Diesel Fuel Chemistry Modeling

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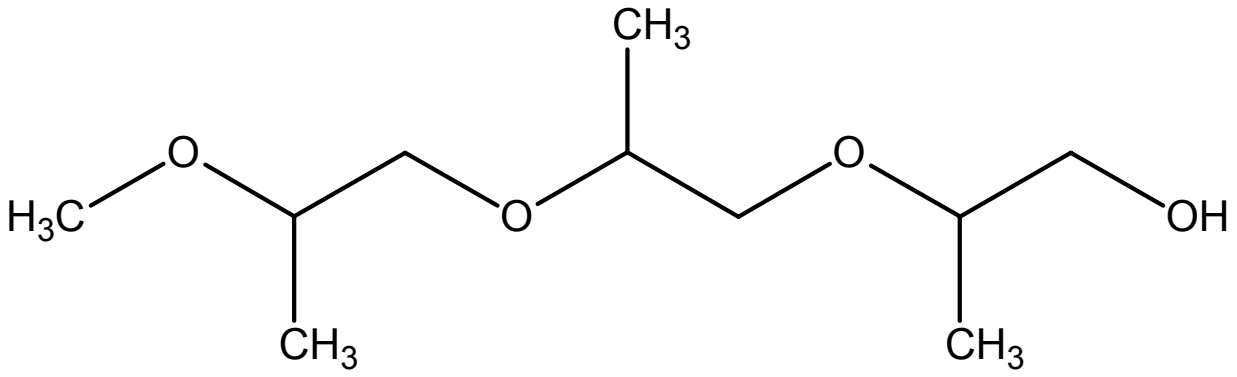
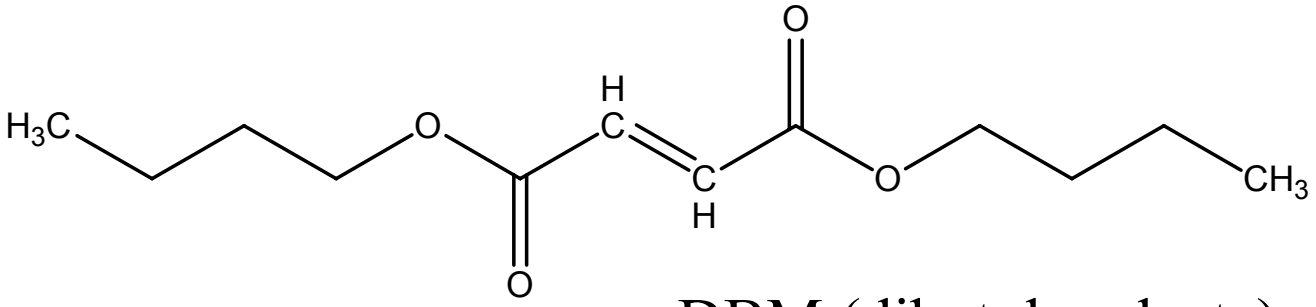
Objectives and Approach

- Use kinetic modeling to address problems in diesel and HCCI combustion
- Specifically address soot and NOx production, ignition
- Focus on problems related to fuel chemistry
- Develop fundamental understanding of interactions between combustion chemistry and fluid mechanics and engine operating parameters
- Transfer fuel chemistry expertise to industrial and university program and individuals

Top oxygenates selected by DOE screening study



TPGME (tri-propylene glycol monomethyl ether)

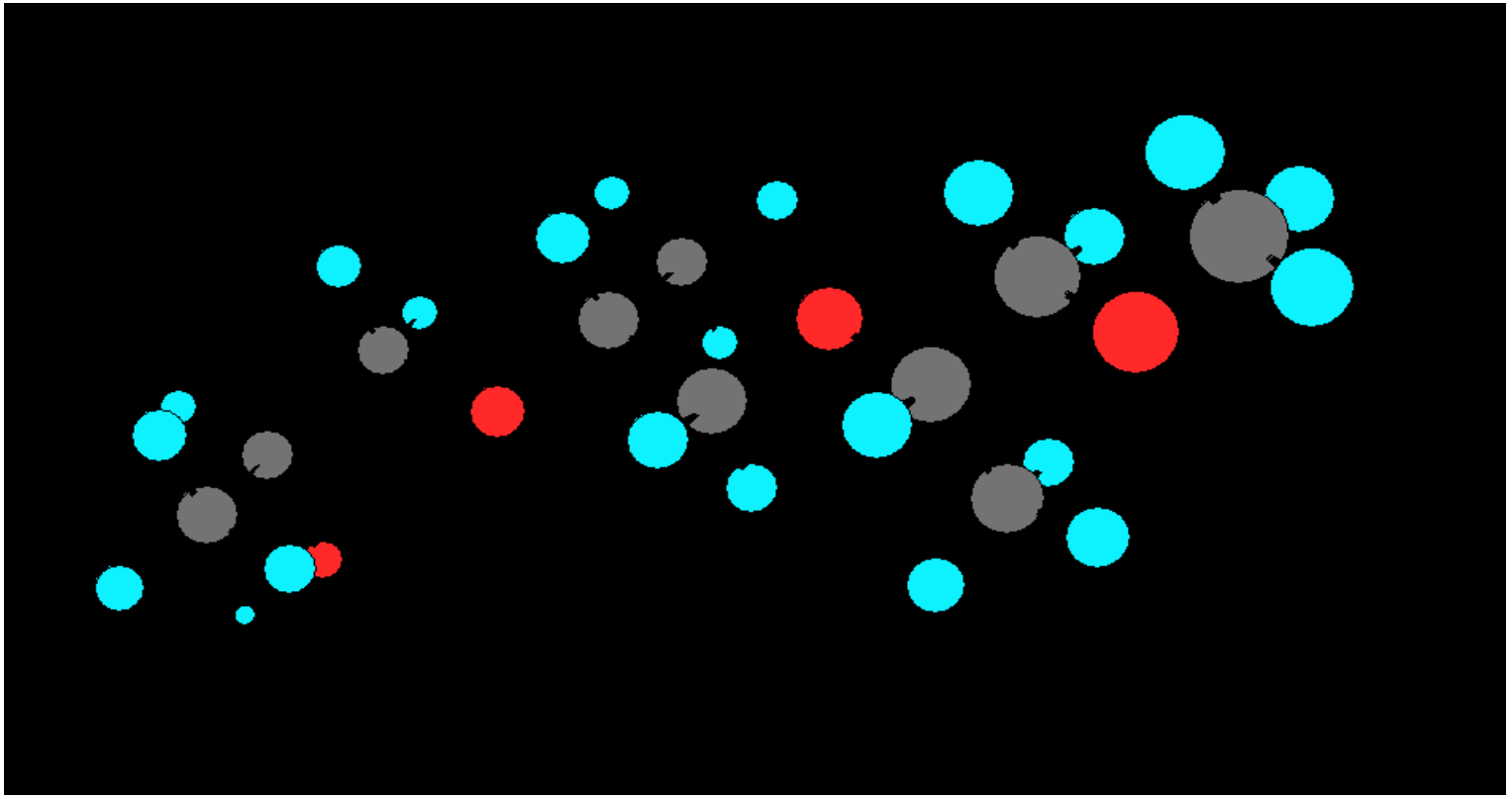


DBM (dibutyl maleate)

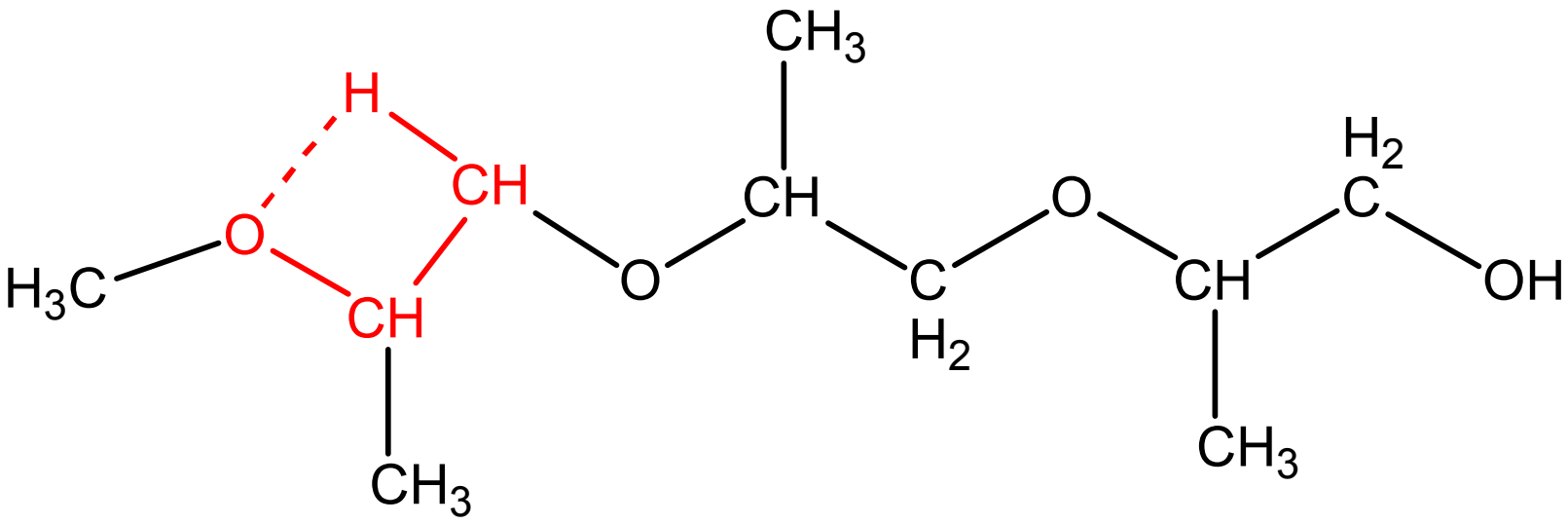
Current interest in TPGME

- Presence of three propene fragments in TPGME suggests it may produce lots of soot precursors
- Three oxygen atoms well distributed in the TPGME molecule
- Plan is to reproduce previous diesel ignition calculations but use TPGME as the oxygenated additive, compare with effectiveness of other oxygenated additives
- Large fuel molecule involves modeling challenges

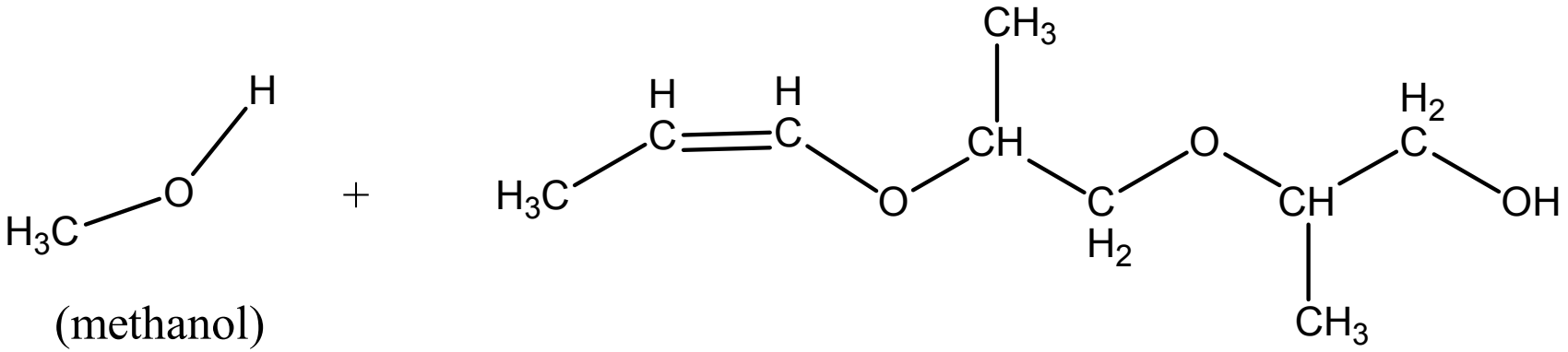
Structure of
Tripropylene Glycol Monomethyl Ether (TPGME)



TPGME is initially consumed by four-centered elimination reactions

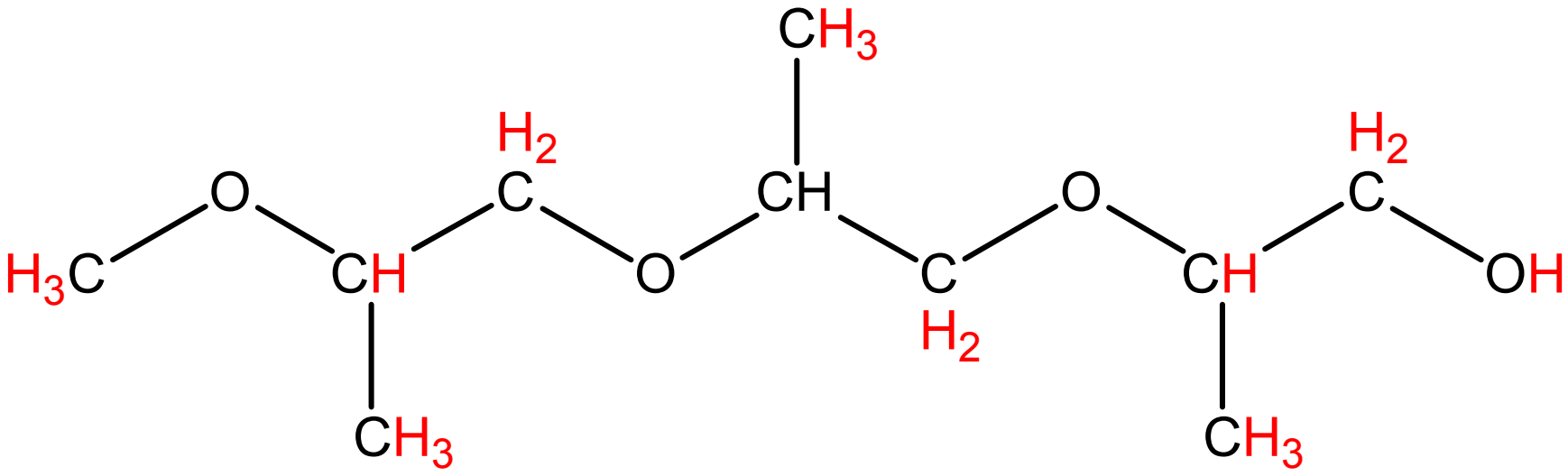


Methanol and an oxygenated product are formed

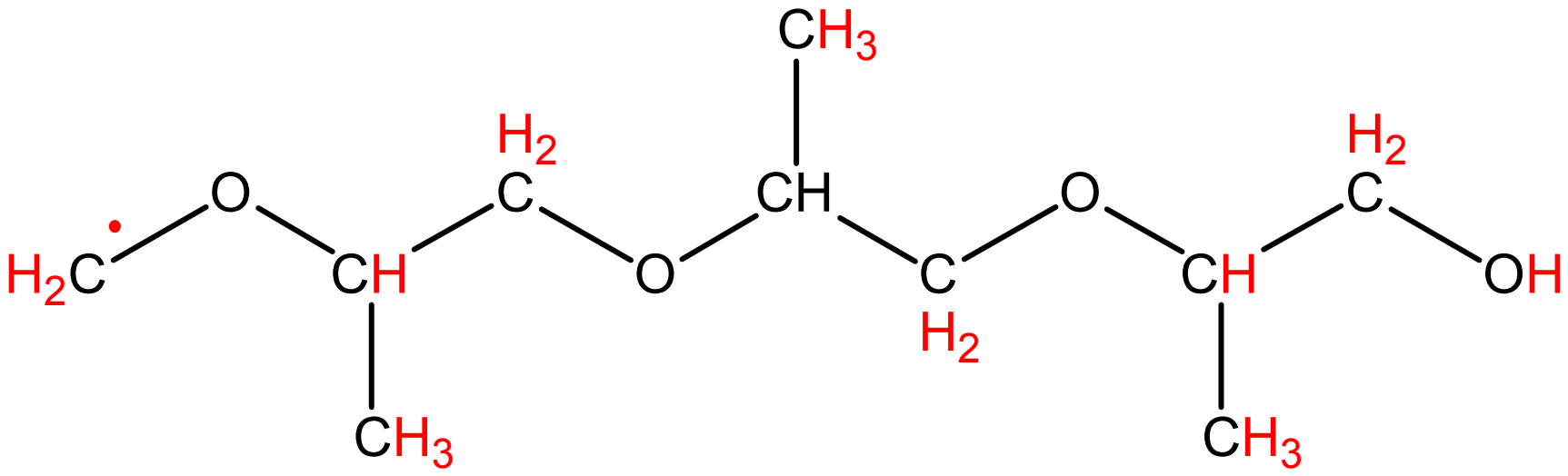


(methanol)

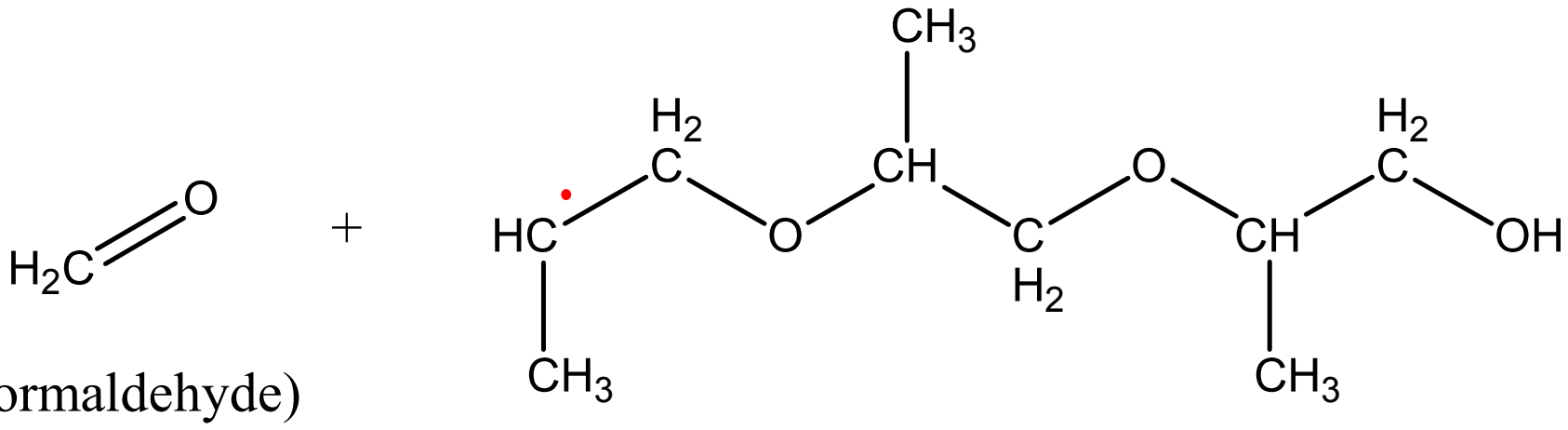
Another class of reactions for TPGME involves H atom abstraction



Consumption of TPGME radicals lead to aldehydes and propylene

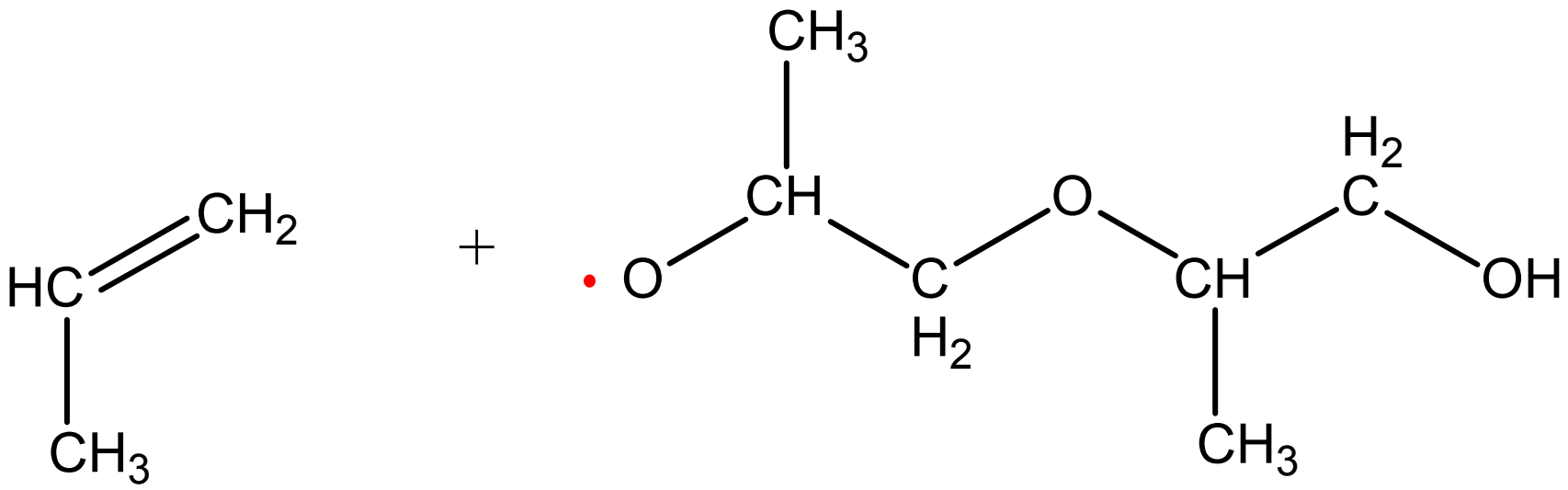


First product of decomposition is formaldehyde which ties up one C atom with oxygen



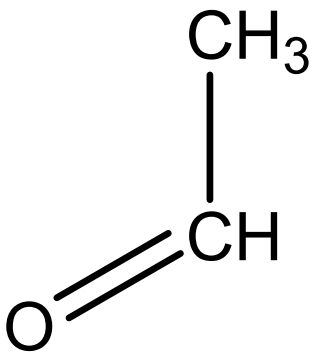
(formaldehyde)

Second product is propene, which is a possible soot precursor



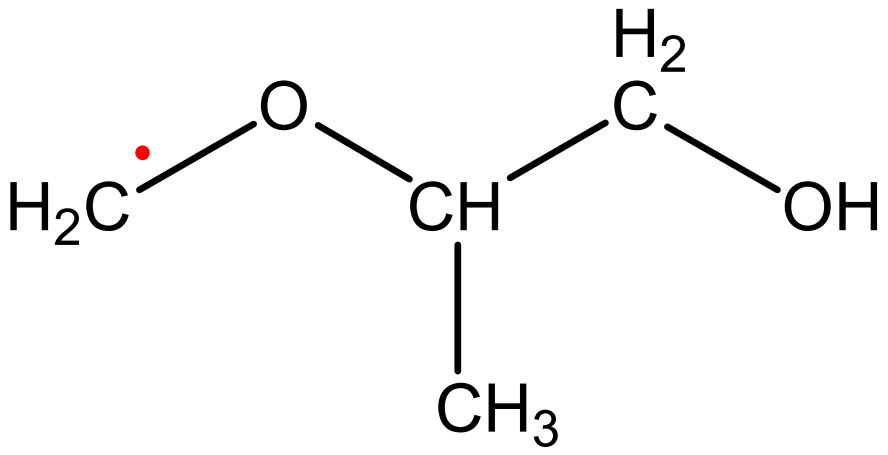
(propylene)

Third product is acetaldehyde which ties up two C atoms that cannot lead to soot

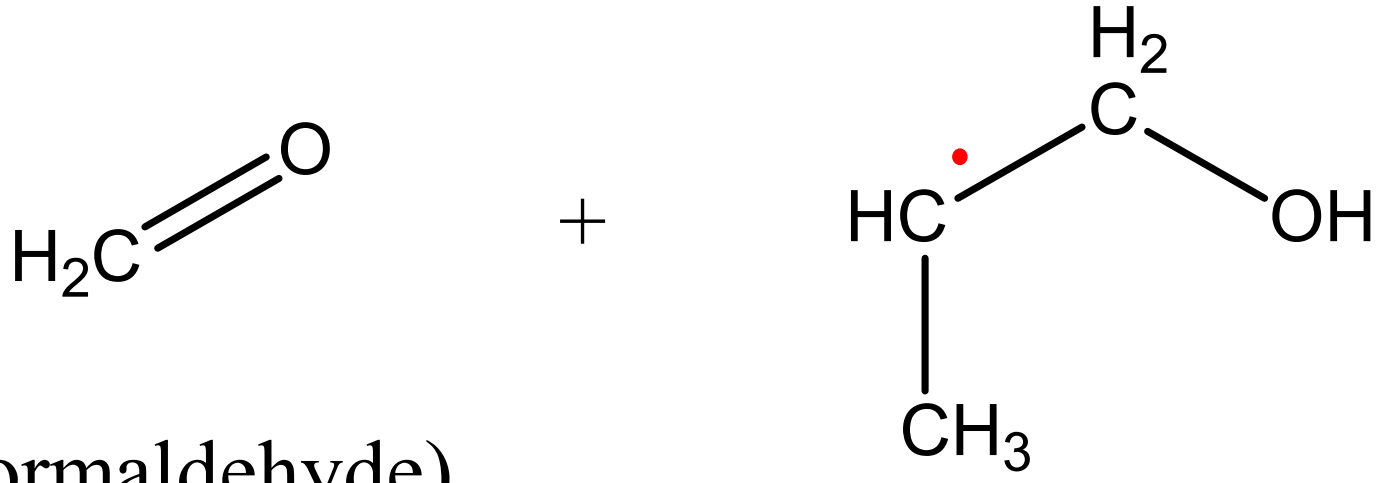


(acetaldehyde)

+

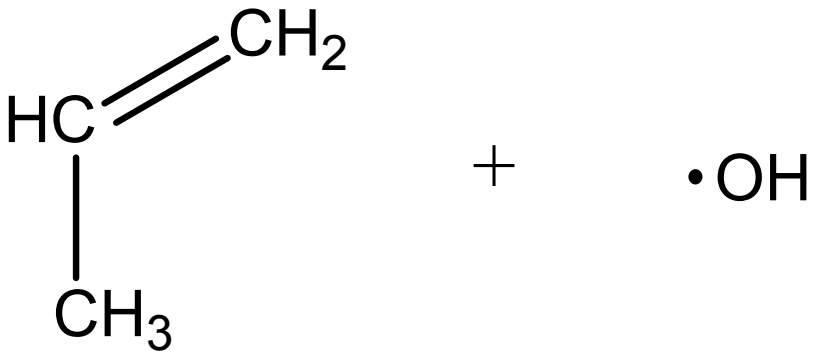


Fourth product is another formaldehyde, a non-sooting intermediate species



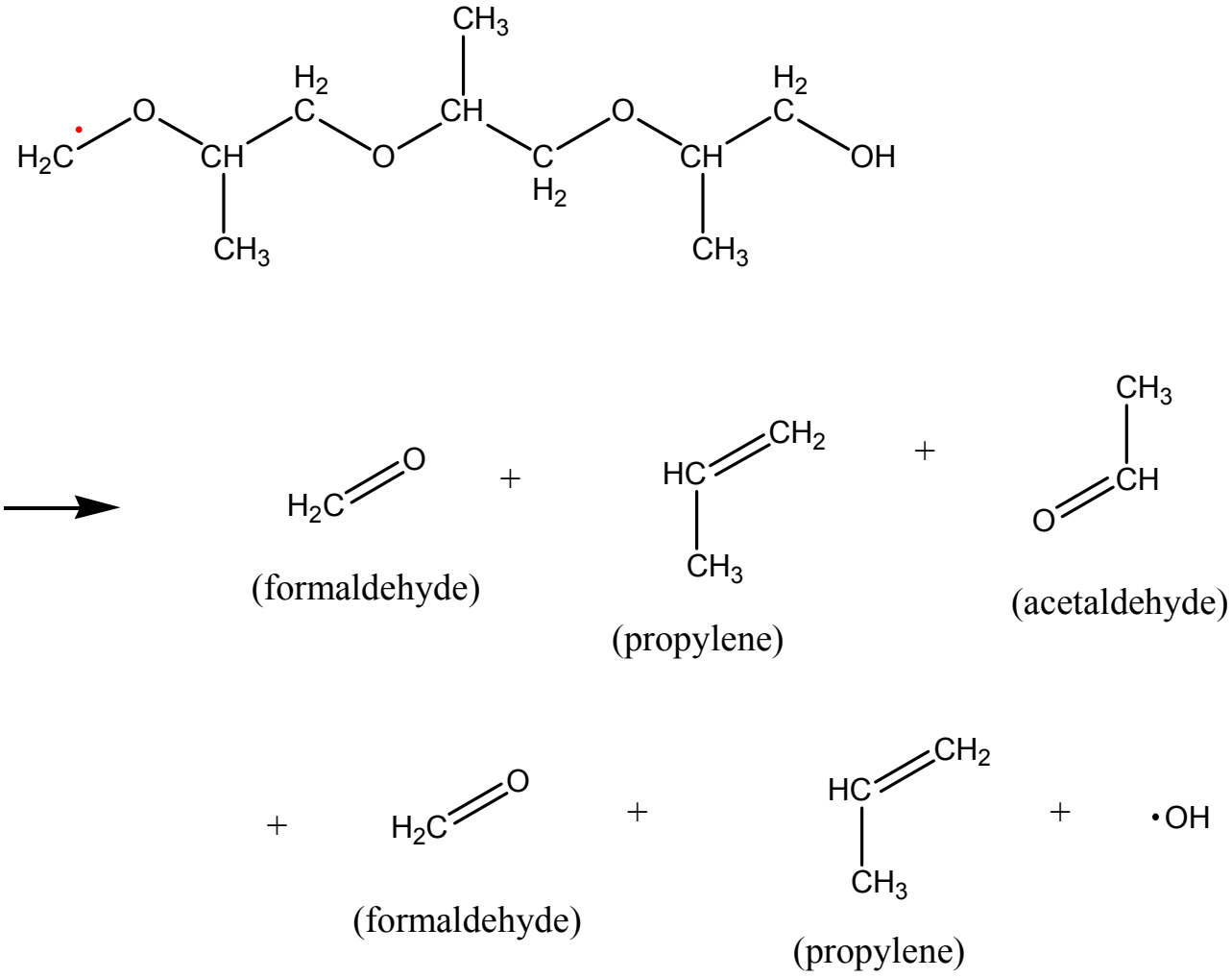
(formaldehyde)

Final products include propene and OH



(propylene)

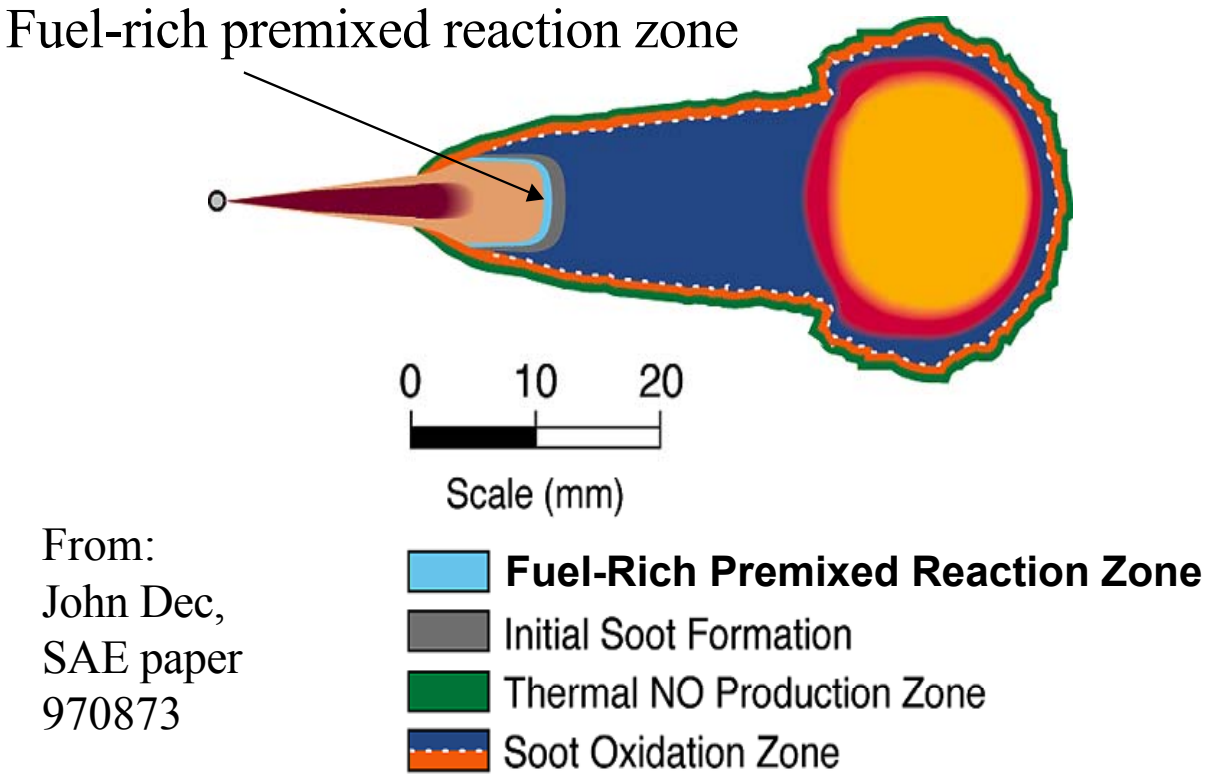
Consumption of 1-TPGME radical



Repeat the same analysis for the other 10 distinct H atoms in TPGME molecule

- A different mixture of products will result for each radical
- Each mixture will have a different impact on soot precursors
- In each case, the O atoms are well dispersed and are very effective in sequestering C atoms in the TPGME
- On average, between one and two propene molecules produced

Predicting the soot precursors is one of the keys to predicting soot emissions from a Diesel engine

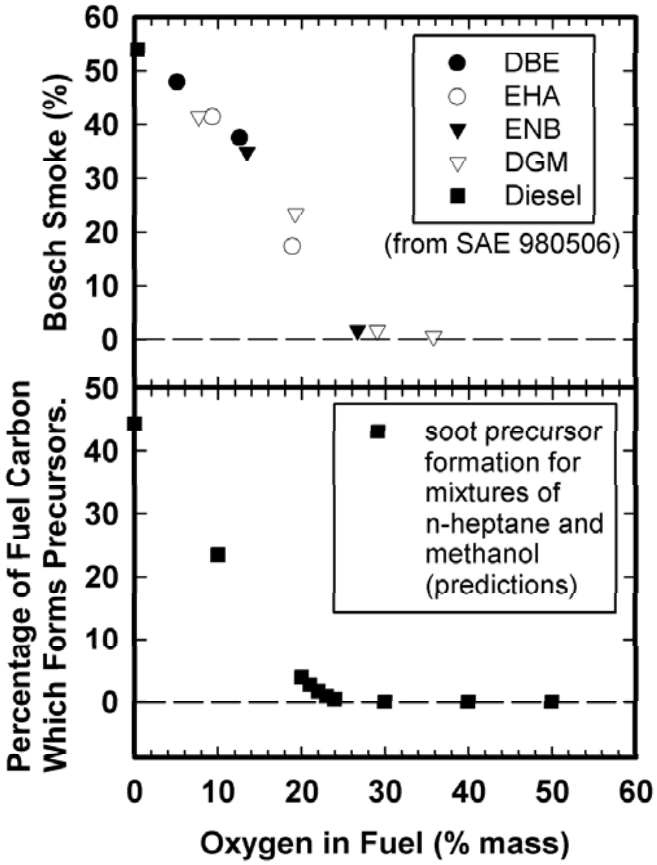


From:
John Dec,
SAE paper
970873

All these chemical reactions are combined to produce a kinetic model for diesel ignition

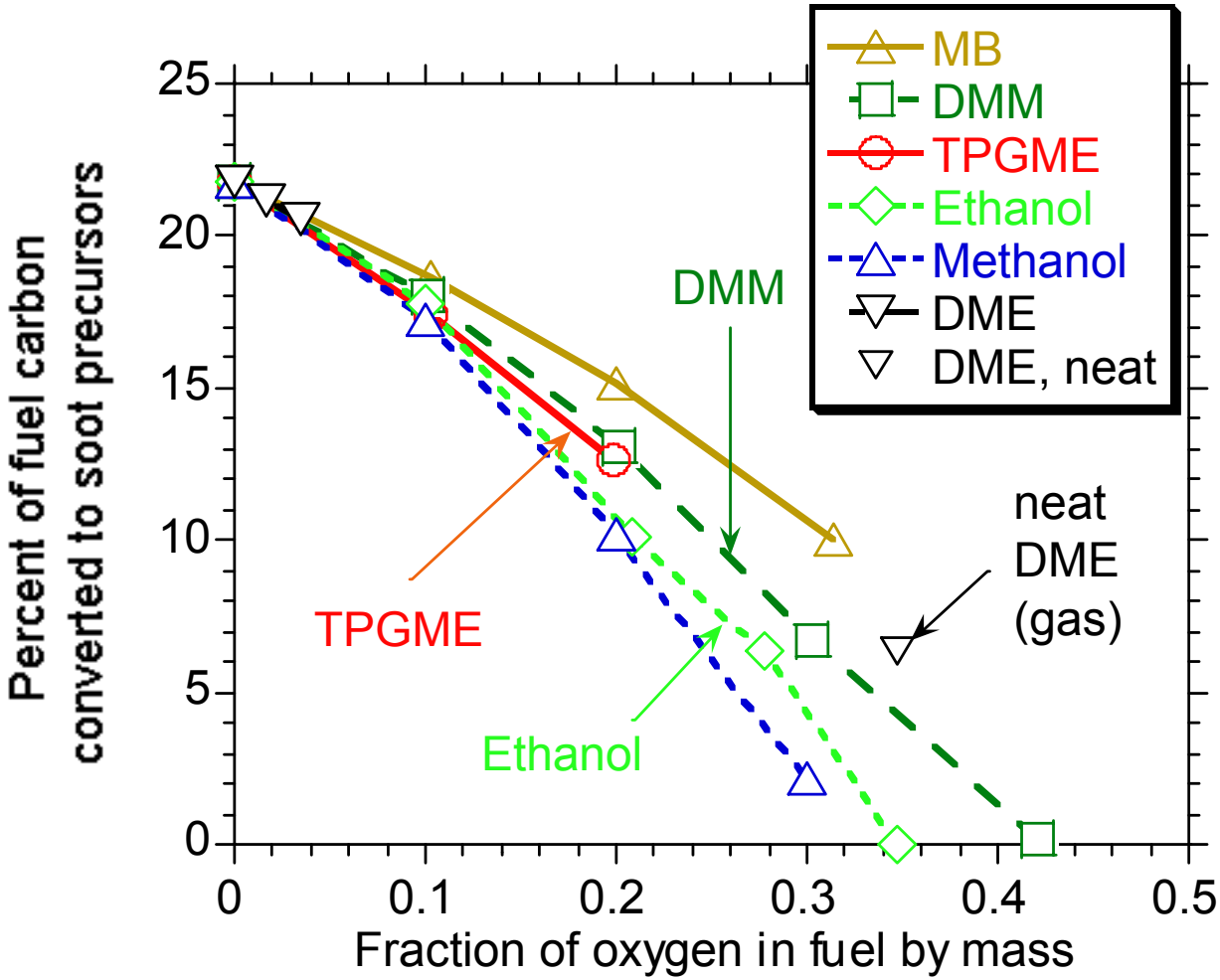
- Diesel fuel is represented by n-heptane
- Rich premixed ignition is computed
- Reaction products are correlated with soot precursors
- Soot precursor products change when oxygenated additives are included in the diesel fuel
- Past studies have shown that oxygenates reduce soot precursors, and all oxygenates previously analysed are approximately equally effective in reducing soot precursor levels

Predicted level of soot precursors correlates well with soot emissions from a Diesel engine



From:
Flynn, Durrett, Dec, Westbrook, et al., SAE paper 1999-01-0509

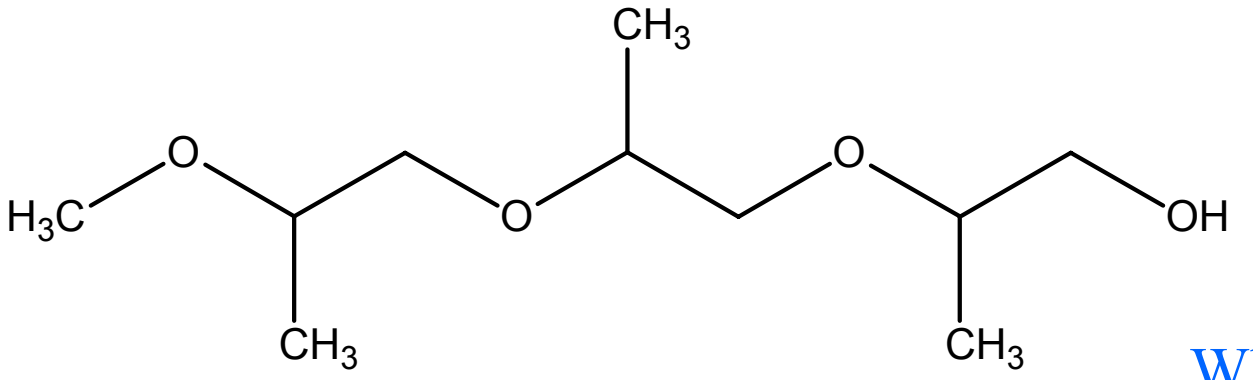
Computed results for soot precursor reduction with TPGME are very similar to other additives



Implications of these modeling results for TPGME

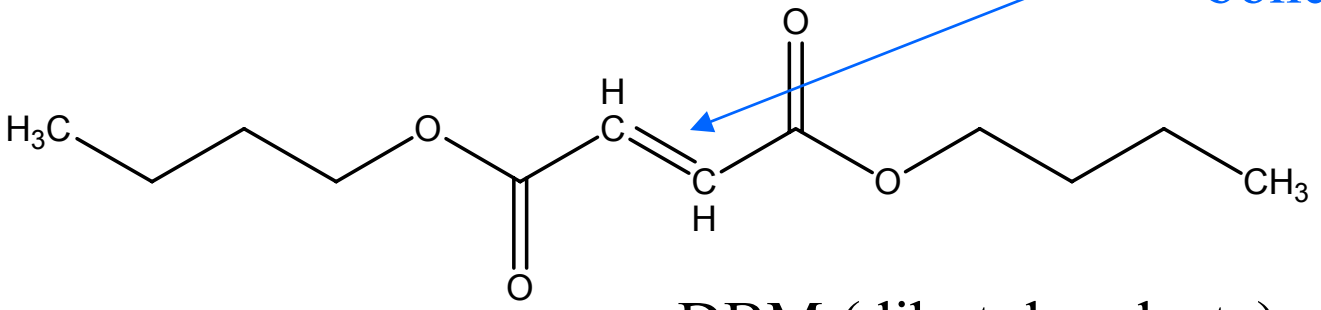
- TPGME reduces soot precursors with effectiveness equal to other oxygenates already studied
- Distribution of O atoms in TPGME is particularly good -- does this suggest other good non-sooting oxygenates?
- These results reinforce general relation of soot reduction to oxygen content in fuel
- Additive may thus be selected to optimize other operational characteristics, such as fuel/additive solubility, vapor pressure, cost, toxicity or other factors

Oxygenates selected by DOE screening study



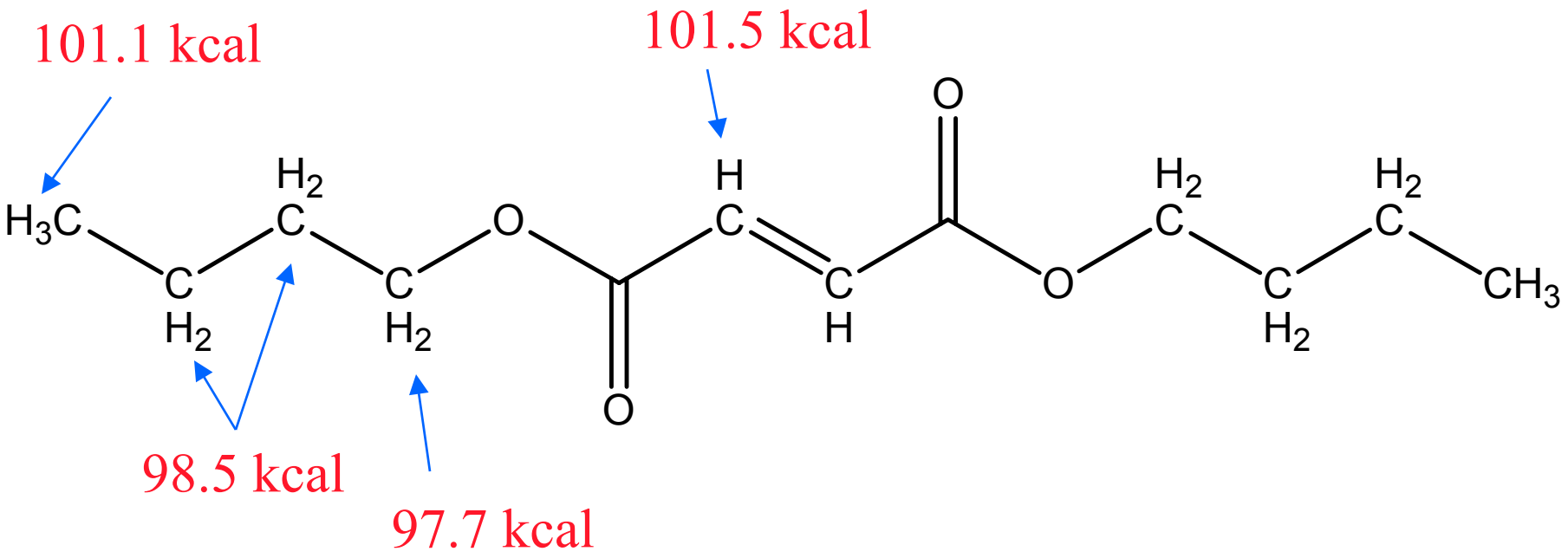
TPGME (tri-propylene glycol monomethyl ether)

What is effect of double bond?

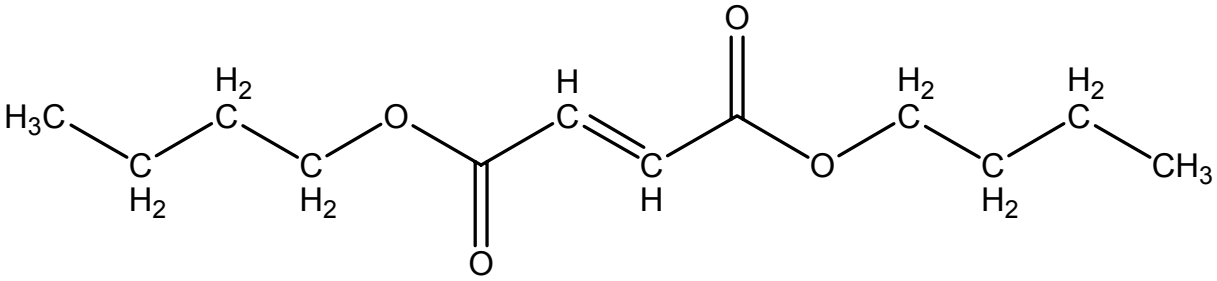


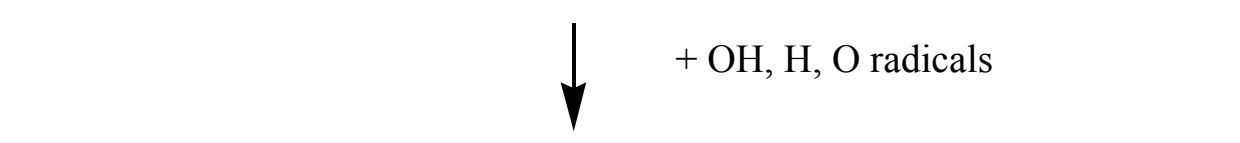
DBM (dibutyl maleate)

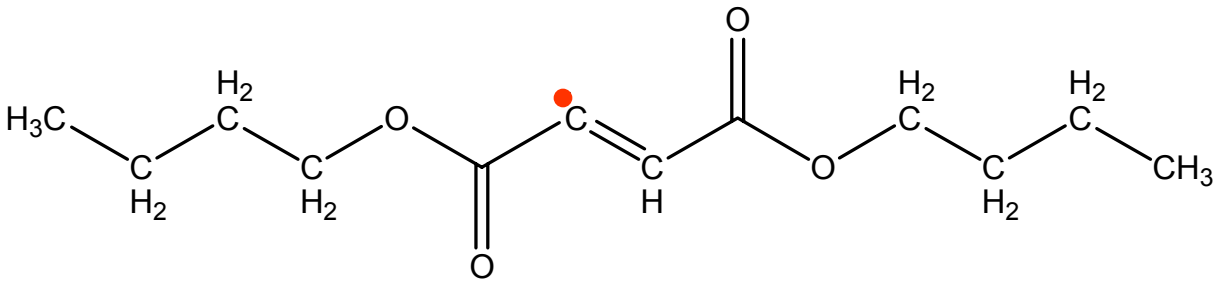
How is DBM likely to be consumed?

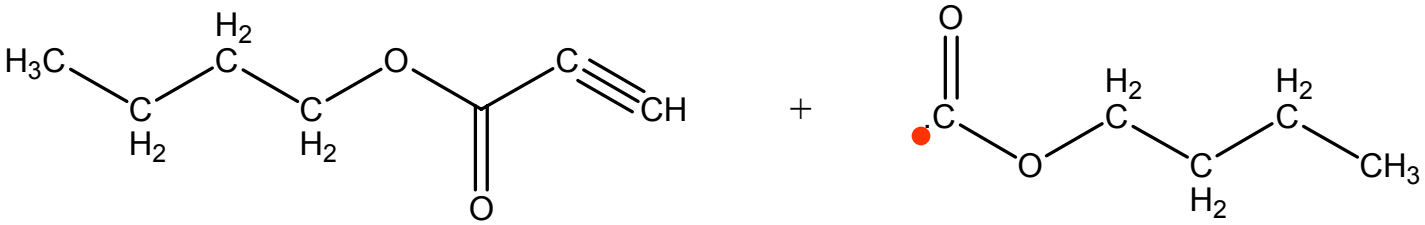


Important path for consumption of DBM:

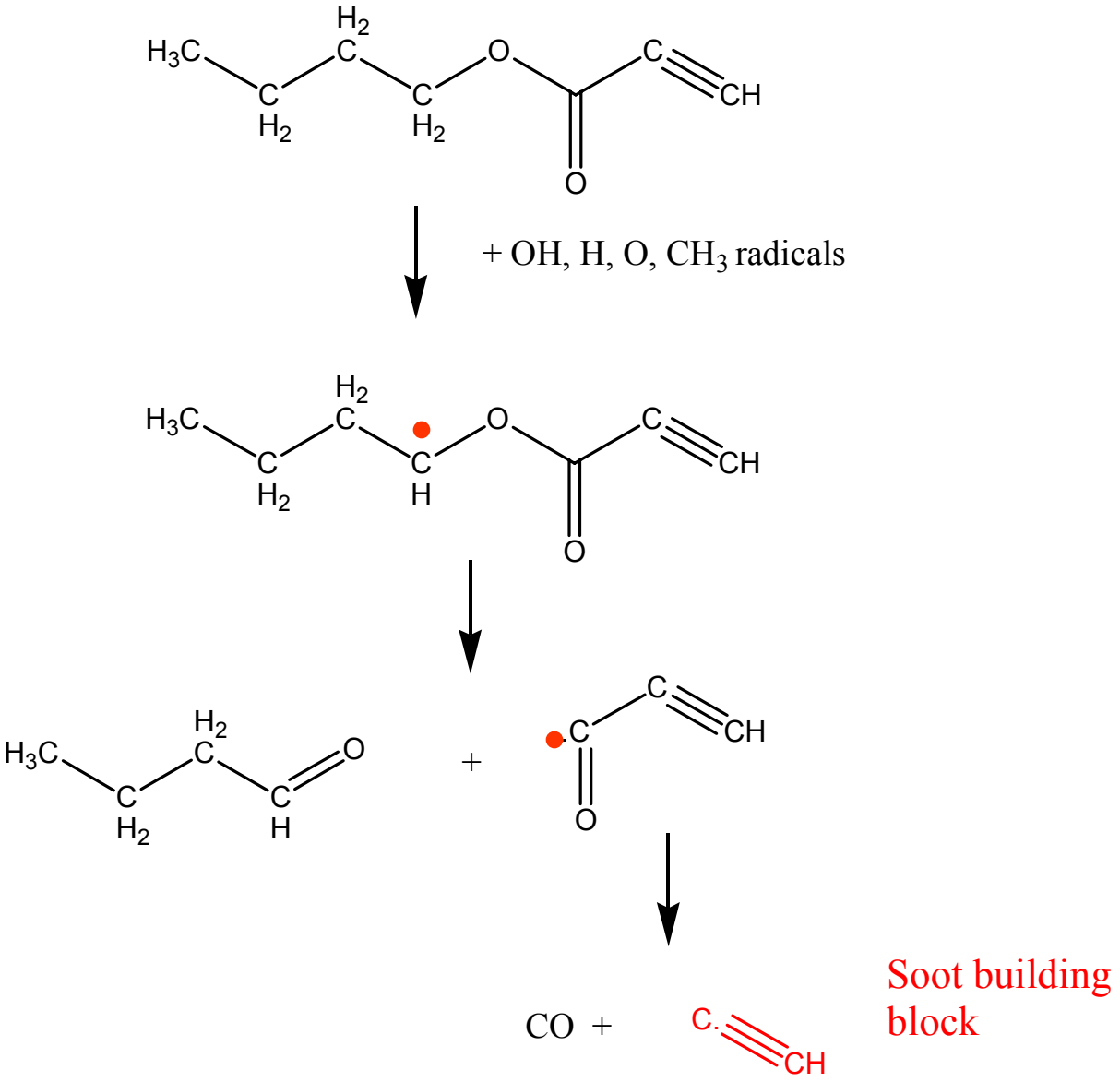




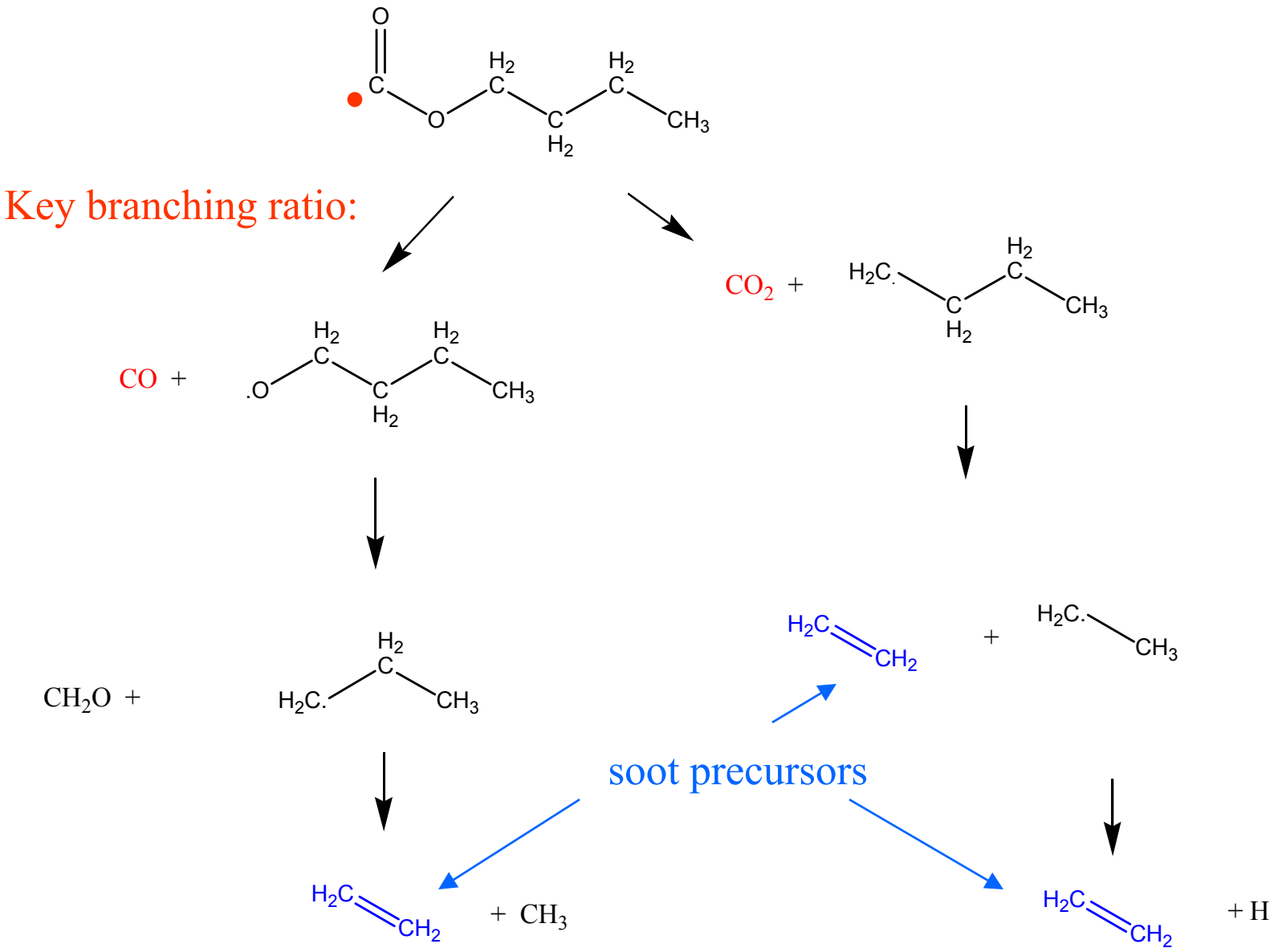




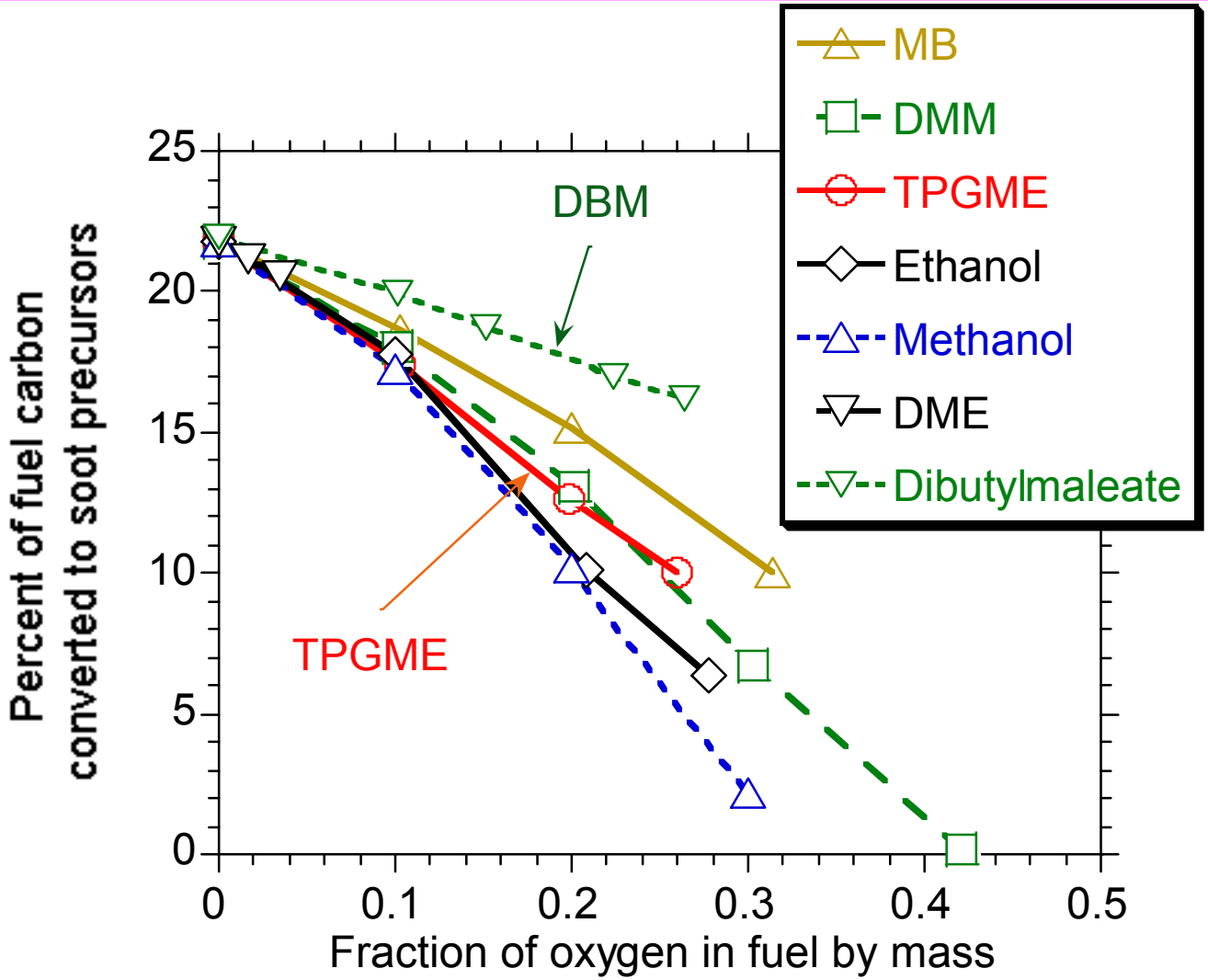
Consumption of vinyl-type DBM radical leads to “soot building block” :



Other DBM radical can lead to one or two vinyl radicals:



Computations show that dibutyl maleate (DBM) is less effective in reducing soot precursors than TPGME or the synthetic biodiesel fuel Methyl butanoate (MB)

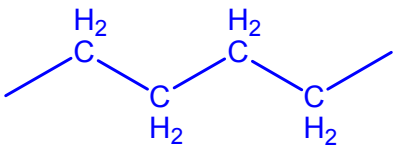


Implications of these modeling results for DBM

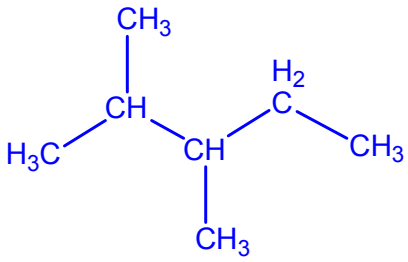
- Double bonds involving O atoms make those O atoms ineffective in trapping C in non-sooting precursors
- Distribution of O atoms in DBM is not very good -- some O atoms progress directly to CO_2
- Double bonds between C atoms in fuel produce higher quantity of soot precursors
- Model results suggest DBM should be somewhat less effective (per O atom present in the fuel) in reducing sooting
- These results have been confirmed in Sandia engine experiments

Classes of hydrocarbons in diesel fuel

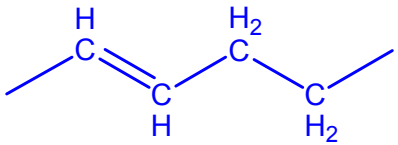
n-paraffin

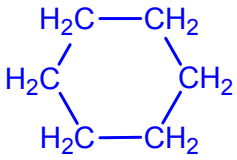


iso-paraffin

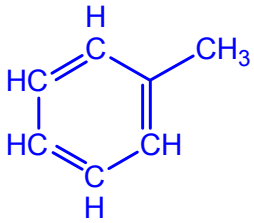


olefin

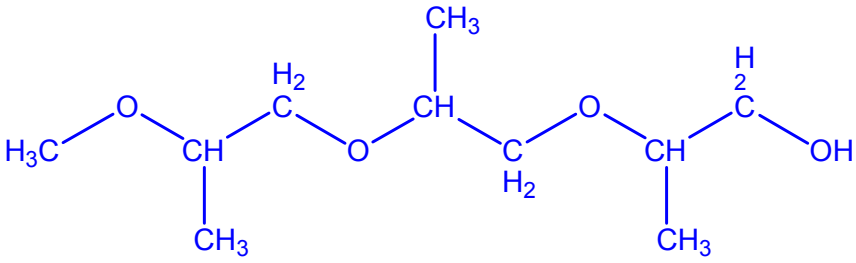




cyclo-alkane



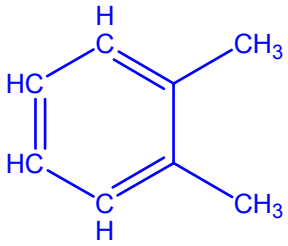
aromatic



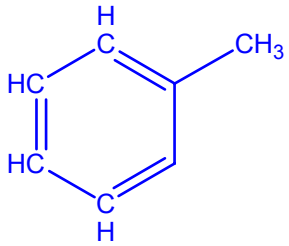
oxygenate

We have been working on kinetic models for two representative aromatic hydrocarbon

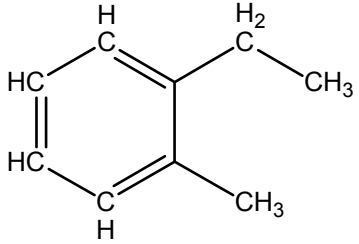
o-xylene



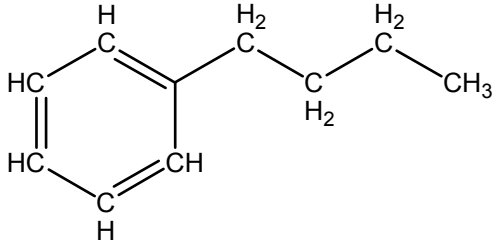
toluene



Recall that production of soot precursors leads to formation of aromatic species such as these, so the presence of these types of species in diesel fuel will certainly lead to soot production



Other aromatics for which experimental data exist to assist in model development



Models for toluene, o-xylene and cyclohexane

- Several papers on toluene combustion published
- Collaboration on o-xylene and cyclohexane with a group at Lille in France
- Both aromatics with side branches much different from benzene
- Parallels with methane
- Mechanisms ready for incorporation into diesel and HCCI fuel and surrogate fuel mixtures

Continuing efforts

- Continue development of TPGME and DBM kinetics
- Continue submodels for aromatics (toluene, xylene) and cyclo-alkanes (methyl cyclohexane, cyclopentane) as important components of diesel fuel
- Work on surrogate mixtures of components to represent a diesel fuel where we can model all of the constituents