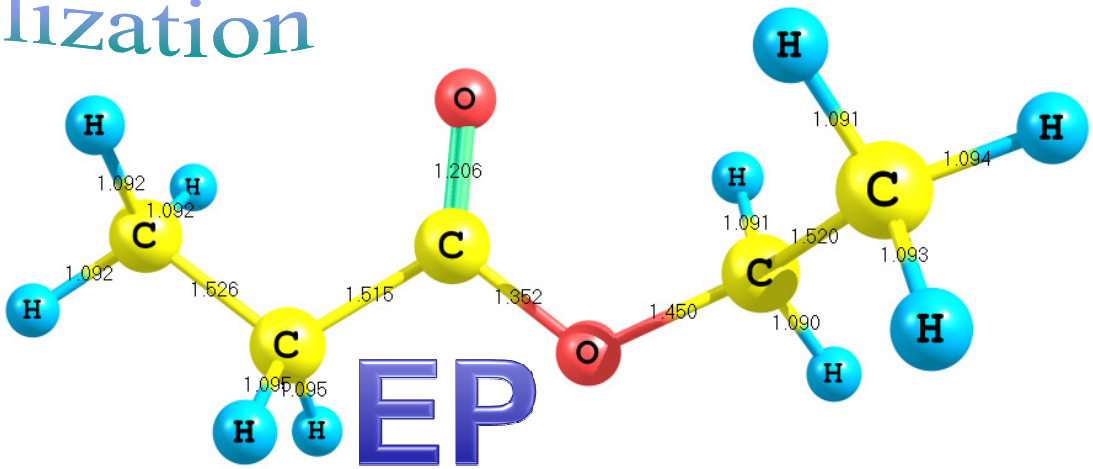
$\Delta H^{\#}$= 48.5 kcal/mol

IPB

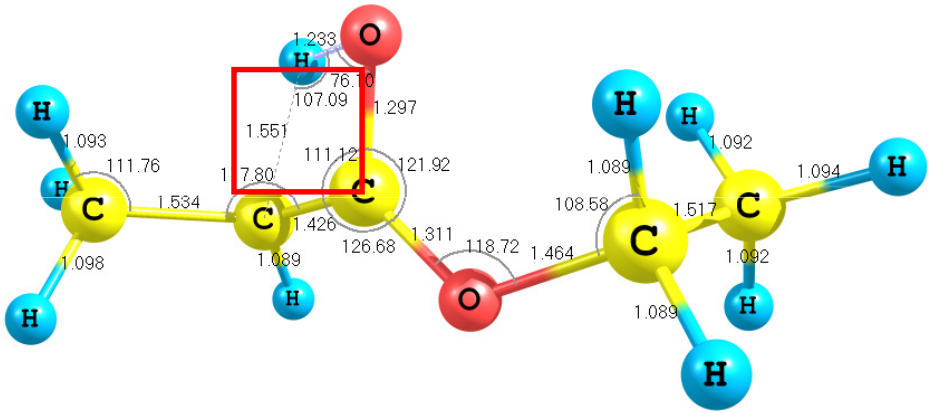


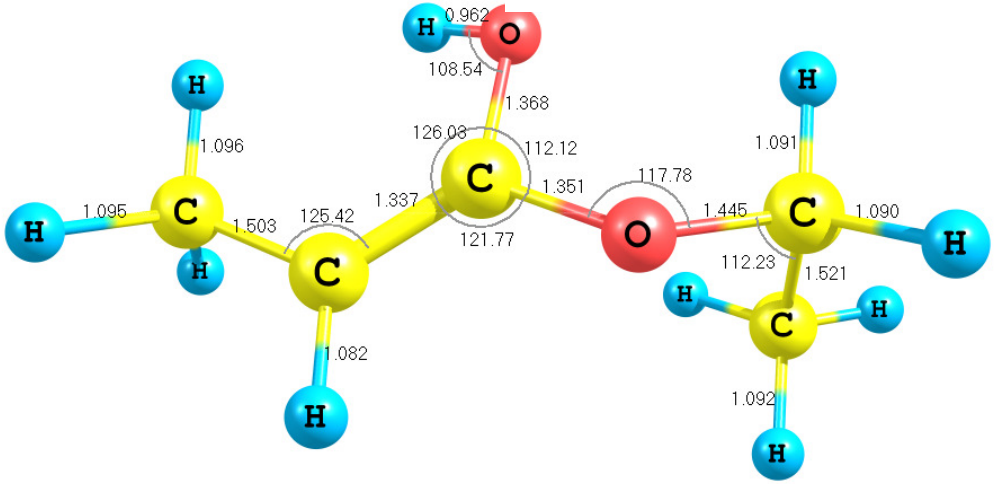
ΔH_r= +15.9 kcal/mol

Enolization



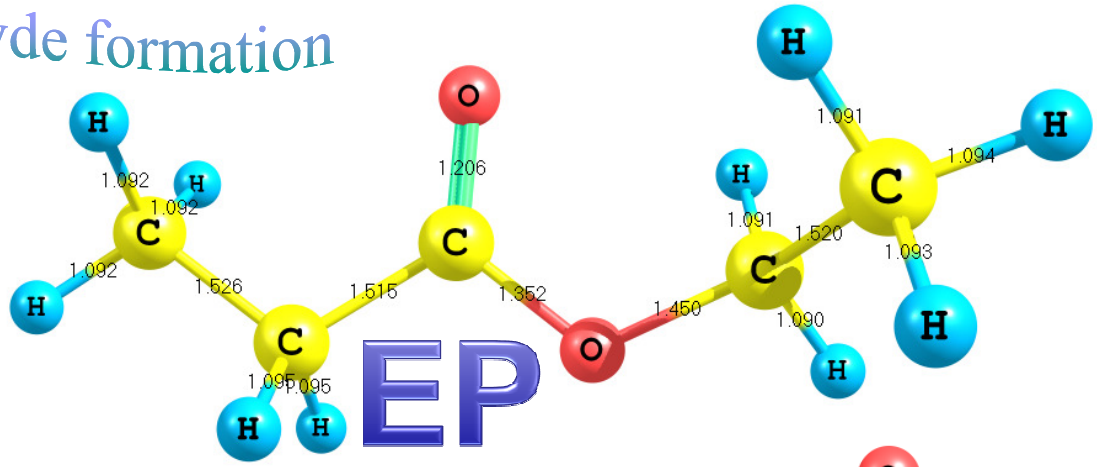
$\Delta H^{\#}$= 75.5 kcal/mol



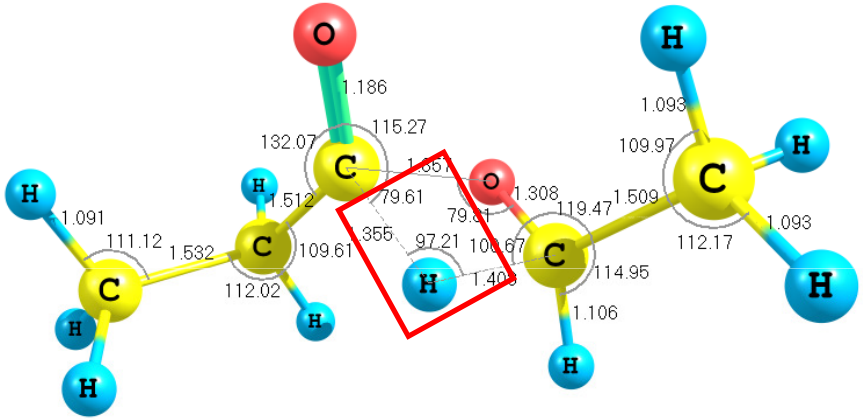


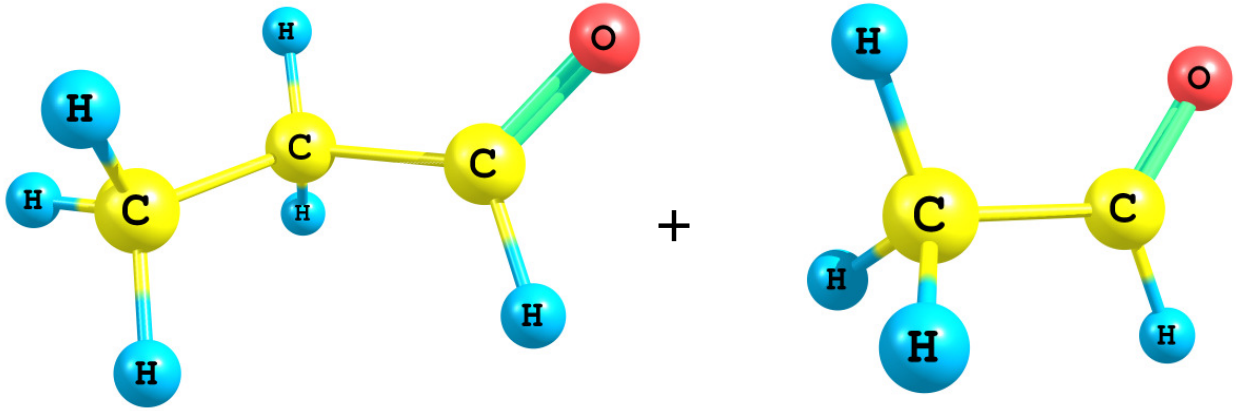
ΔH_r= +28.9 kcal/mol

Aldehyde formation



$\Delta H^{\#}$= 71.7 kJ/mol

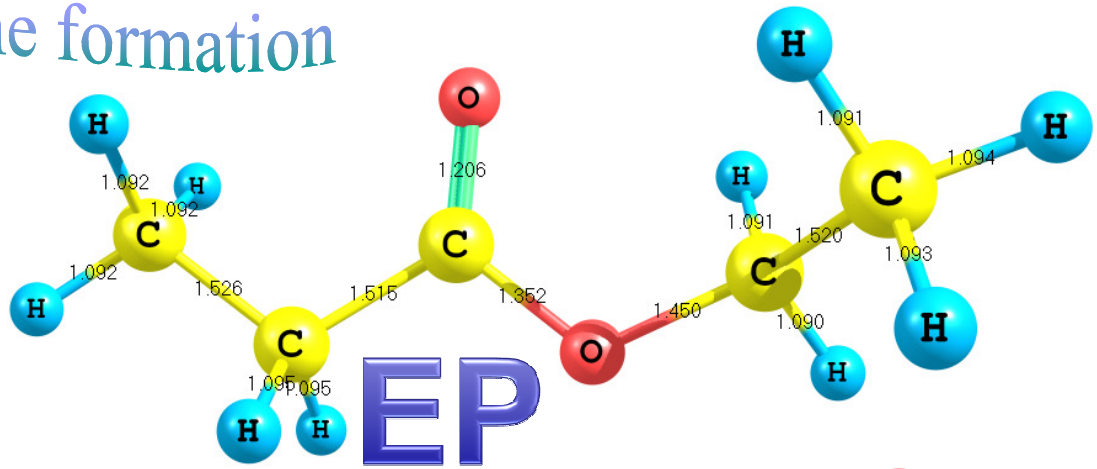




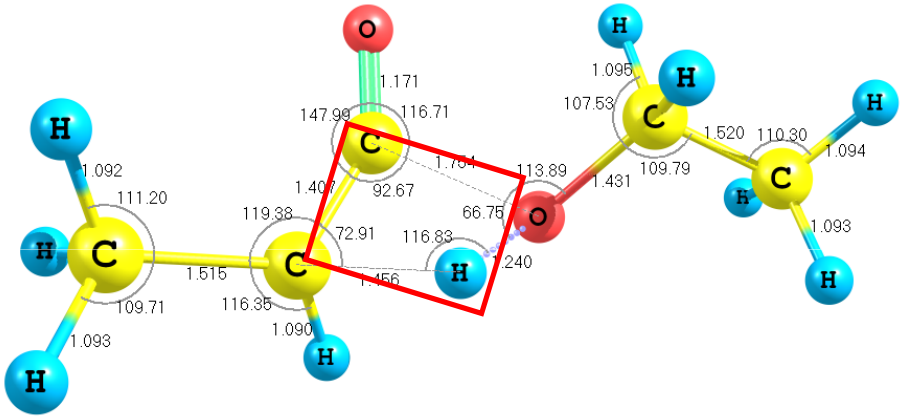
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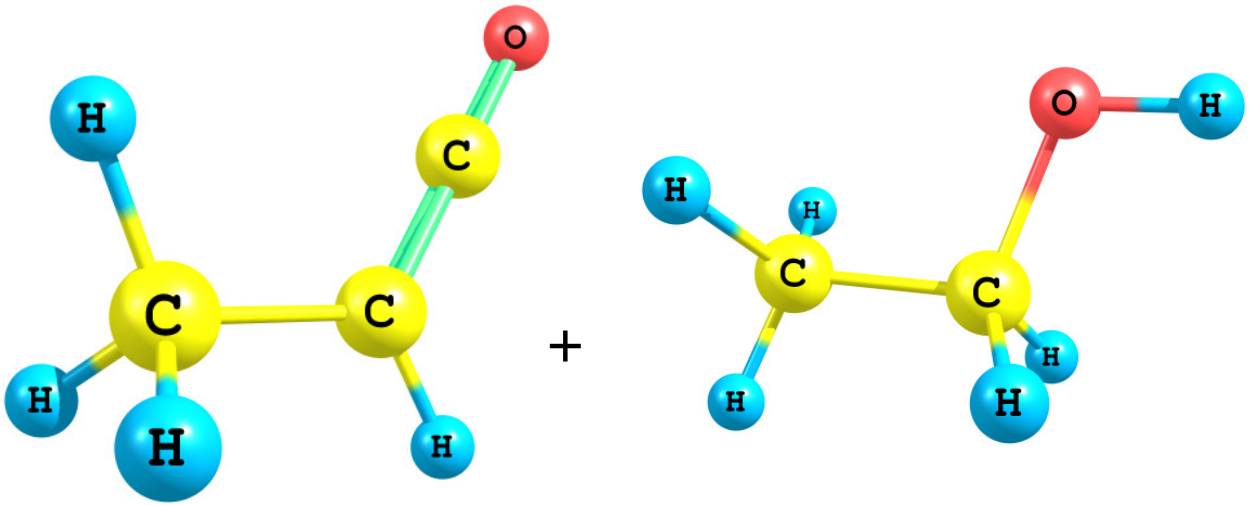
ΔH_r= +26.3 kcal/mol

Ketene formation



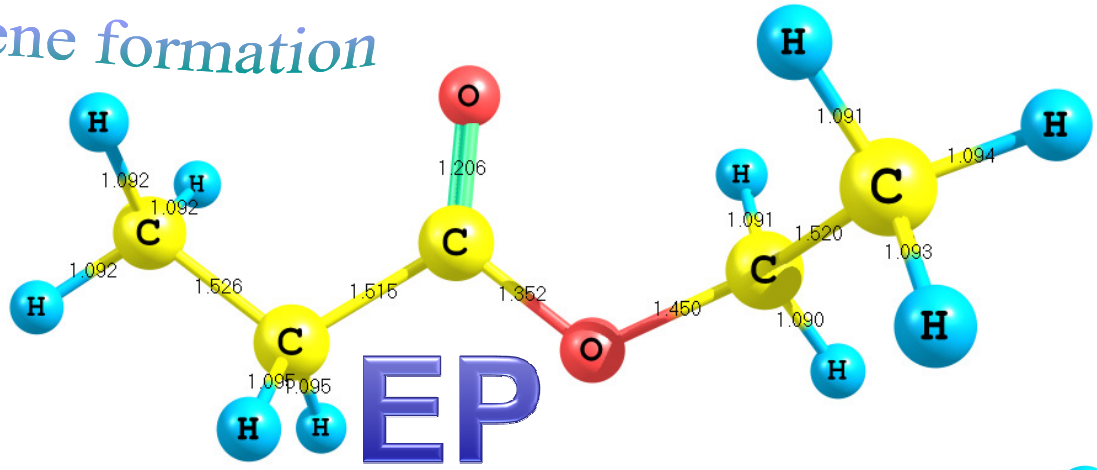
$\Delta H^{\#}$= 73.6 kcal/mol



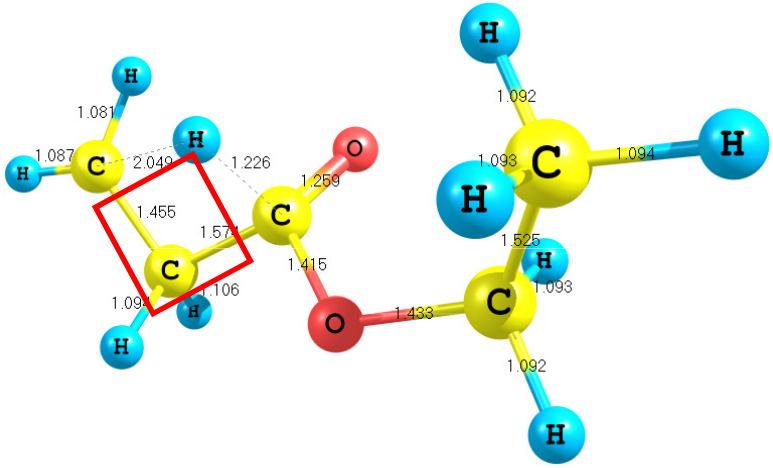


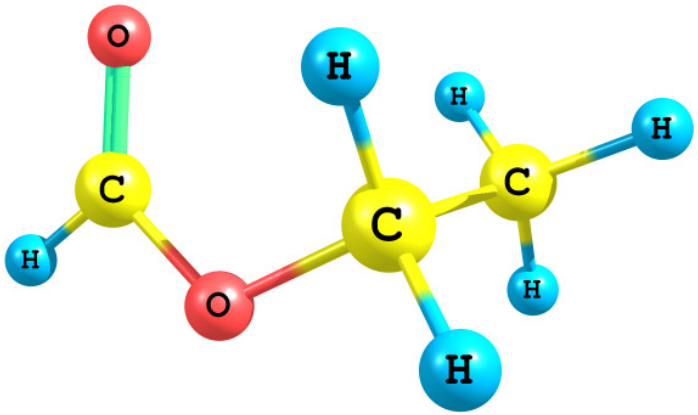
ΔH_r= +39.9 kJ/mol

Ethylene formation

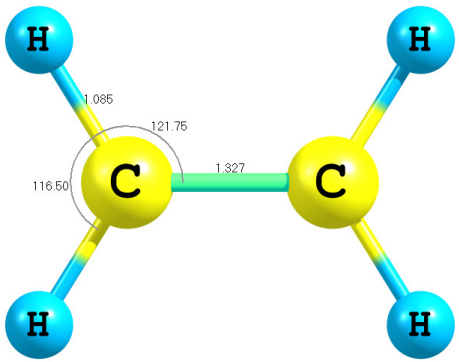


$\Delta H^{\#}$= 101.8 kcal/mol



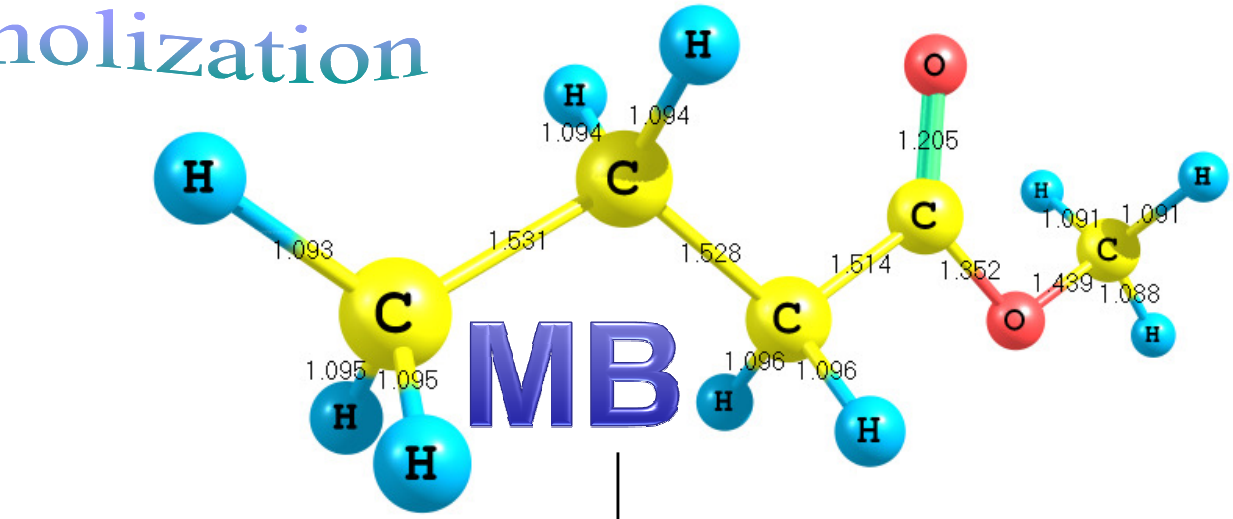


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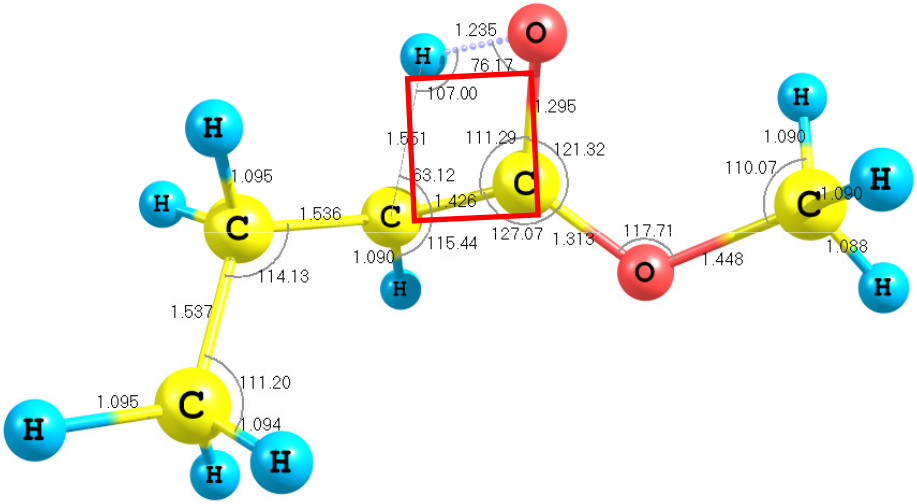


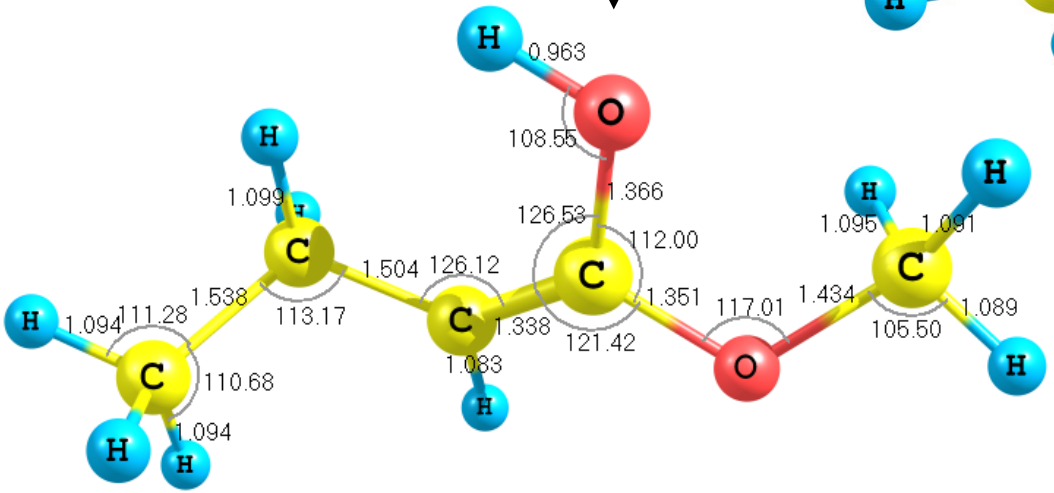
ΔH_r= +80.5 kcal/mol

Enolization



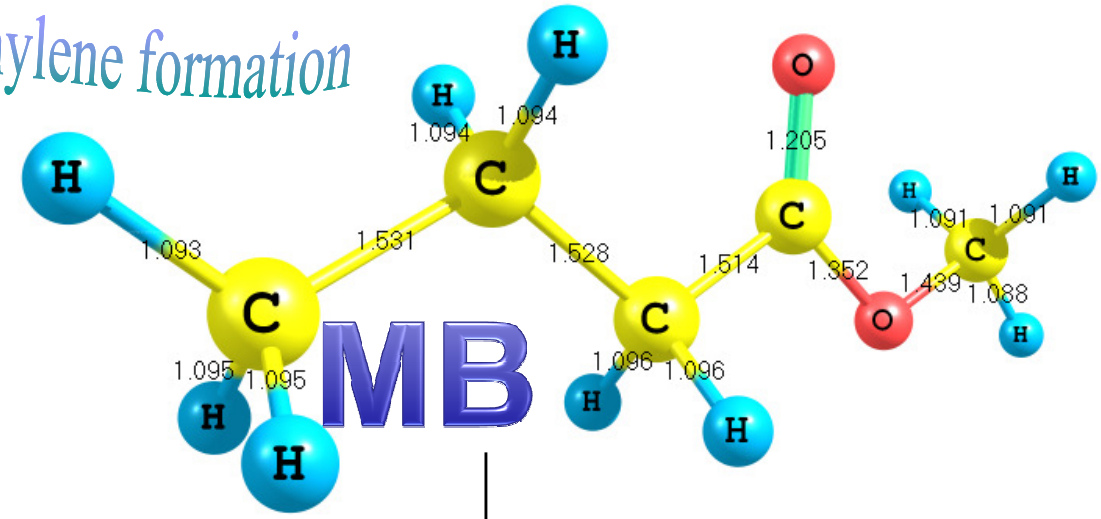
$\Delta H^{\#}$= 74.6 kcal/mol



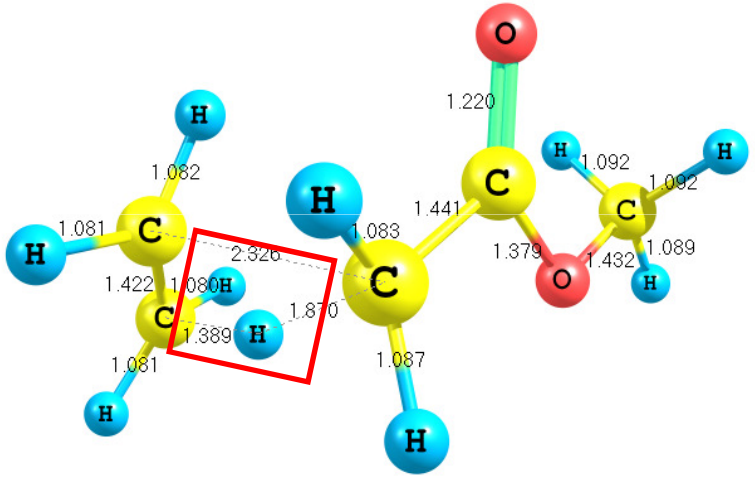


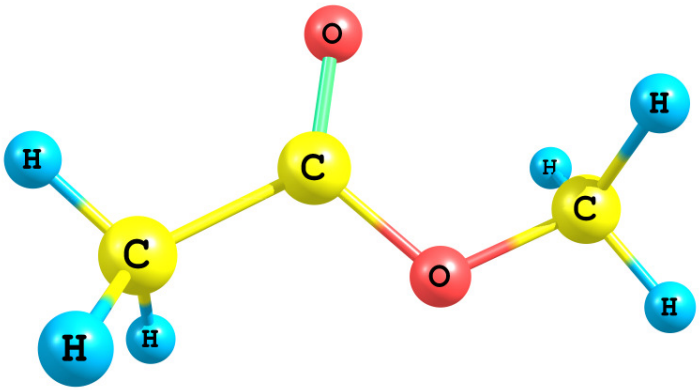
ΔH_r= +29.2 kcal/mol

Ester+ethylene formation

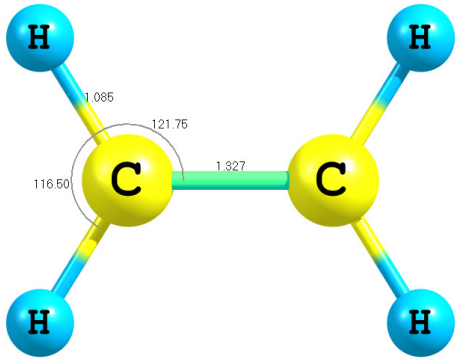


$\Delta H^{\#}$= 104.4 kcal/mol



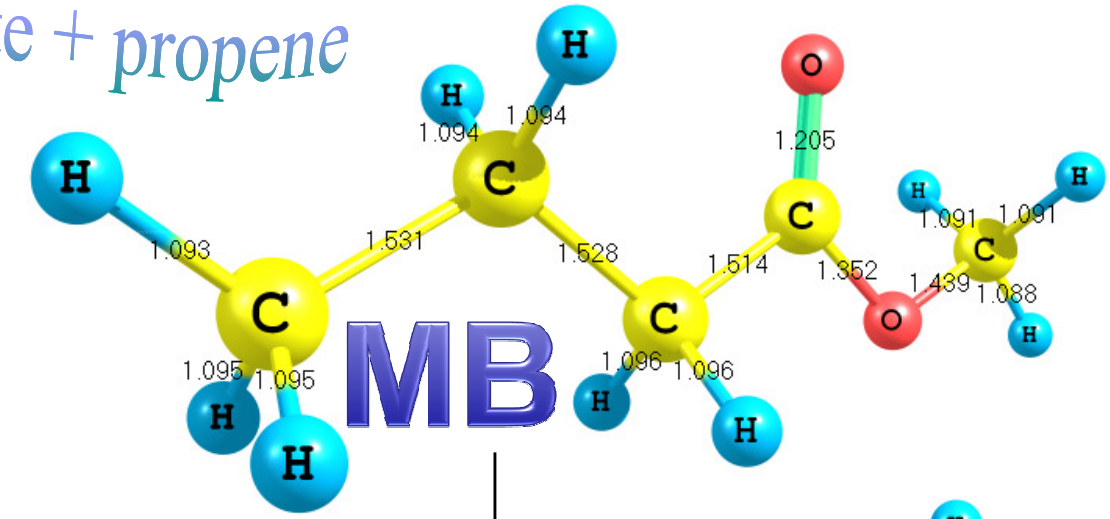


+

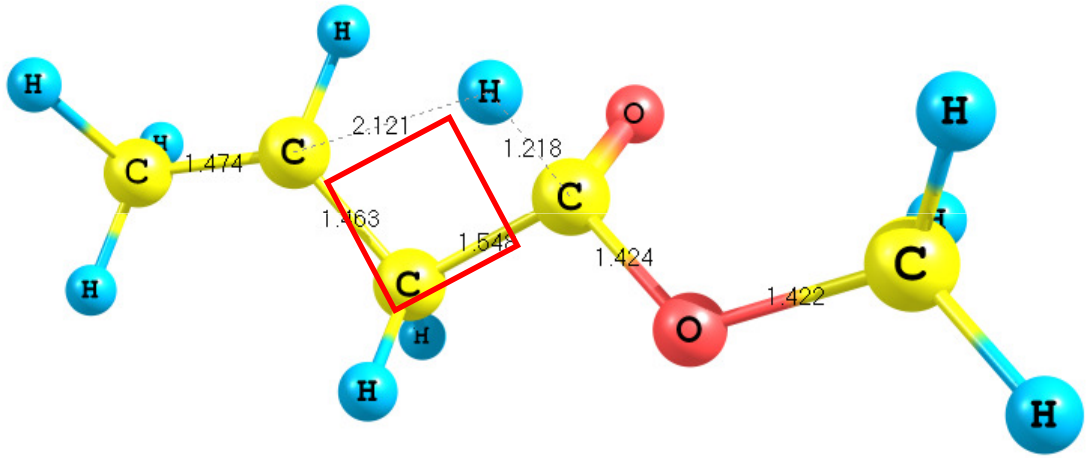


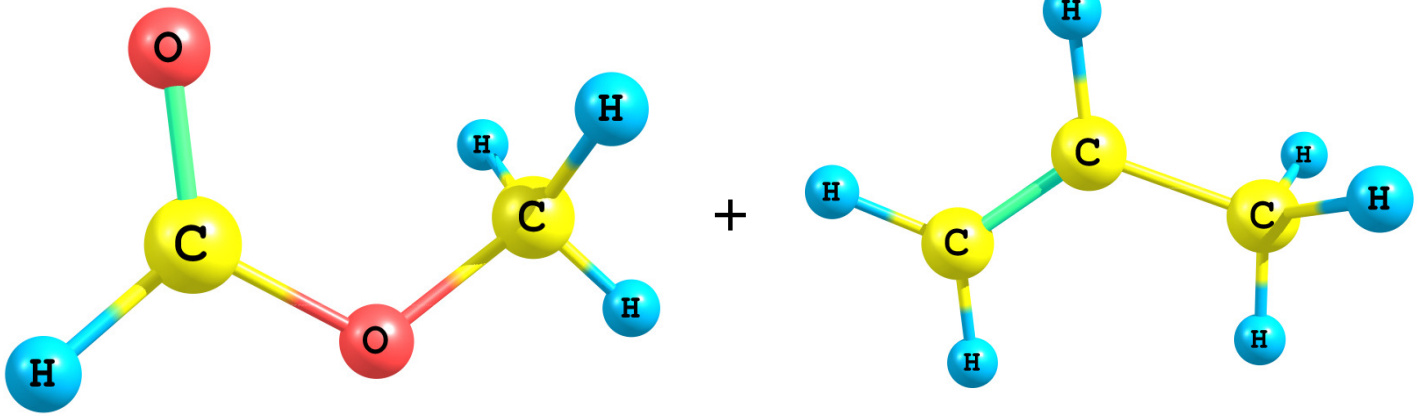
ΔH_r= +22.9 kcal/mol

Formate + propene



$\Delta H^{\#}$= 95.8 kcal/mol

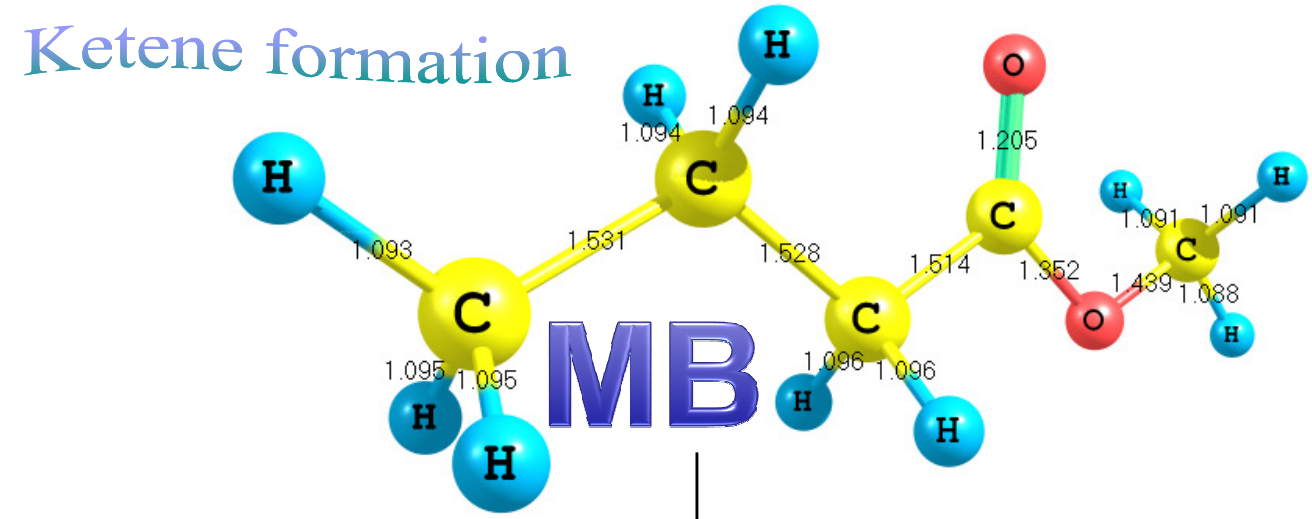




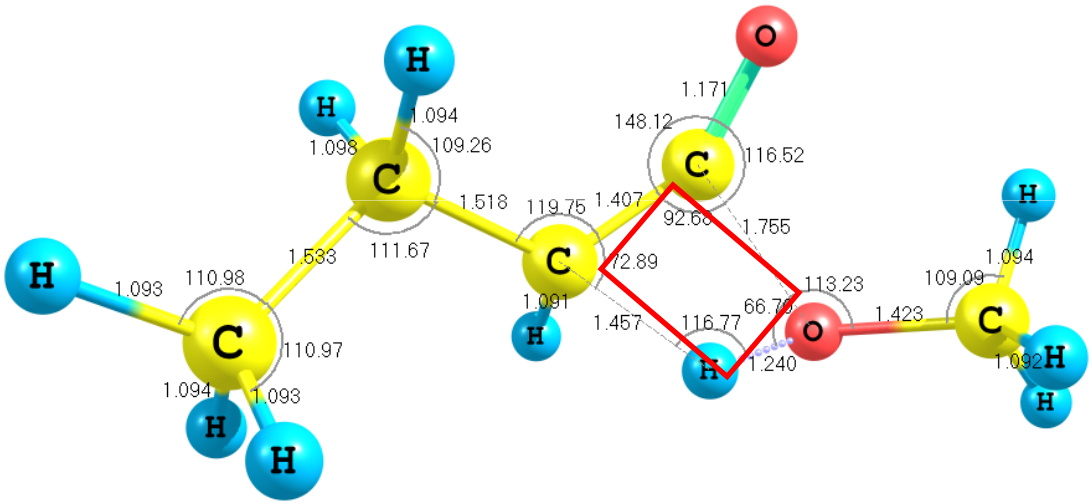
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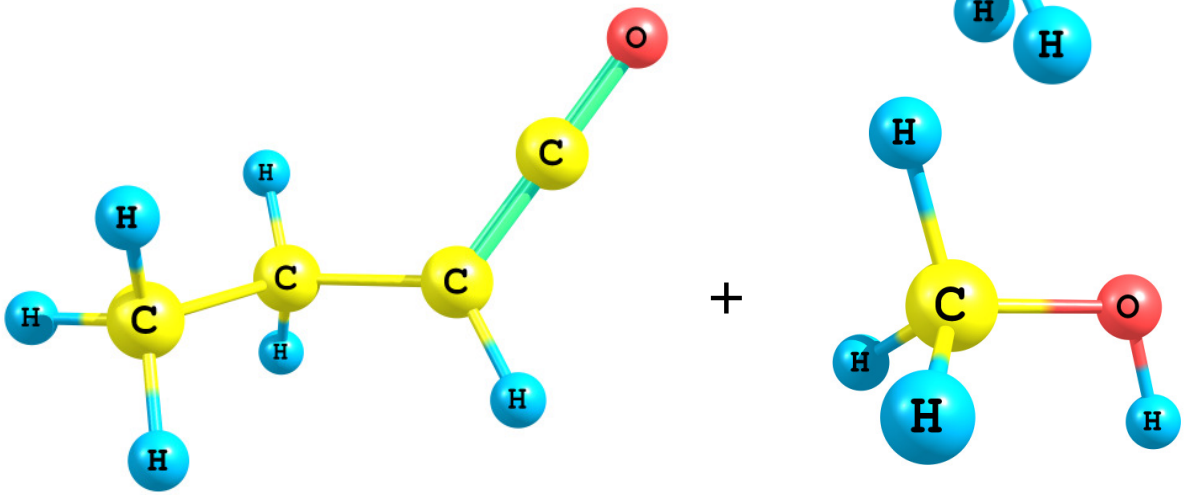
ΔH_r= +80.5 kcal/mol

Ketene formation



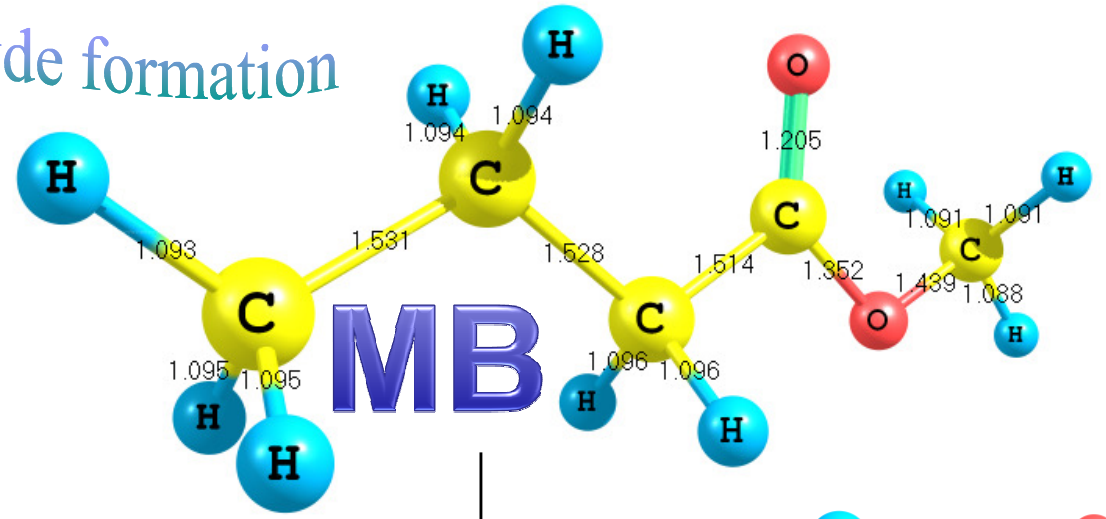
$\Delta H^{\#}$= 74.1 kcal/mol



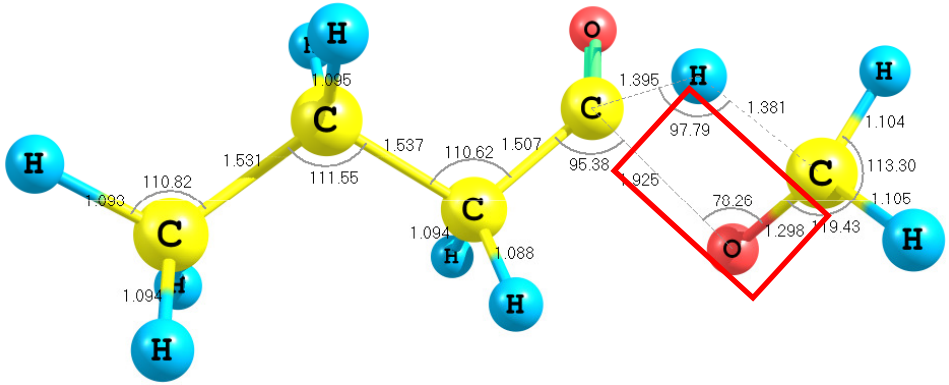


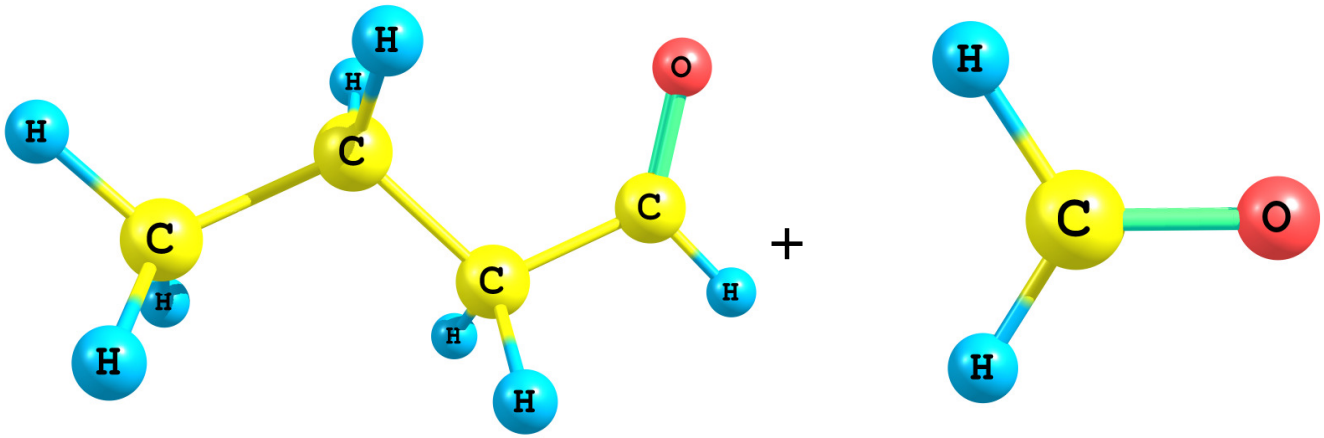
ΔH_r= +39.7 kcal/mol

Aldehyde formation

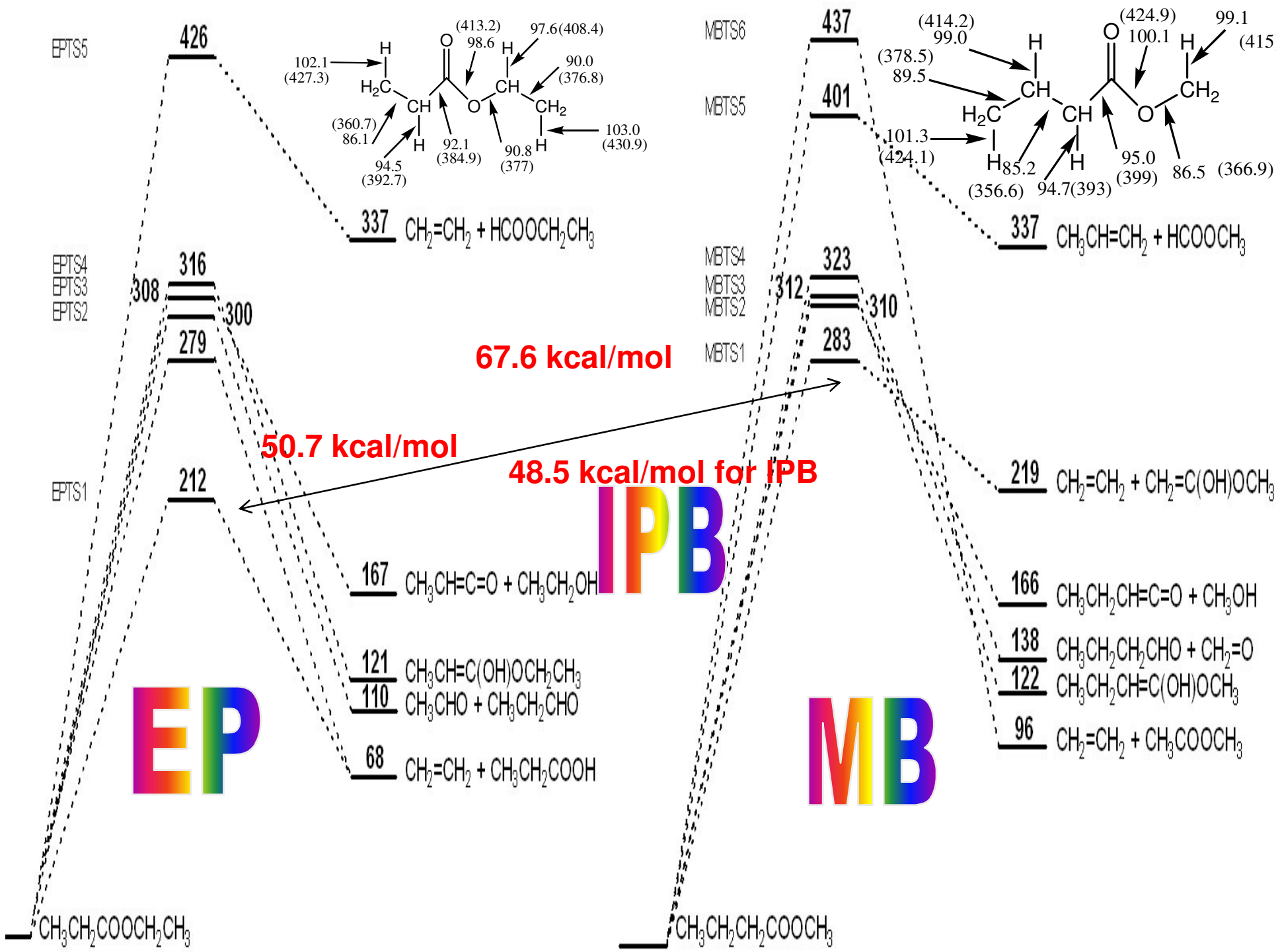


$\Delta H^{\#}$= 74.1 kcal/mol





ΔH_r= +33.0 kcal/mol


EPTS5
426
EPTS4
EPTS3
EPTS2
316
308
300
279
EPTS1
212
337 CH2=CH2 + HCOOCH2CH3
167 CH3CH=C=O + CH3CH2OH
121 CH3CH=C(OH)OCH2CH3
110 CH3CHO + CH3CH2CHO
68 CH2=CH2 + CH3CH2COOH
CH3CH2COOCH2CH3
EP
(413.2)
98.6
97.6(408.4)
102.1
(427.3)
90.0
(376.8)
(360.7)
86.1
92.1
(384.9)
90.8
(377)
103.0
(430.9)
94.5
(392.7)
67.6 kcal/mol
50.7 kcal/mol
48.5 kcal/mol for IPB
IPB
MBTS6
437
MBTS5
401
MBTS4
MBTS3
MBTS2
323
312
310
MBTS1
283
337 CH3CH=CH2 + HCOOCH3
219 CH2=CH2 + CH2=C(OH)OCH3
166 CH3CH2CH=C=O + CH3OH
138 CH3CH2CH2CHO + CH2=O
122 CH3CH2CH=C(OH)OCH3
96 CH2=CH2 + CH3COOCH3
CH3CH2CH2COOCH3
MB
(414.2)
99.0
(424.9)
100.1
99.1
(415
(378.5)
89.5
101.3
(424.1)
85.2
(356.6)
94.7(393)
95.0
(399)
86.5
(366.9)

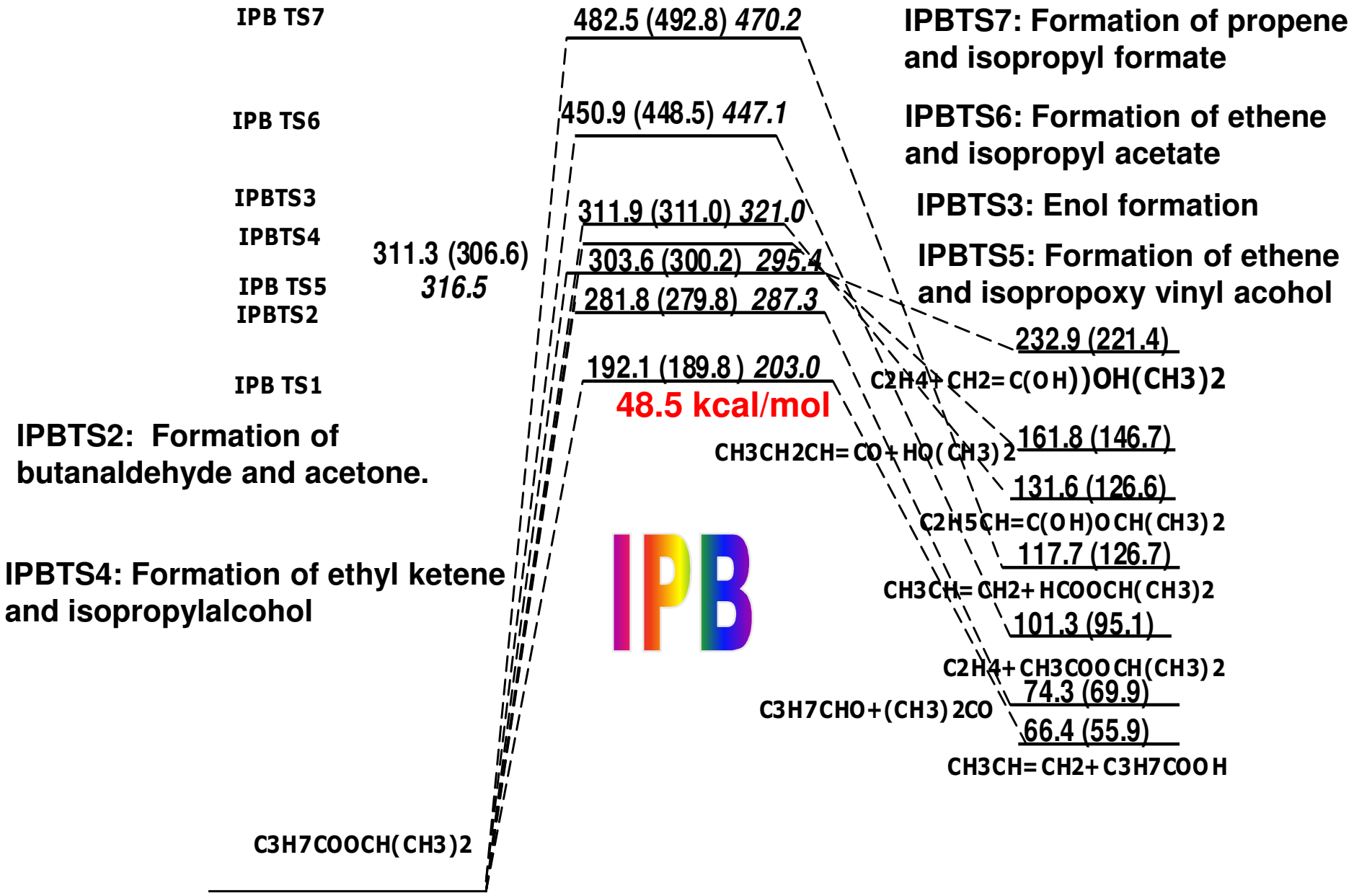


Figure 12: Energy profile for unimolecular decomposition of **IPB** (ΔE_0, $\Delta E^{\#}_0$, kJ/mol) at BMK/6-31+G(d,p), BMK/6-311++G (2d, 2p)//BMK /6-31+G(d,p) (given in parentheses) and CBS-QB3 (Italic).

Conclusions

- **The three esters EP, MB, IPB give alkene as a main product.**
- **Simple bond fission costs less energy than lower ester formation.**
- **Alcohols, lower esters, aldehydes, ketene are also produced at higher temperatures.**
- **IPB can be decomposed faster than the other two esters, 203. Vs. 210 and 285 kJ/mol for propene and ethene formation.**
- **Aldehyde formation is easier from EP than MB because C-O is weaker in the former ester, 420 vs. 424 kJ/mol .**

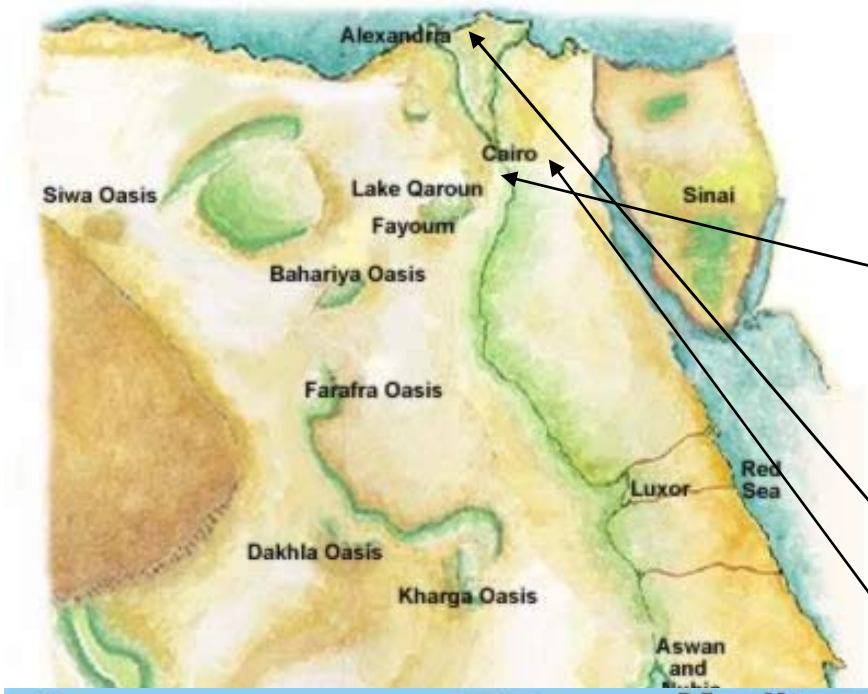
Ongoing work

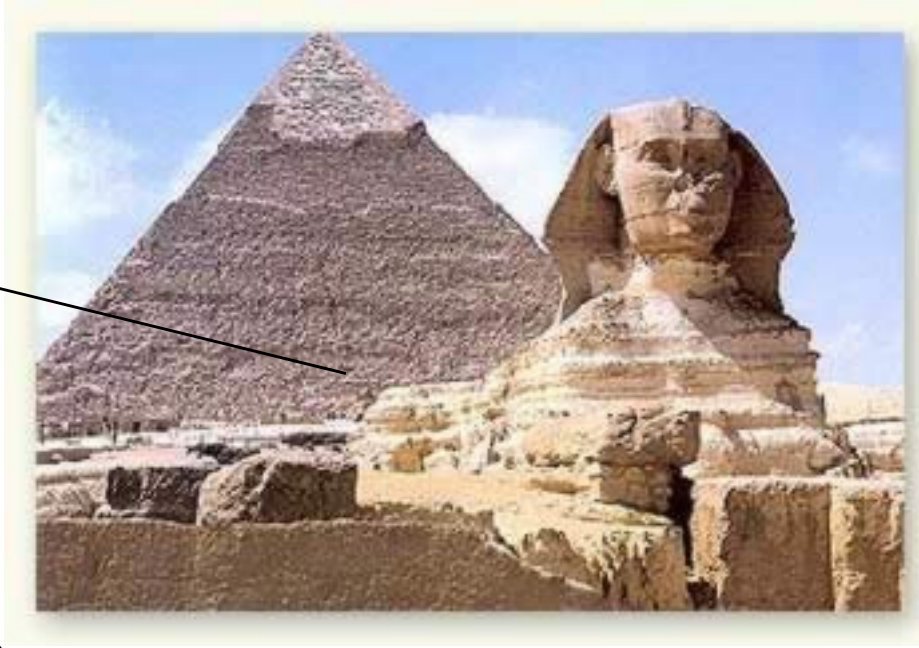
• Reactions of different radicals with O_2 molecules and subsequent degradation to exit channel of CO_2 and H_2O .

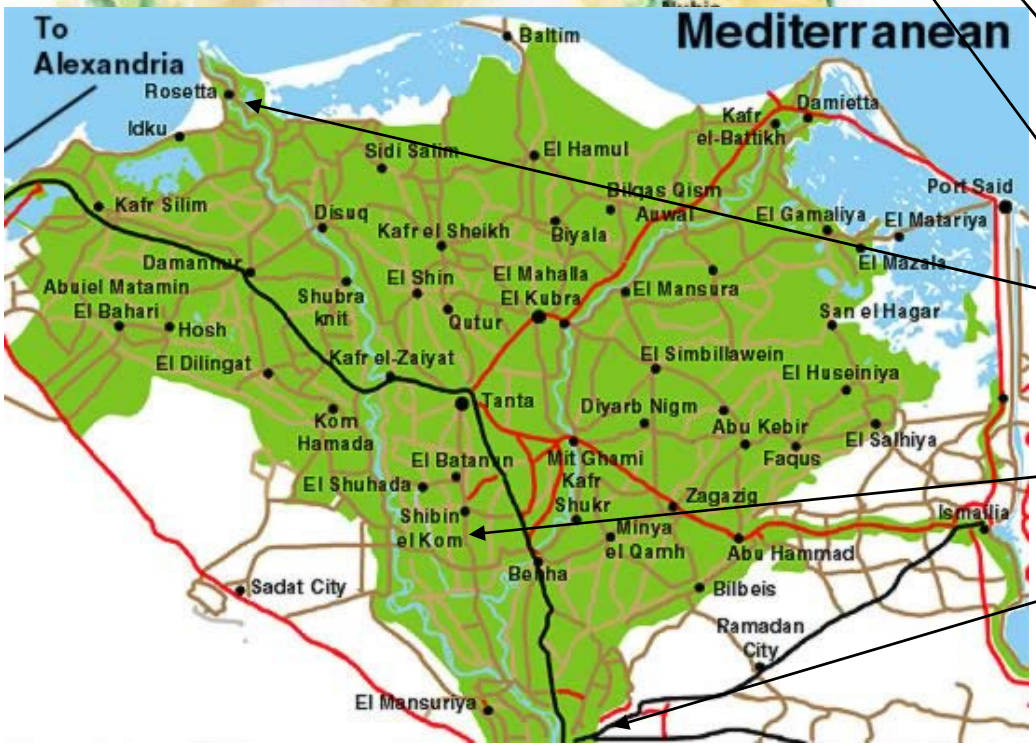
• Reactions of 2-butanaol, isobutanol, and esters with different oxidants: OH, O, O_2, H, O2H, CH3 radicals.

Future projects

•Thermochemisrty and kinetics of the 2ºry reactions (beta-sessions) of radicals.
• Water-assisted reactions for elimination reactions.
• Quest for efficient catalysts for biodeisel production (transesterification).
•Competition between propagation and termination processes.







Alexandria

Shebin El-Kom

Cairo


Thank you for your attention