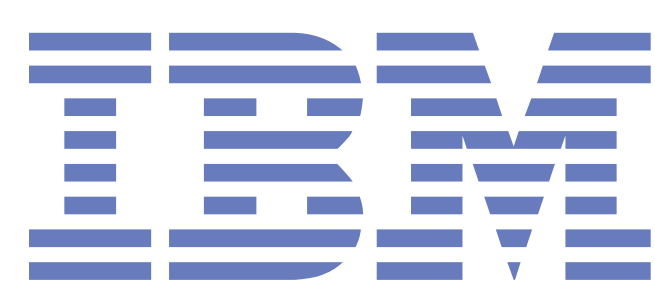


Reaction Pathways for the Pyrolysis of Glycerol, Propylene Glycol and Triacetin in the Gas Phase and at Solid Surfaces

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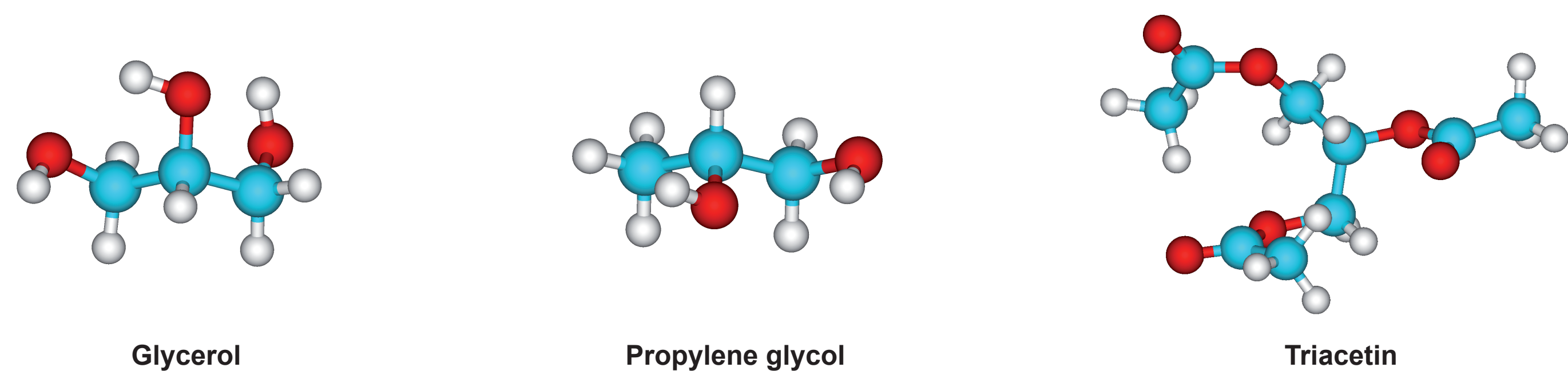
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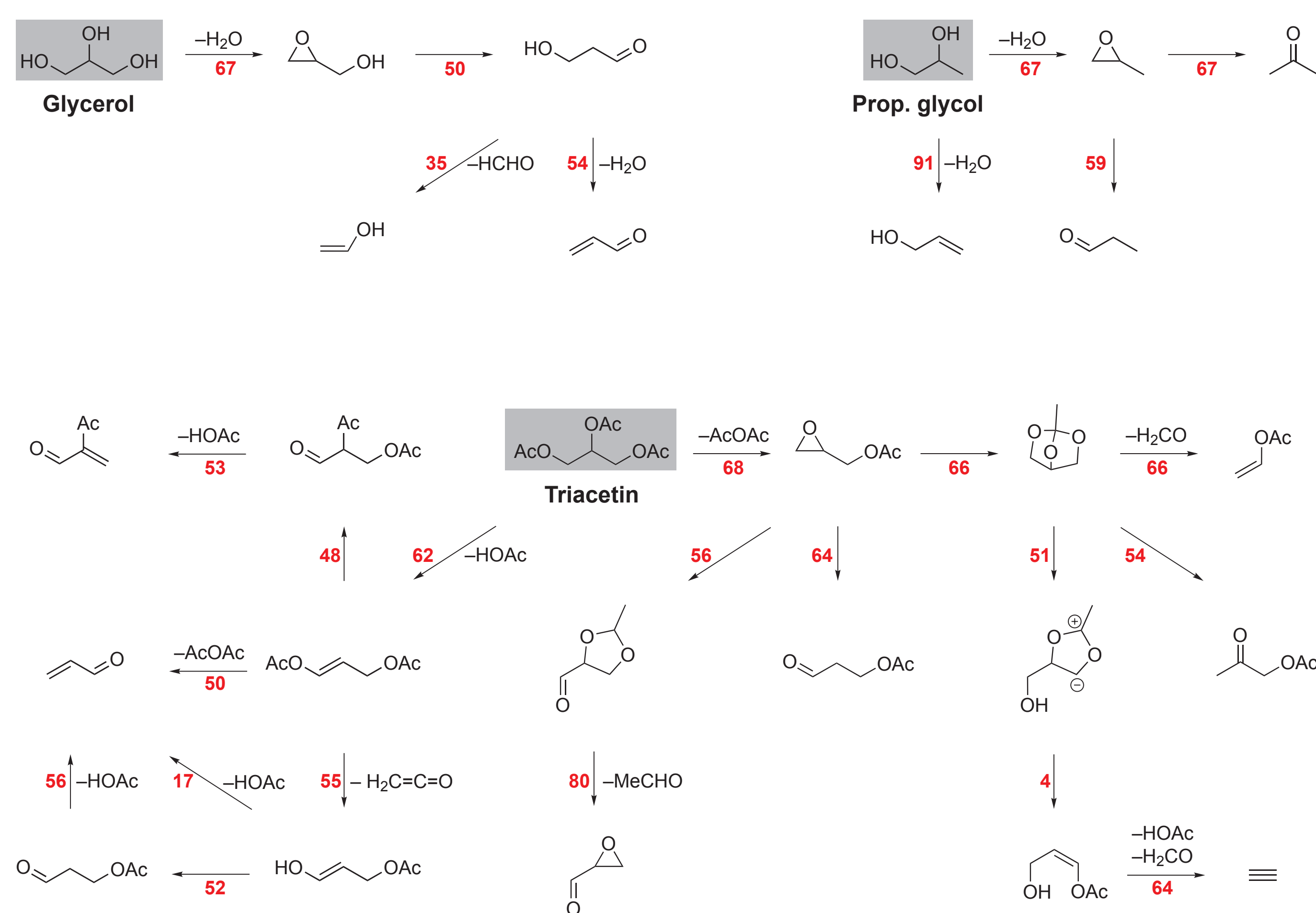
Why simulate the pyrolysis for these substances?



- Glycerol, propylene glycol, and triacetin are commonly used as solvents, food additives, and humectants in the food and tobacco industries. Their use often involves potential exposure to high temperatures.
- Several experimental investigations have been performed providing a broad spectrum of glycerol and propylene glycol gas phase decomposition products depending on the pyrolytic conditions. These experimental results, however, are often contradictory.
- Previous theoretical investigations do not entirely account for the pyrolytic products observed or imply specific catalytic conditions [1,2]. Determined barrier heights are larger than experimental evidence suggests. So far, neither experimental nor computational studies are available for the pyrolysis of triacetin.
- How are the decomposition patterns predicted for the gas phase influenced by the presence of solids, e.g., amorphous carbon, amorphous silica, or crystalline zirconia?

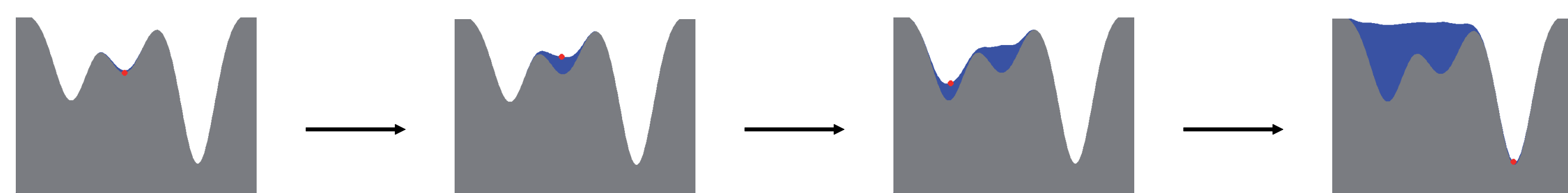
Results

Gas phase decomposition schemes and PBE0 Gibbs free energy **barriers** (in kcal/mol, $T = 800$ K):



Simulation of pyrolysis — how?

Exploration of new reaction pathways using DFT (PBE) metadynamics [3,4]



Metadynamics in short:

$$V(s, t) = \omega N(s, t) = \omega \int_0^t dt' \delta_{s, s(t')}$$

deposition rate histogram Gaussian or similar...

Refinement of trajectories for reactive events:

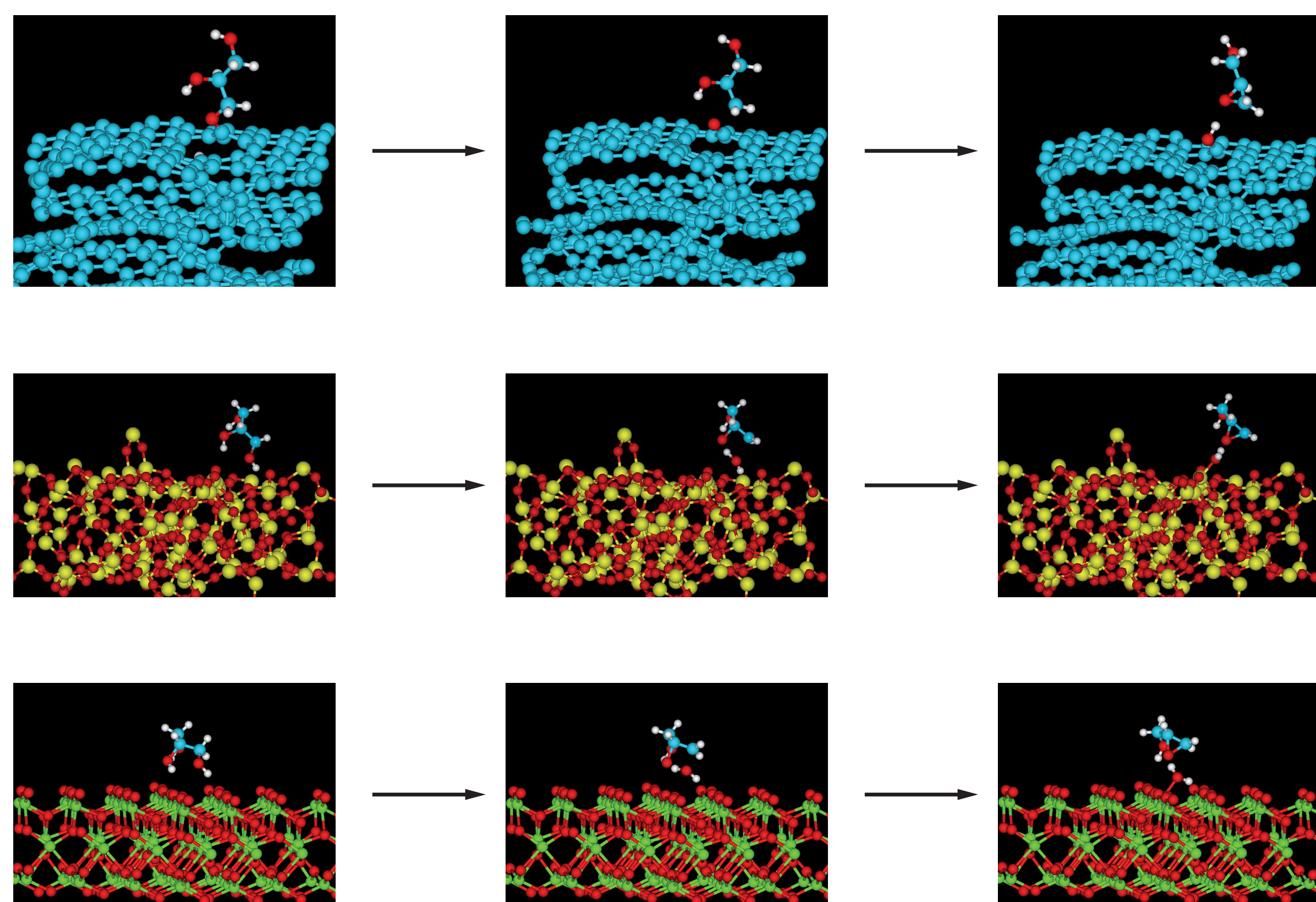
Molecules in the gas phase -

Geometry optimizations and frequency calculations (80 Rydberg/PBE; 100 Rydberg/PBE0; Troullier-Martins type pseudopotentials, CPMD code), transition structures from eigenmode following

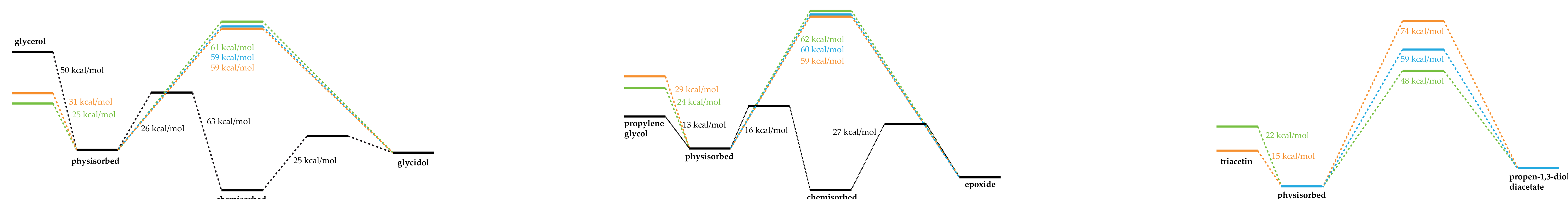
Molecules at solid surfaces -

Geometry optimizations, transition structure location from a nudged elastic band approach (SZV/PBE; CP2K code), single point energy calculations (80 Rydberg/PBE; CPMD code)

The initial glycerol decomposition step over amorphous carbon (top), amorphous silica (middle), and crystalline zirconia (bottom): glycerol → transition structure → glycidol



Reaction profiles for the initial steps of the decomposition schemes in the **gas phase**, at the amorphous **carbon**, amorphous **silica**, and crystalline **zirconia** surfaces:



Conclusions

- Decomposition of glycerol [5] and propylene glycol via epoxide intermediates (rate limiting)
- Formaldehyde and vinyl alcohol as major glycerol decomposition products, formation of acrolein predicted to be competitive at very high temperatures only; propanal and only minor amounts of acetone predicted as products from propylene glycol
- Triacetin thermically slightly less stable than glycerol or propylene glycol; complex decomposition pattern characterized by stepwise eliminations of acetic acid or acetaldehyde
- Due to high surface reactivity with alcohols, significant decrease of barrier heights at the amorphous carbon surface compared to gas phase decomposition steps; virtually no influence of oxide materials on barriers for glycerol and propylene glycol, slight sensitivity in the case of triacetin

References

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