

SFB

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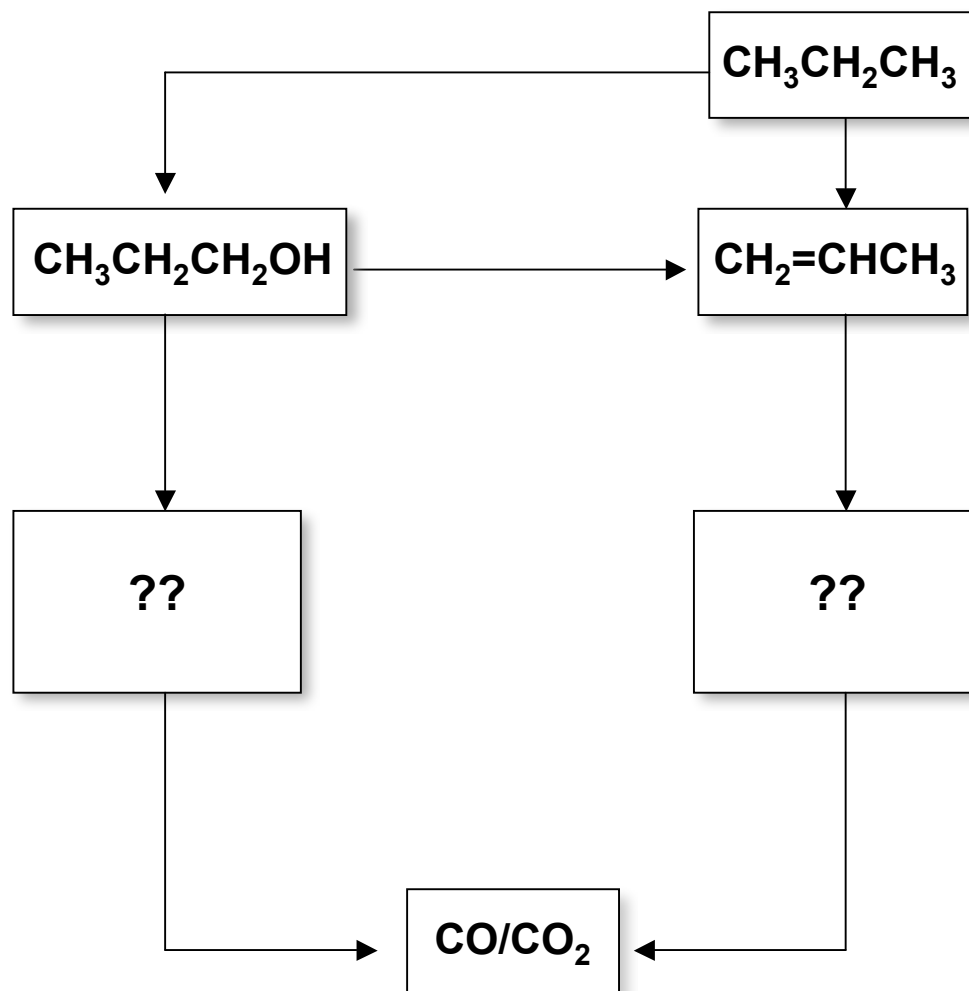


Selective Oxidation of Propene by Vanadium Oxide Sites Supported on Silica

Jianwen Liu, Fawzi Mohamed, Joachim Sauer

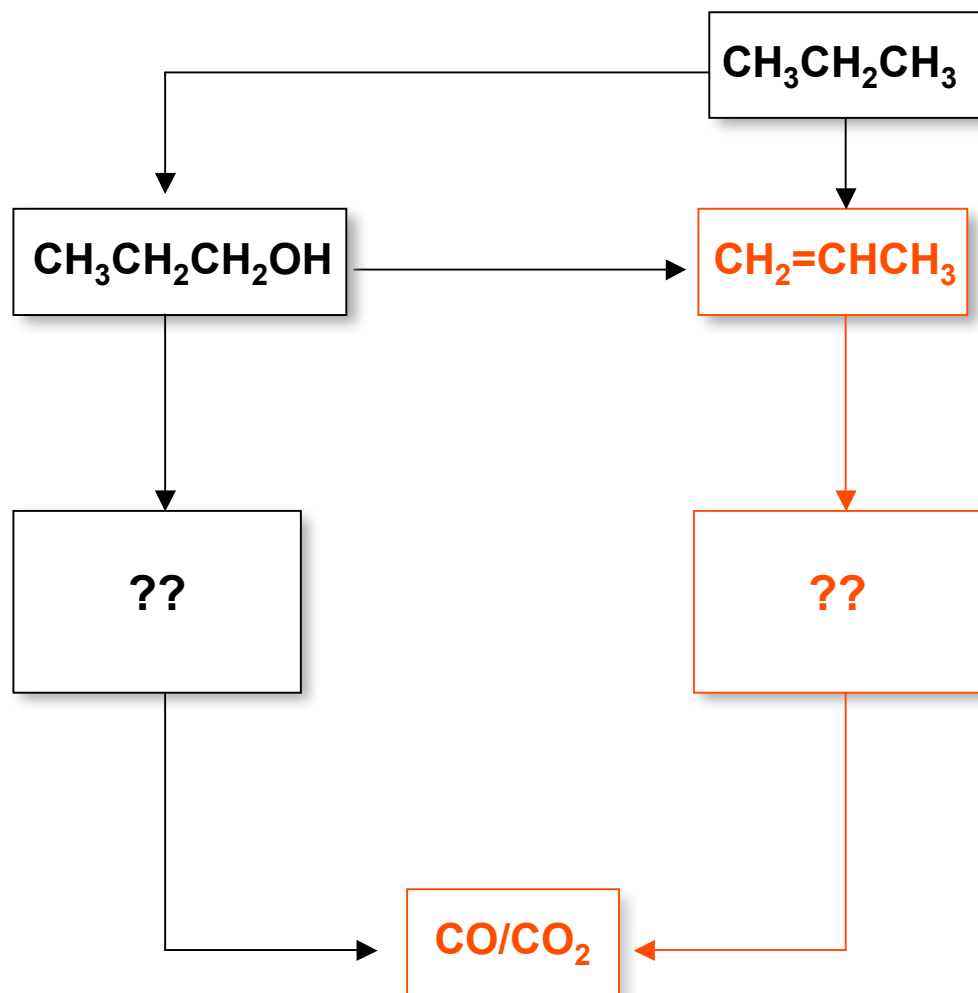
Schmöckwitz 15. 02. 2010

Motivation



- X. Rozanska, R. Rortrie and J. Sauer, J. Phys. Chem. C, 111(2007)6041.
- X. Rozanska, E. V. Kondratenko and J. Sauer, J. Catal. 256 (2008) 84.
- X. Rozanska and J. Sauer, Int. J. Quant. Chem. 108 (2008) 2223.
- X. Rozanska and J. Sauer, J. Phys. Chem. A 113 (2009) 11586.

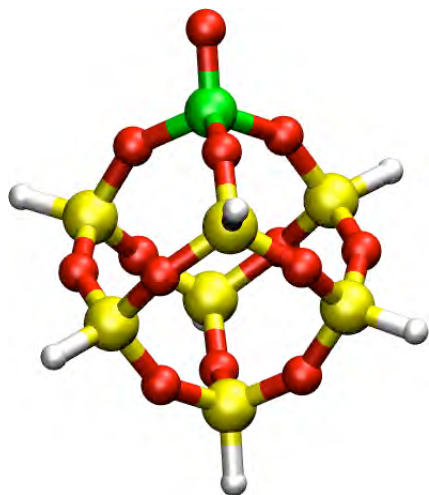
Motivation



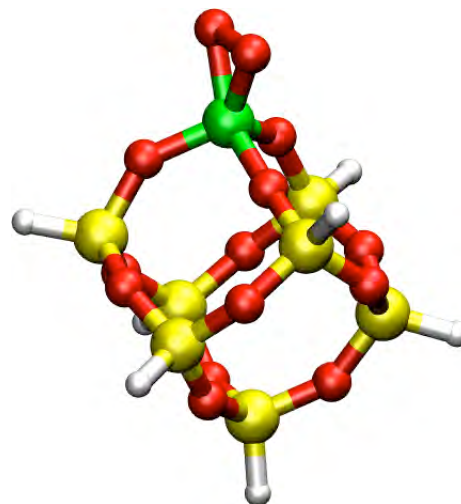
- X. Rozanska, R. Rortrie and J. Sauer, J. Phys. Chem. C, 111(2007)6041.
- X. Rozanska, E. V. Kondratenko and J. Sauer, J. Catal. 256 (2008) 84.
- X. Rozanska and J. Sauer, Int. J. Quant. Chem. 108 (2008) 2223.
- X. Rozanska and J. Sauer, J. Phys. Chem. A 113 (2009) 11586.

Calculation Details

1. DFT+D using Turbomole (B3LYP / TZVP, PBE / TZVP)
2. Meta-dynamics simulation using CP2K
(PBE+D / DZVP-MOLOPT-SR-GTH)
3. Silsesquioxane model



Vanadyl



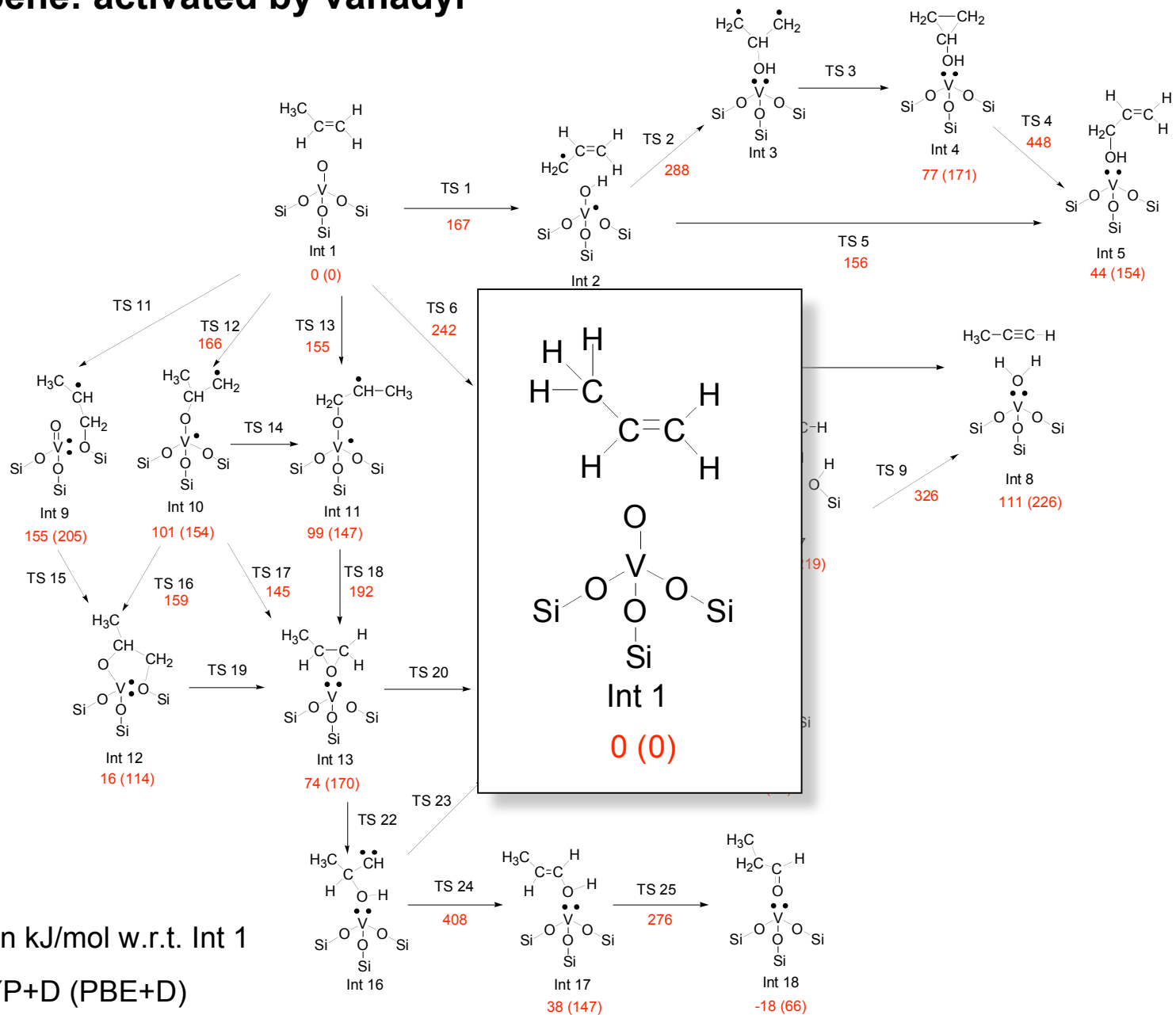
Peroxovanadate

J. Döbler, M. Pritzsche, J. Sauer, J. Am. Chem. Soc., 127(2005)10861.

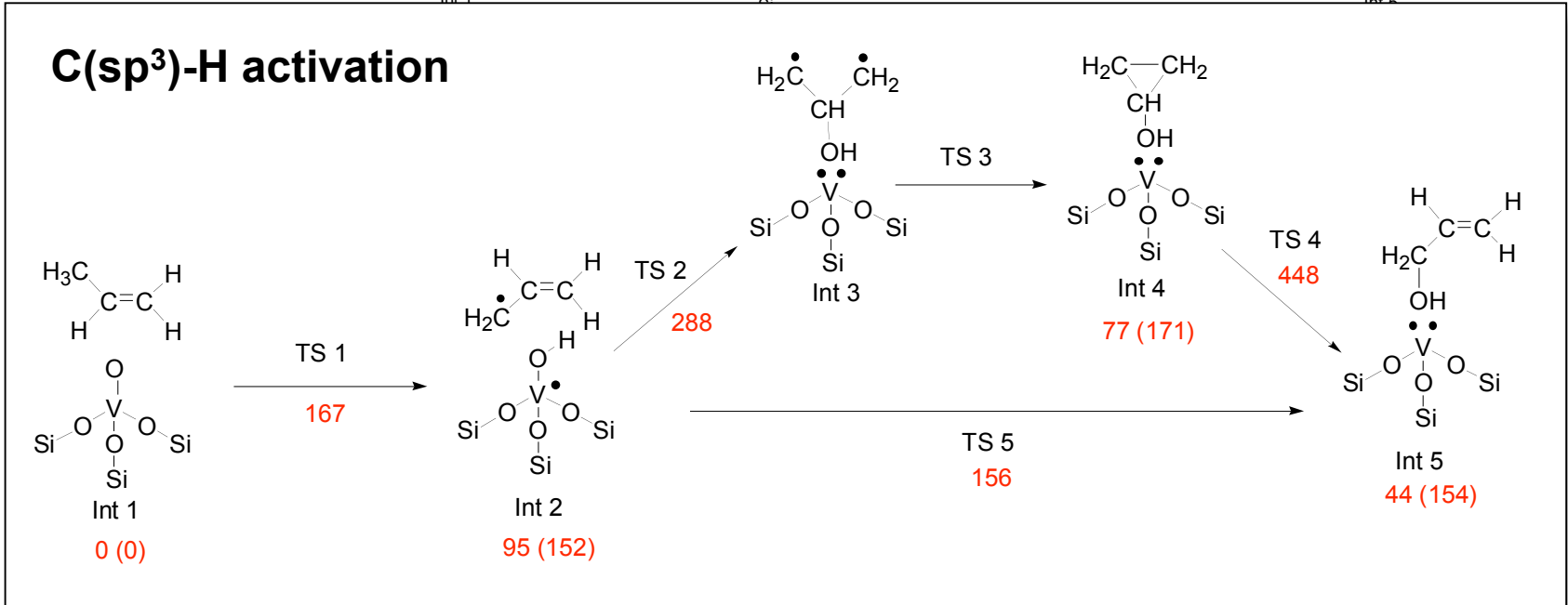
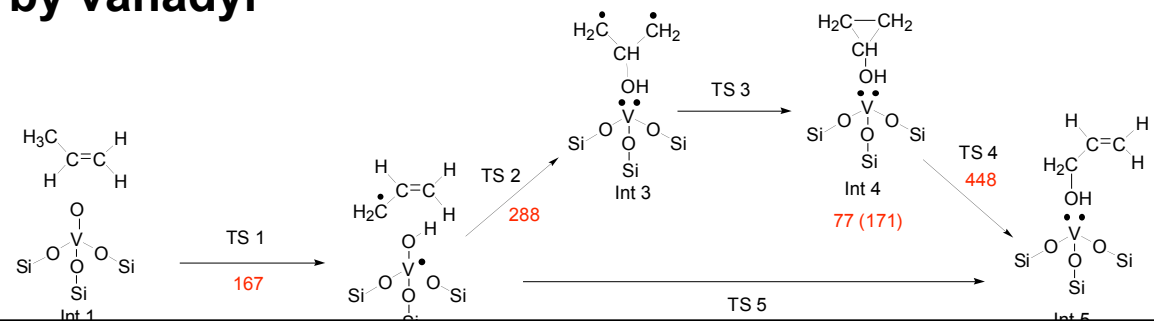
N. Magg et al., J. Catal. 226(2004)88.

X. Rozanska, R. Rortrie and J. Sauer, J. Phys. Chem. C, 111(2007)6041.

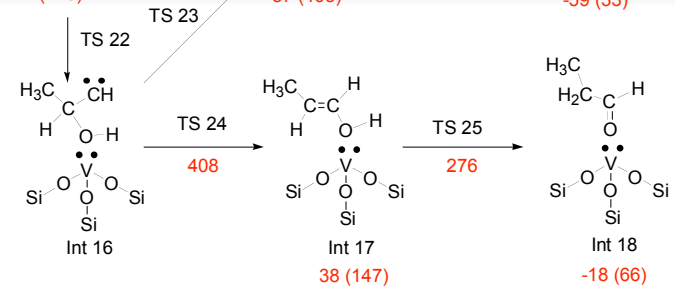
Propene: activated by vanadyl



Propene: activated by vanadyl

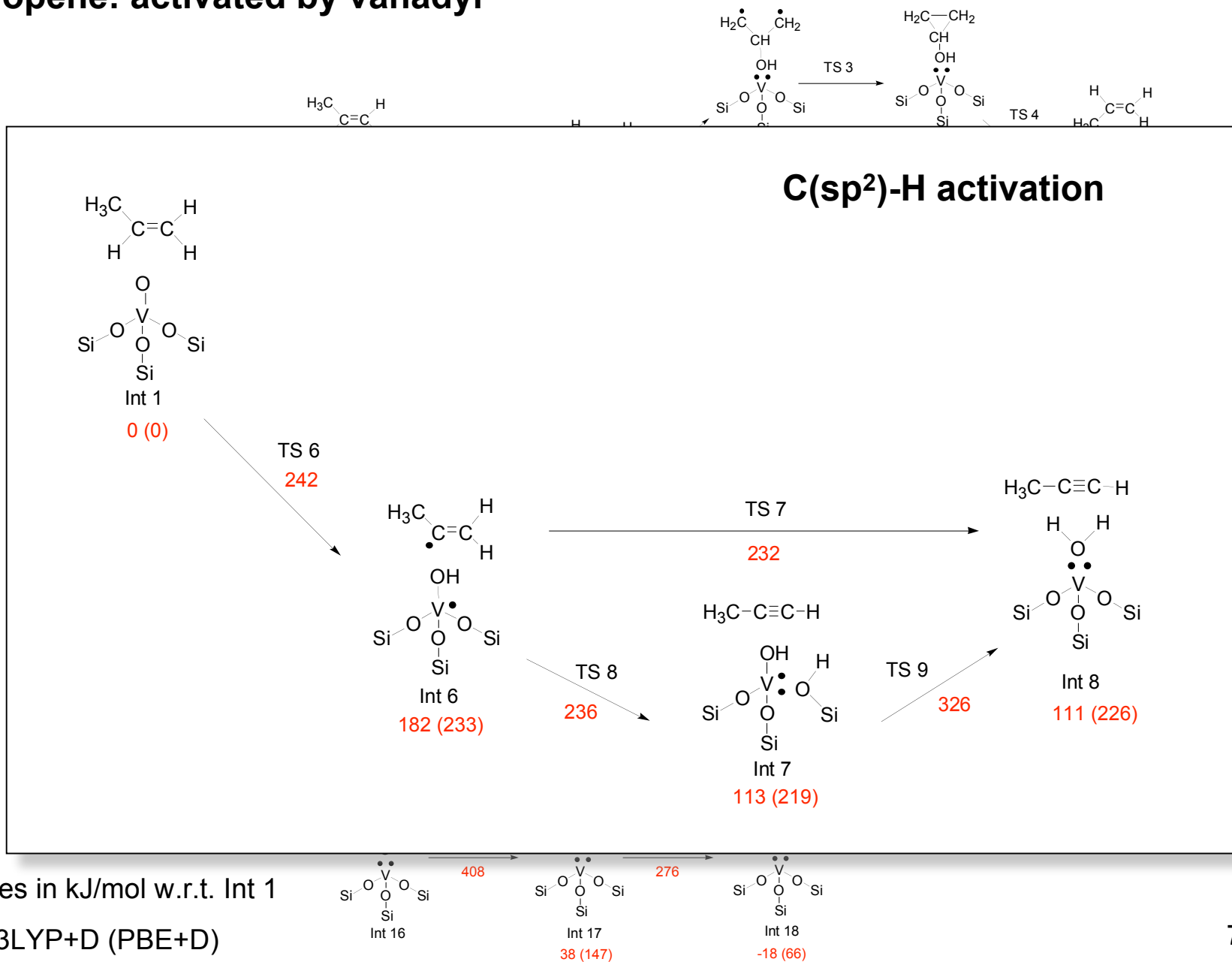


16 (114) 74 (170) 87 (103) -59 (33)

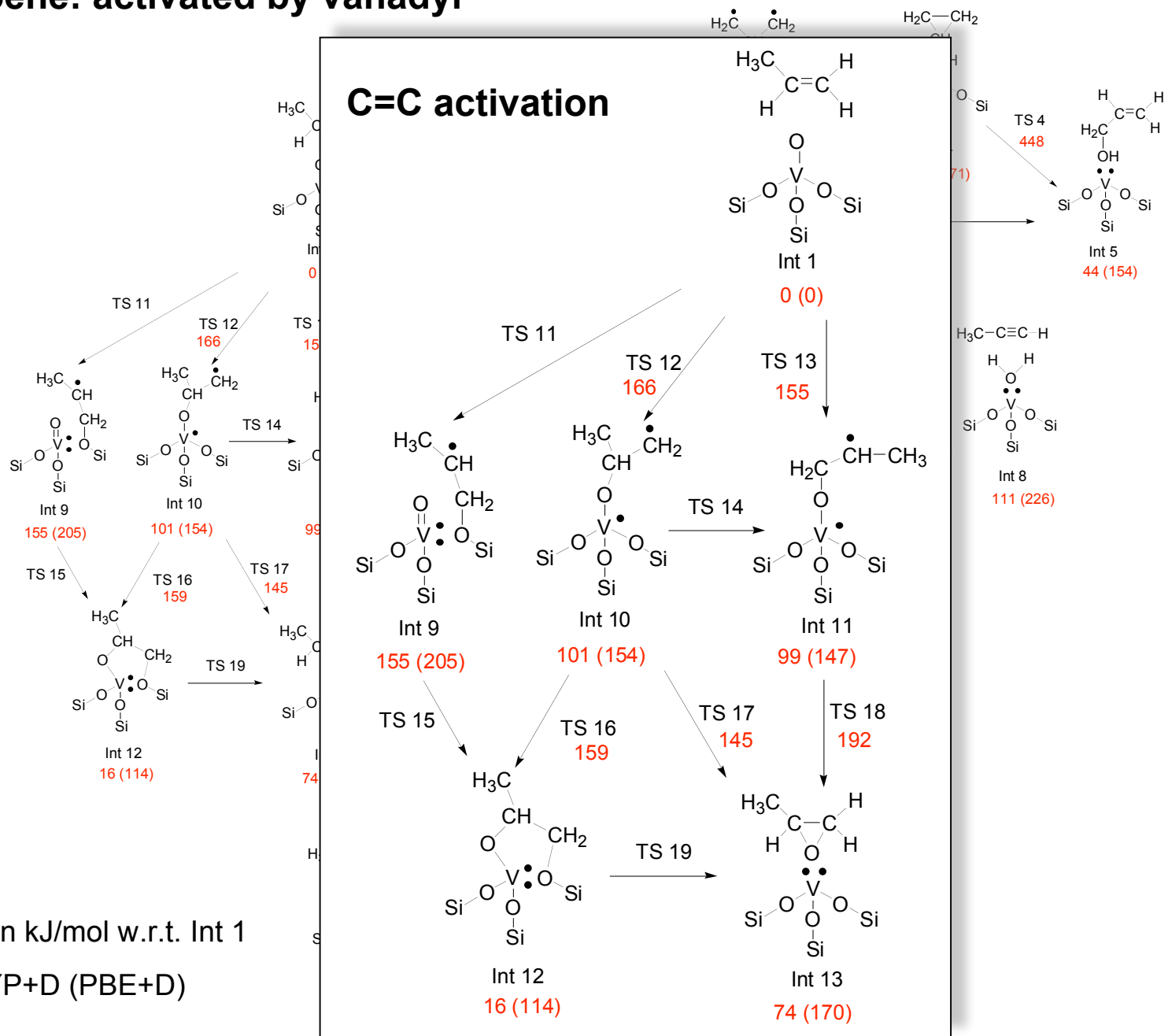


Energies in kJ/mol w.r.t. Int 1
B3LYP+D (PBE+D)

Propene: activated by vanadyl

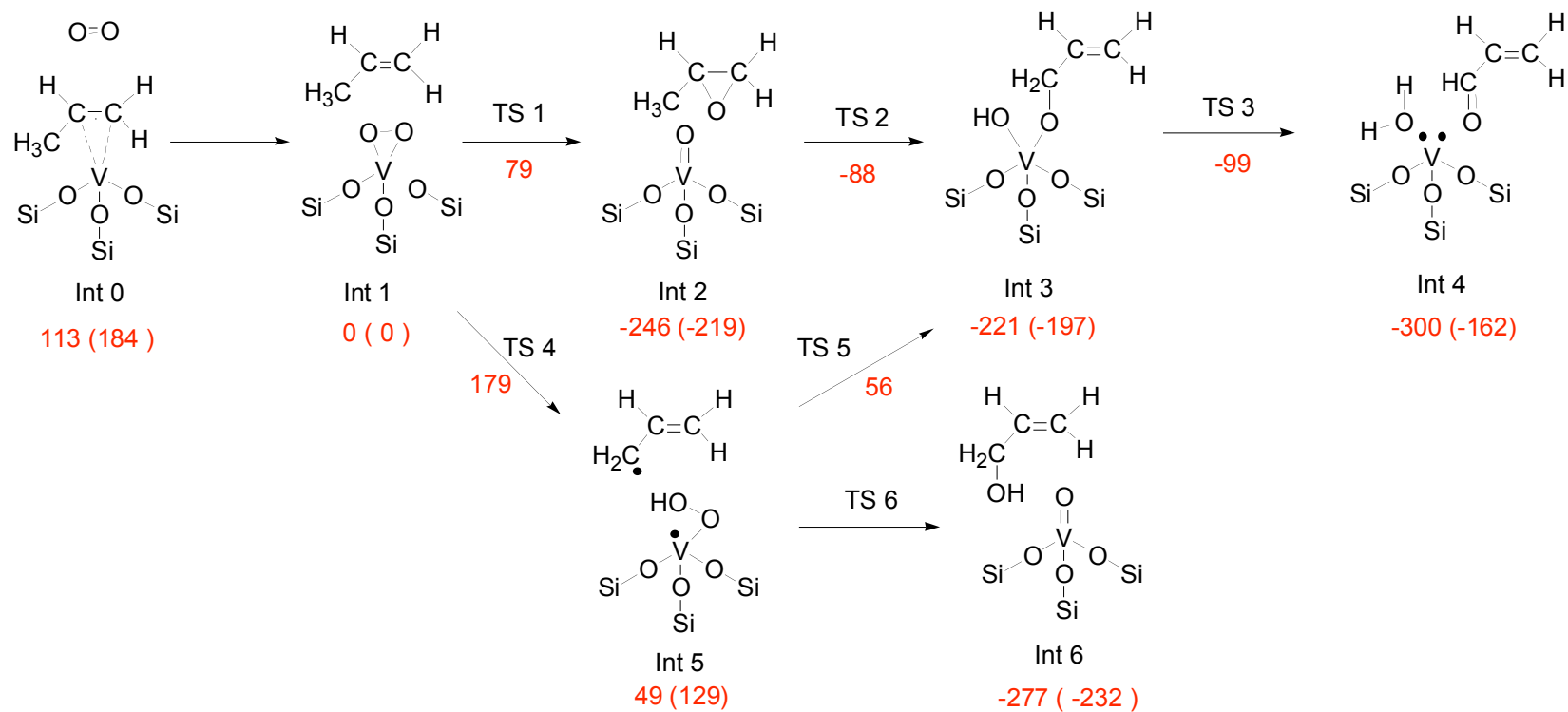


Propene: activated by vanadyl



Energies in kJ/mol w.r.t. Int 1
B3LYP+D (PBE+D)

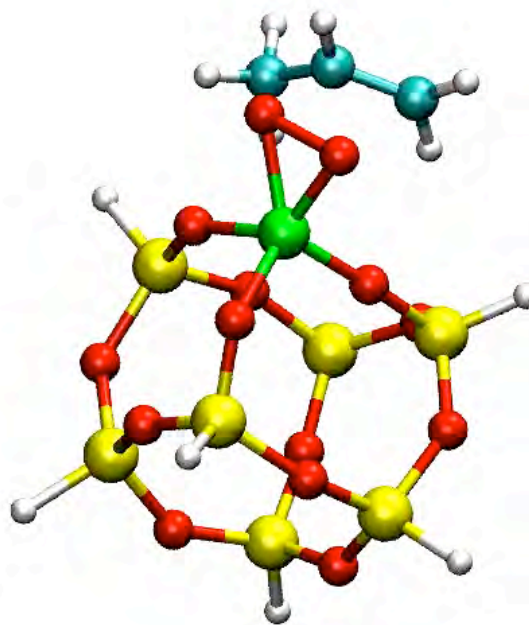
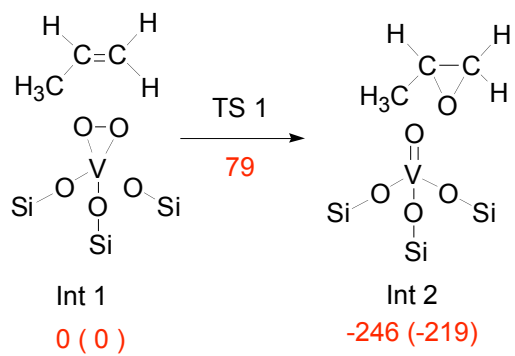
Propene: activated by peroxovanadate



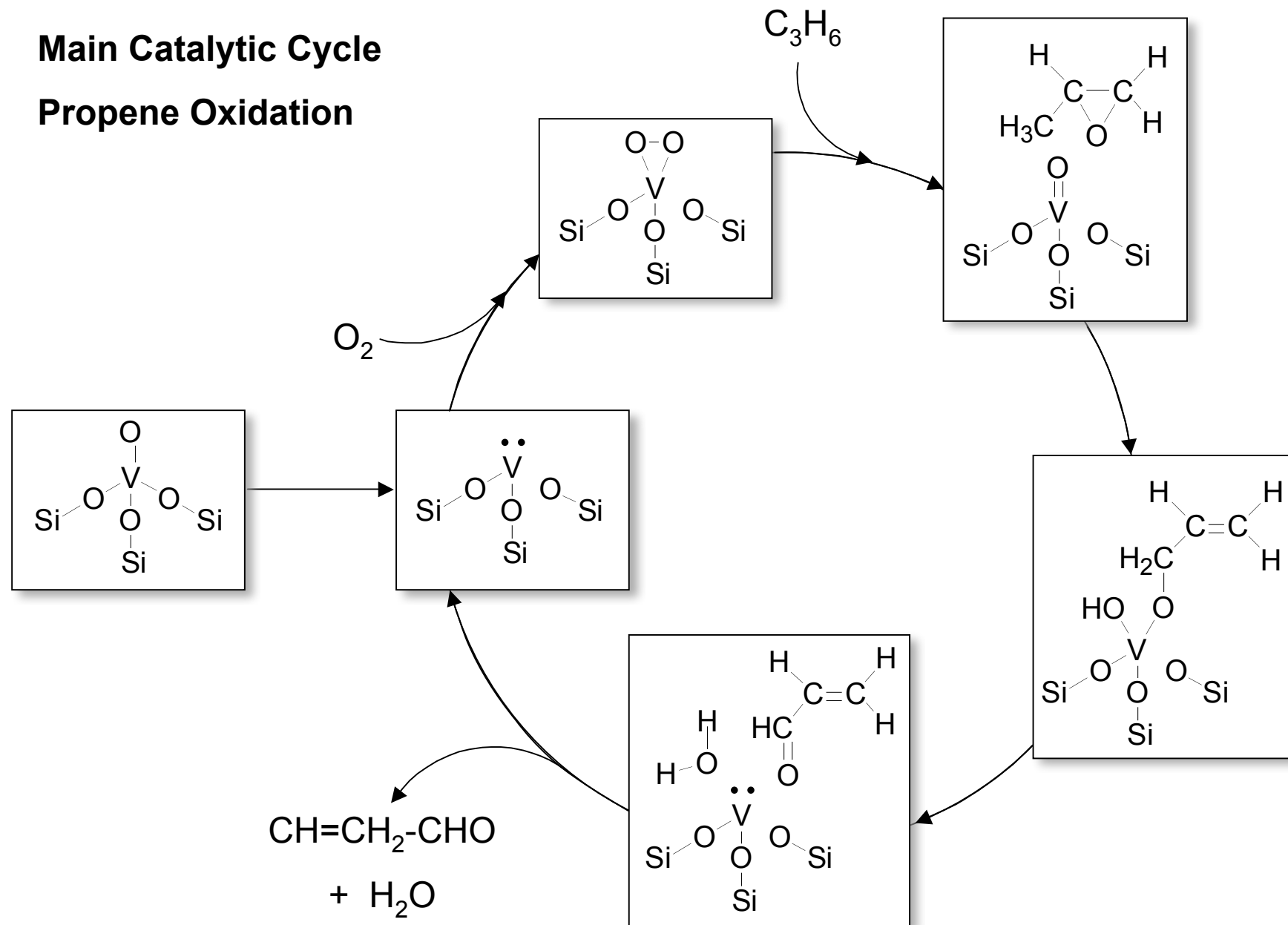
Energies in kJ/mol w.r.t. Int 1

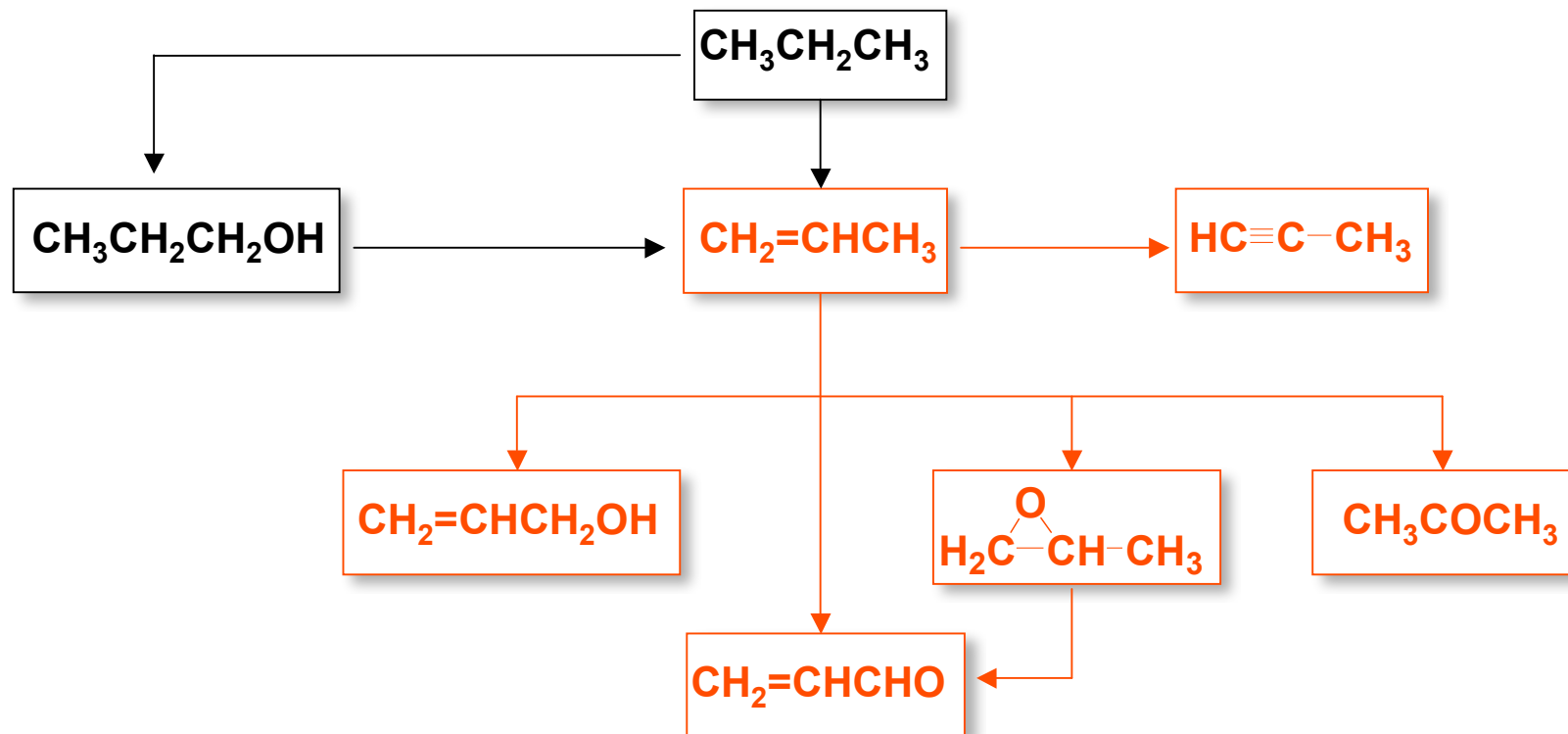
B3LYP+D (PBE+D)

MTD simulation

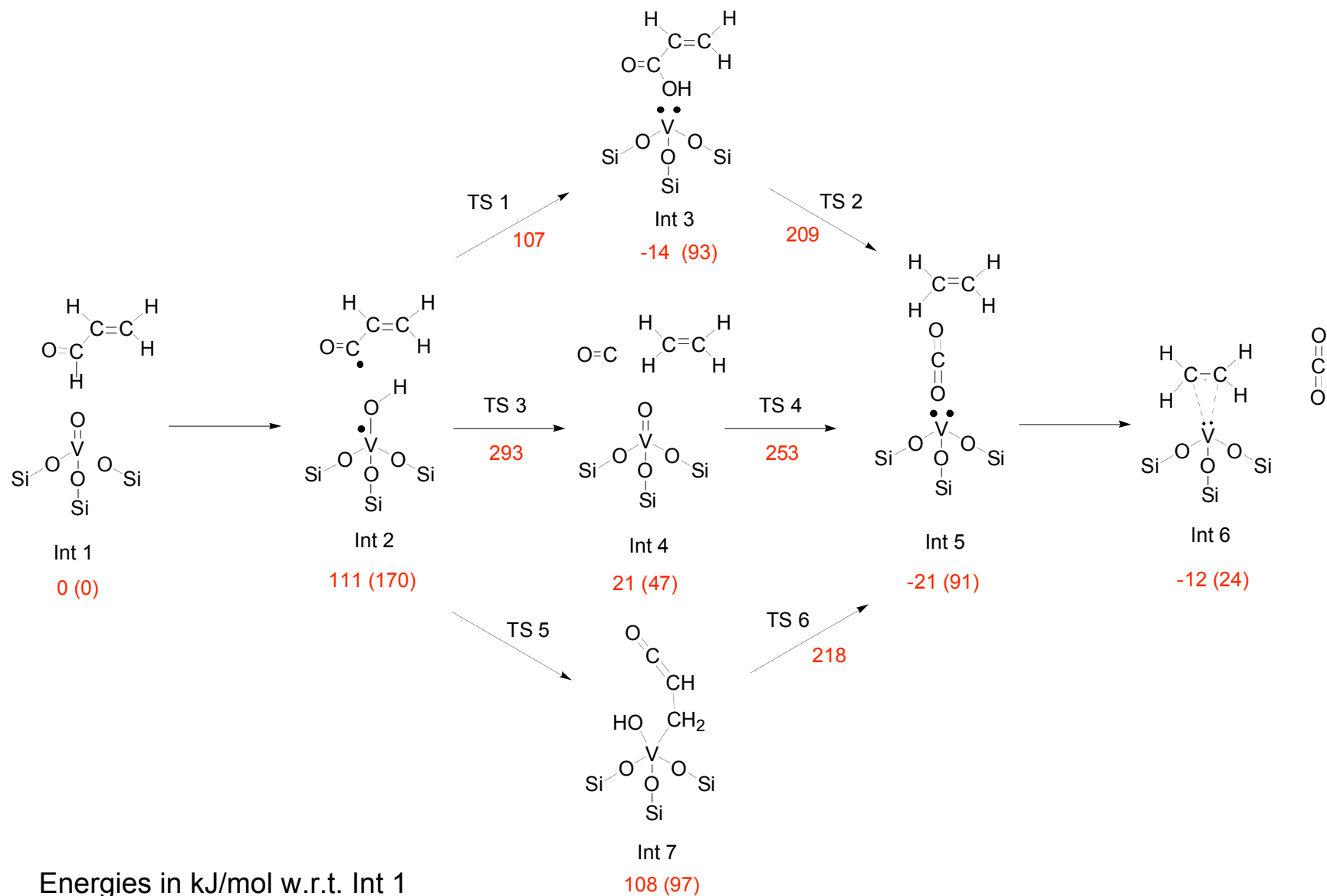


Main Catalytic Cycle
Propene Oxidation





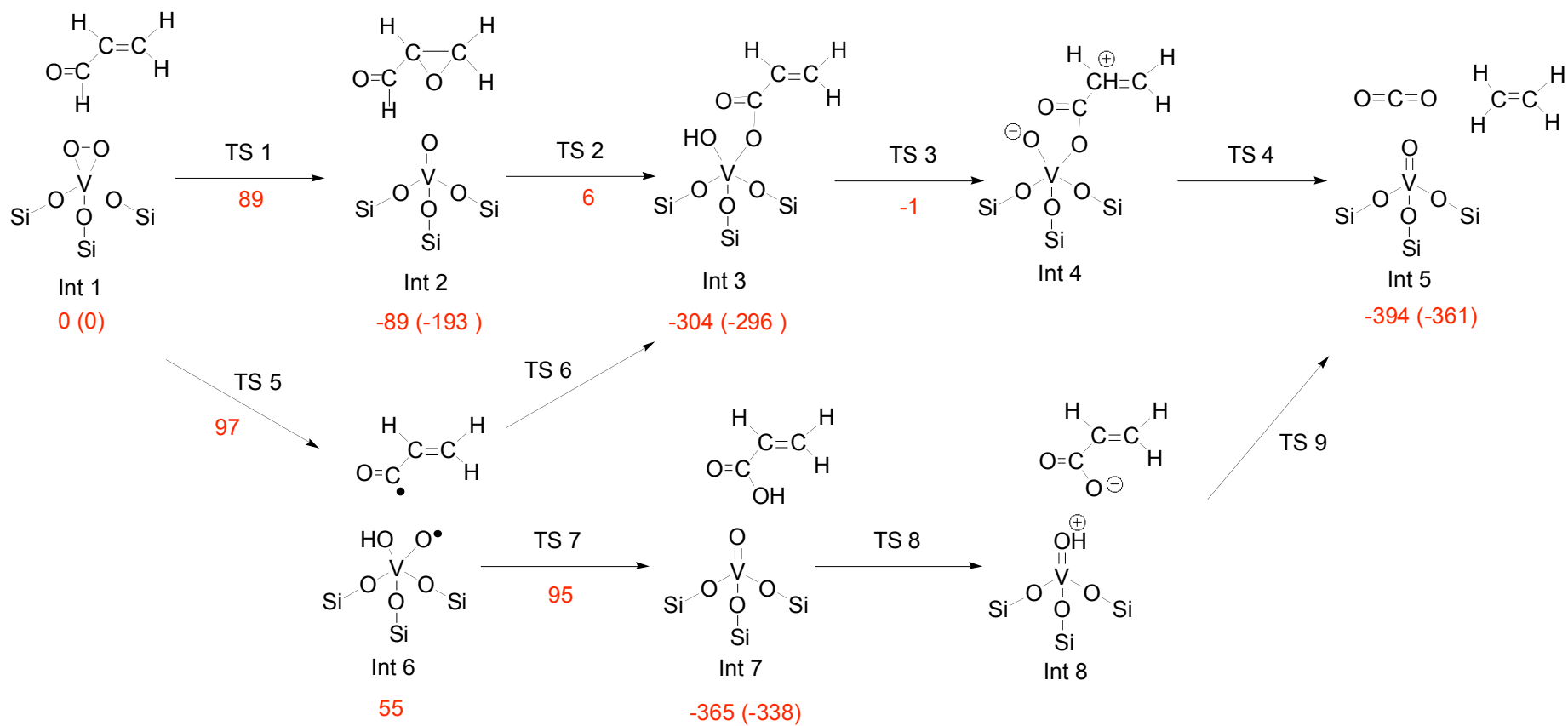
Acrolein: activated by vanadyl



Energies in kJ/mol w.r.t. Int 1

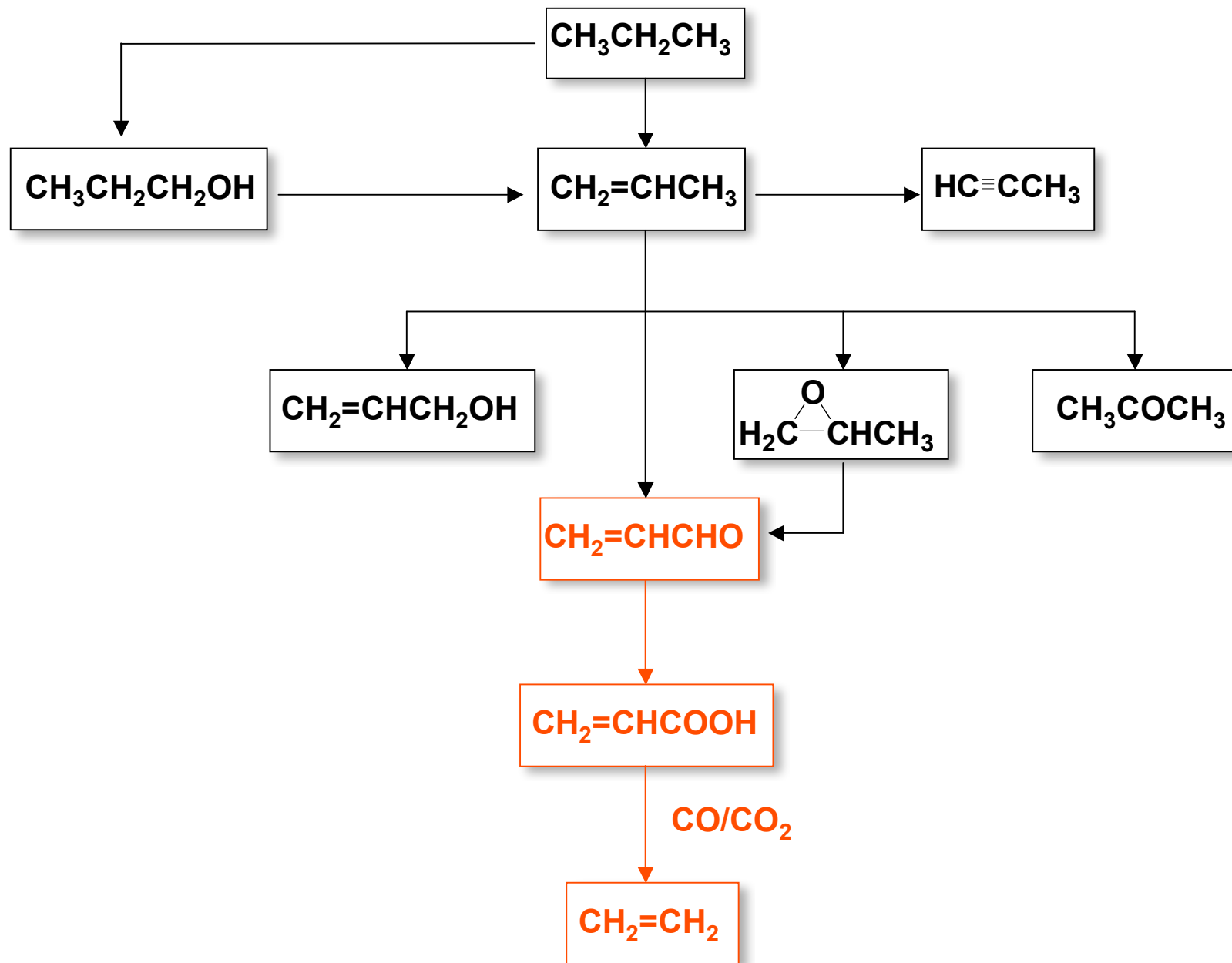
B3LYP+D (PBE+D)

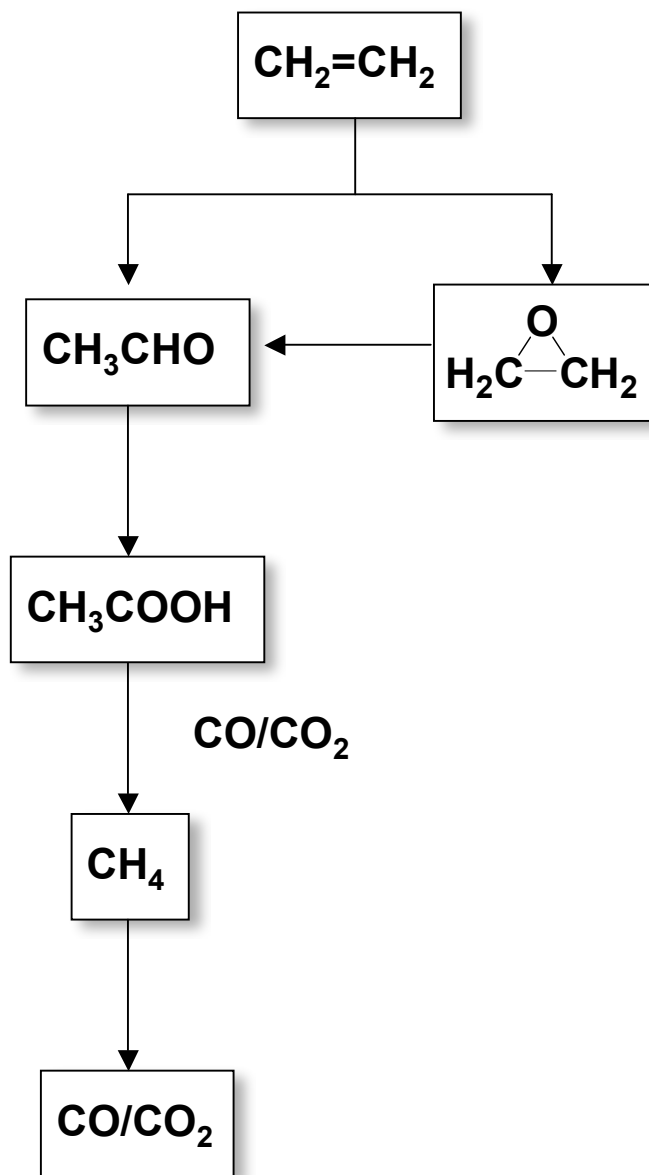
Acrolein: activated by peroxovanadate

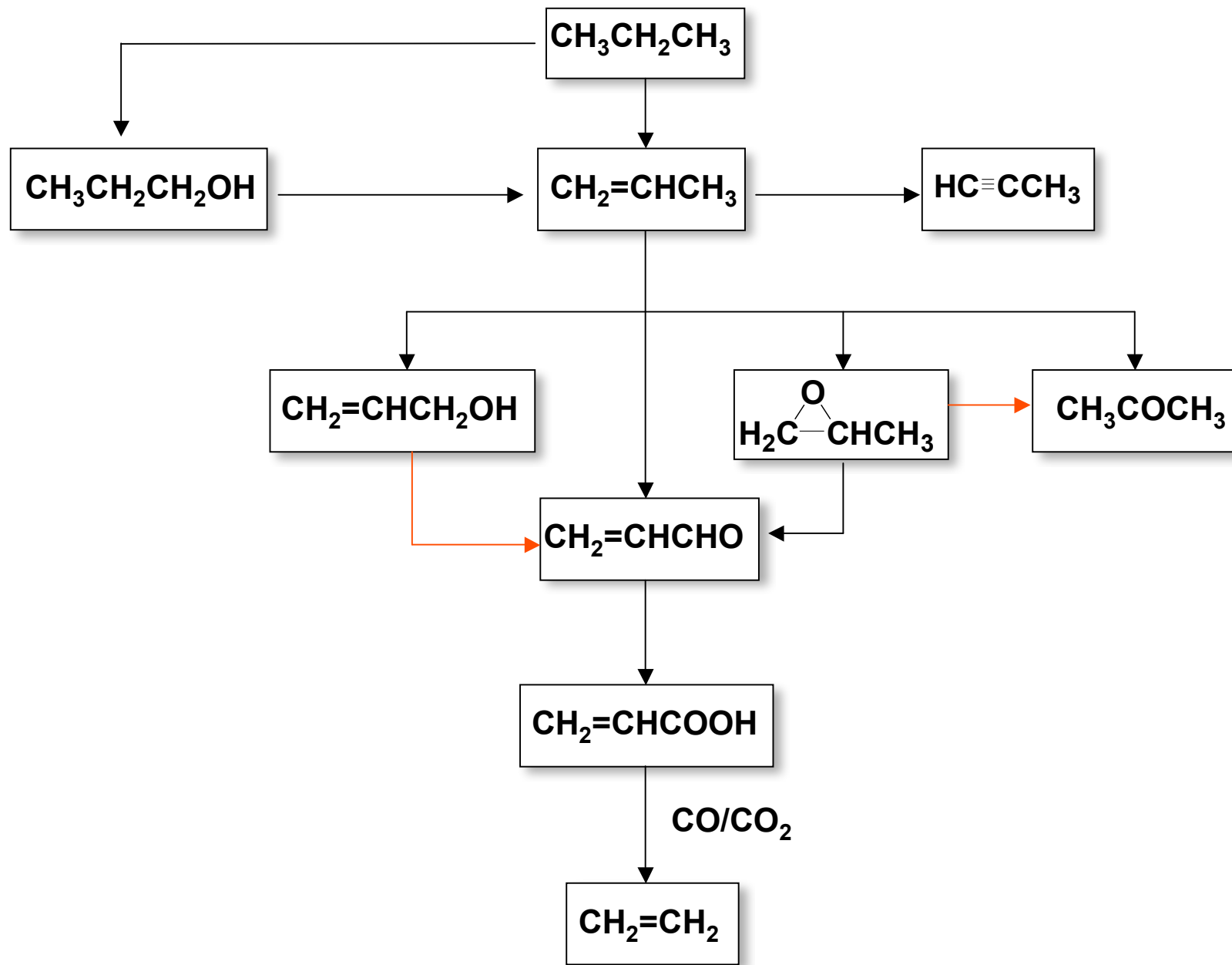


Energies in kJ/mol w.r.t. Int 1

B3LYP+D (PBE+D)



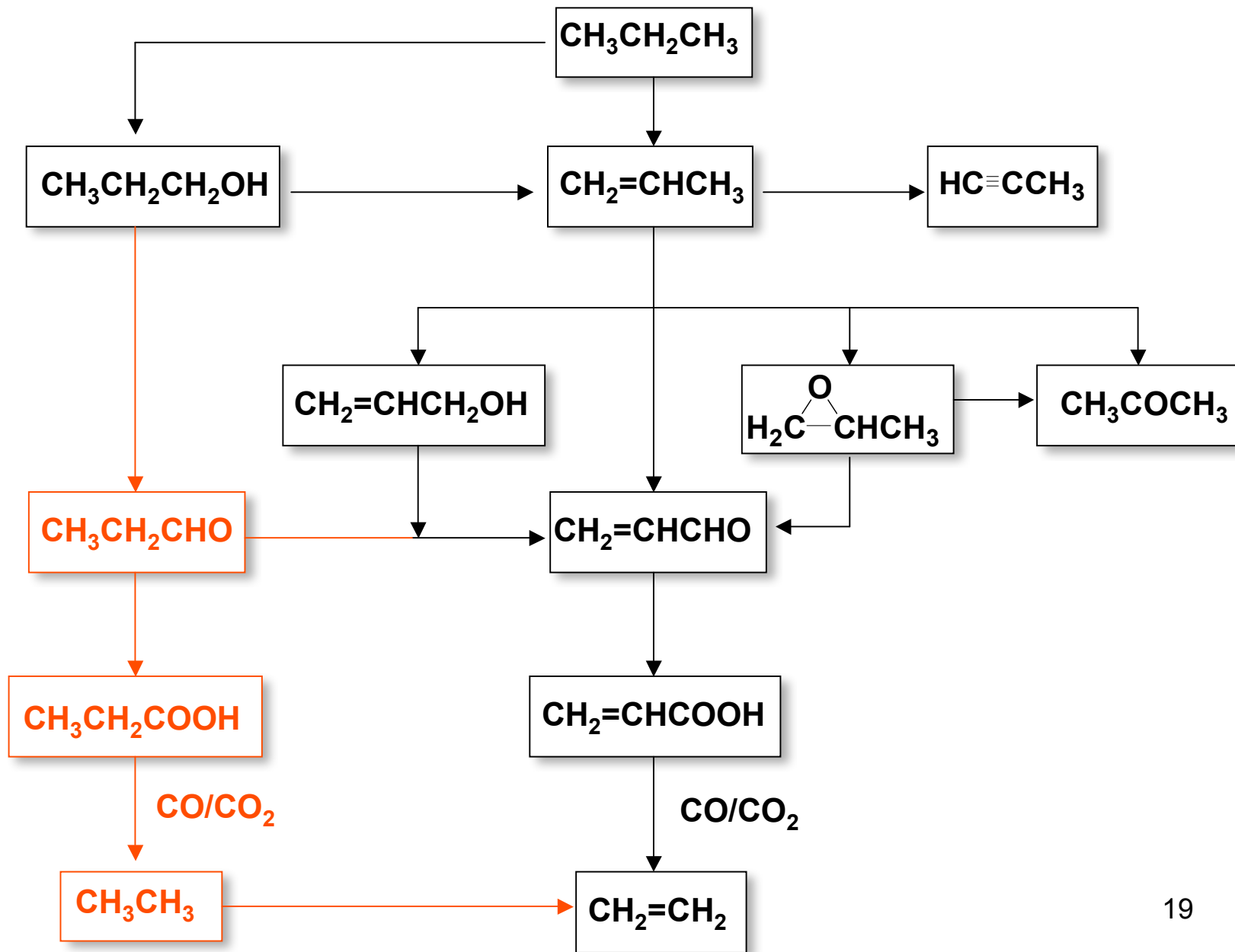




Conclusions

- **Main catalytic cycle is mapped out for propene oxidation.**
- **Peroxovanadate is highly active for propene oxidation .**
- **Direct oxidation of propene will mainly produce acrolein with by-products propyne, acetone, propene oxide and allyl alcohol.**
- **Further oxidation of acrolein to acrylic acid is possible.**

Prospective



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