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Detailed and Simplified Chemical Kinetics of Aviation Fuels and Surrogates: *ab initio* calculations of hydrogen extraction from n-propyl benzene

September 2012

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Motivation

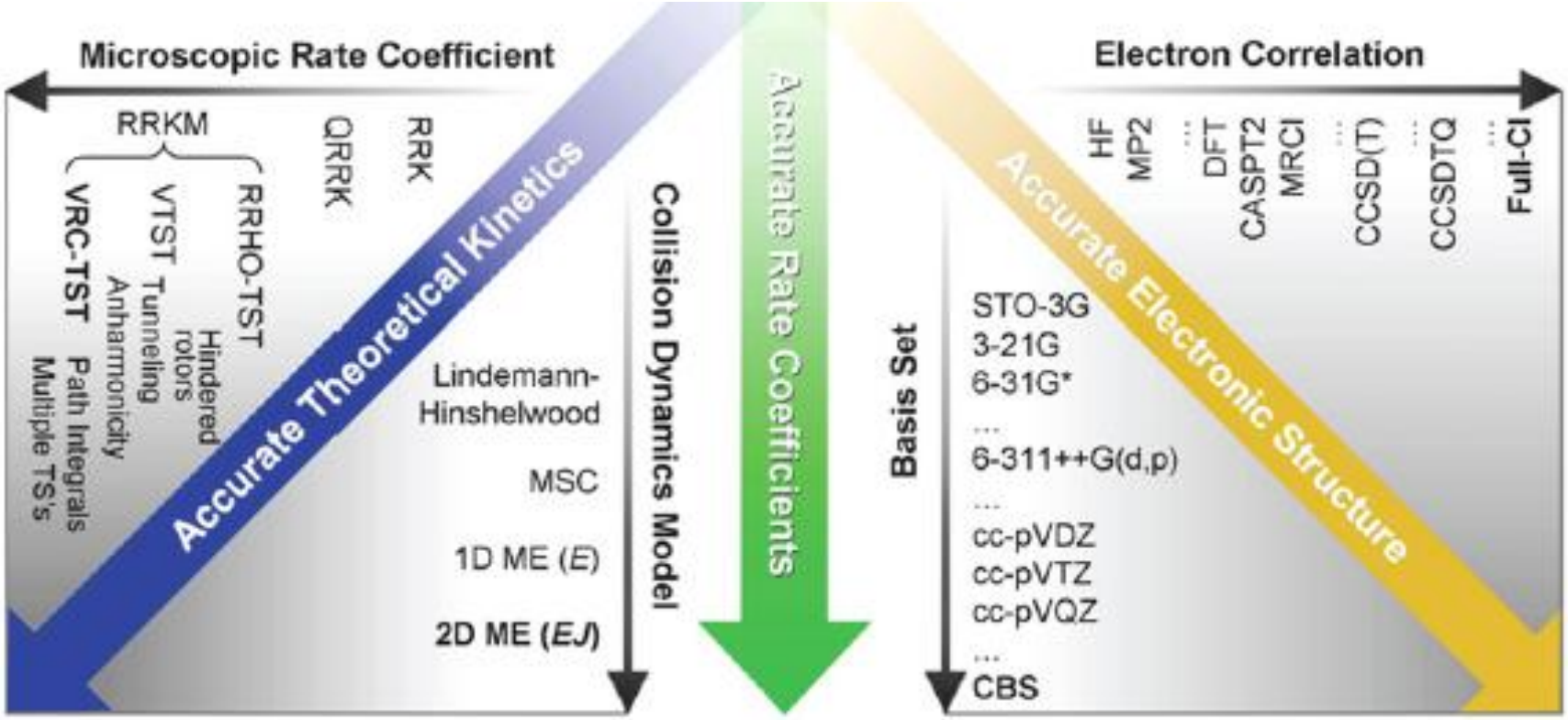
Technical Objectives

- To contribute to the development of detailed and simplified chemical mechanisms for fuel components.
- To study the trade-off between accuracy and tractability of *ab initio* calculations for practical fuel components used in aviation and surrogate blends.
- To seek to reduce the empiricism associated with mechanism construction while retaining a decent rate of progress.

Sample System

- Exploration of bimolecular exchange reactions in involved in the initial breakdown of n-propyl-benzene (nPB) concerning hydrogen exchange with common radicals such as H and CH_3.
- The choice of n-propyl benzene stems from its use in EU and US surrogate fuel formulations.

Strategy for Increased Accuracy of Rate Coefficients (Zador et al. 2011)



Explore the trade-off between speed and accuracy for four system tenants:

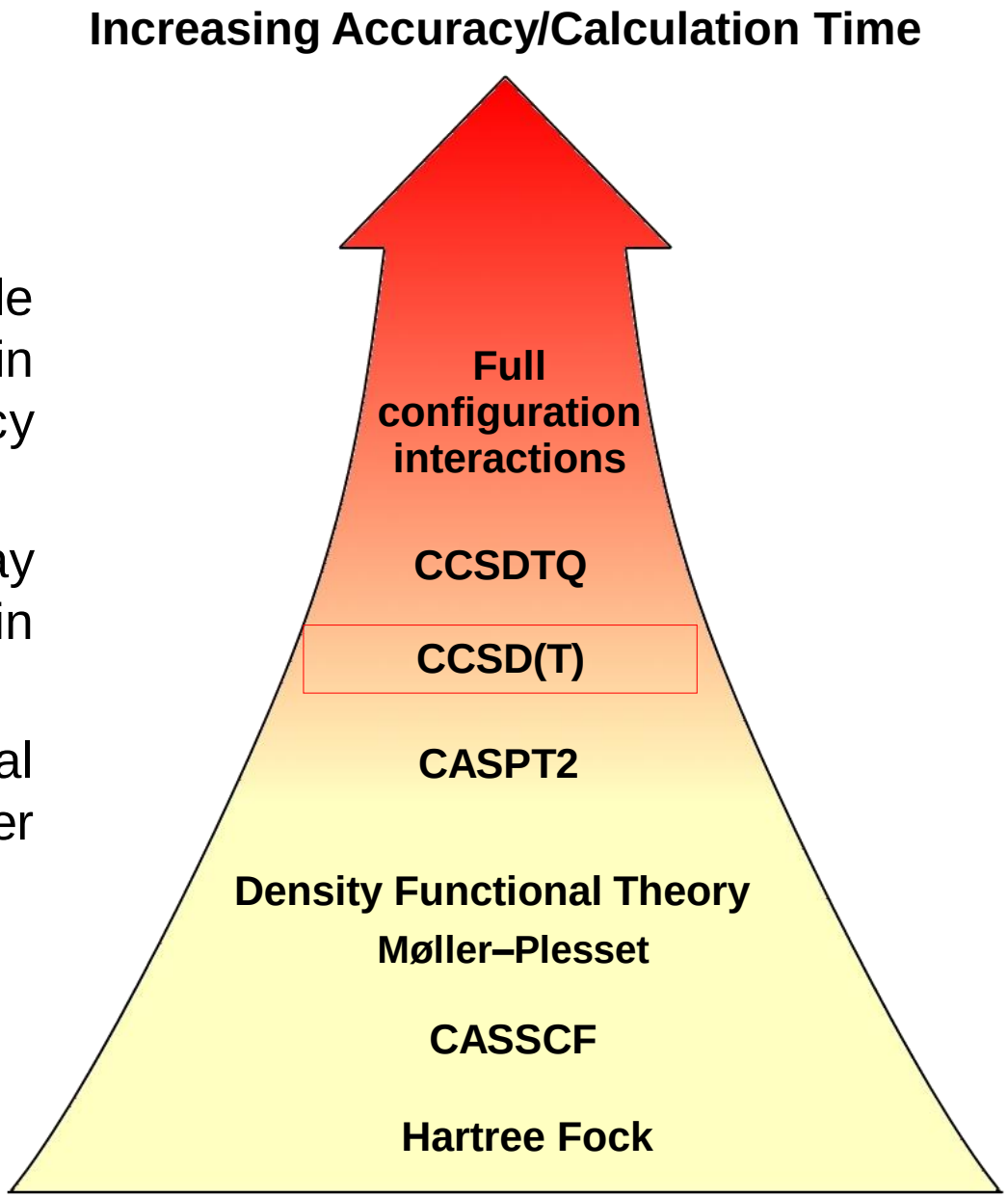
- Quantum mechanical methodology (DFT and coupled cluster (CC) methods).
- The size of the basis set.
- Rate coefficient determination methods.
- Quantum tunnelling corrections.

Kinetic and thermochemical data produced using the selected methods

Quantum Mechanical Methods

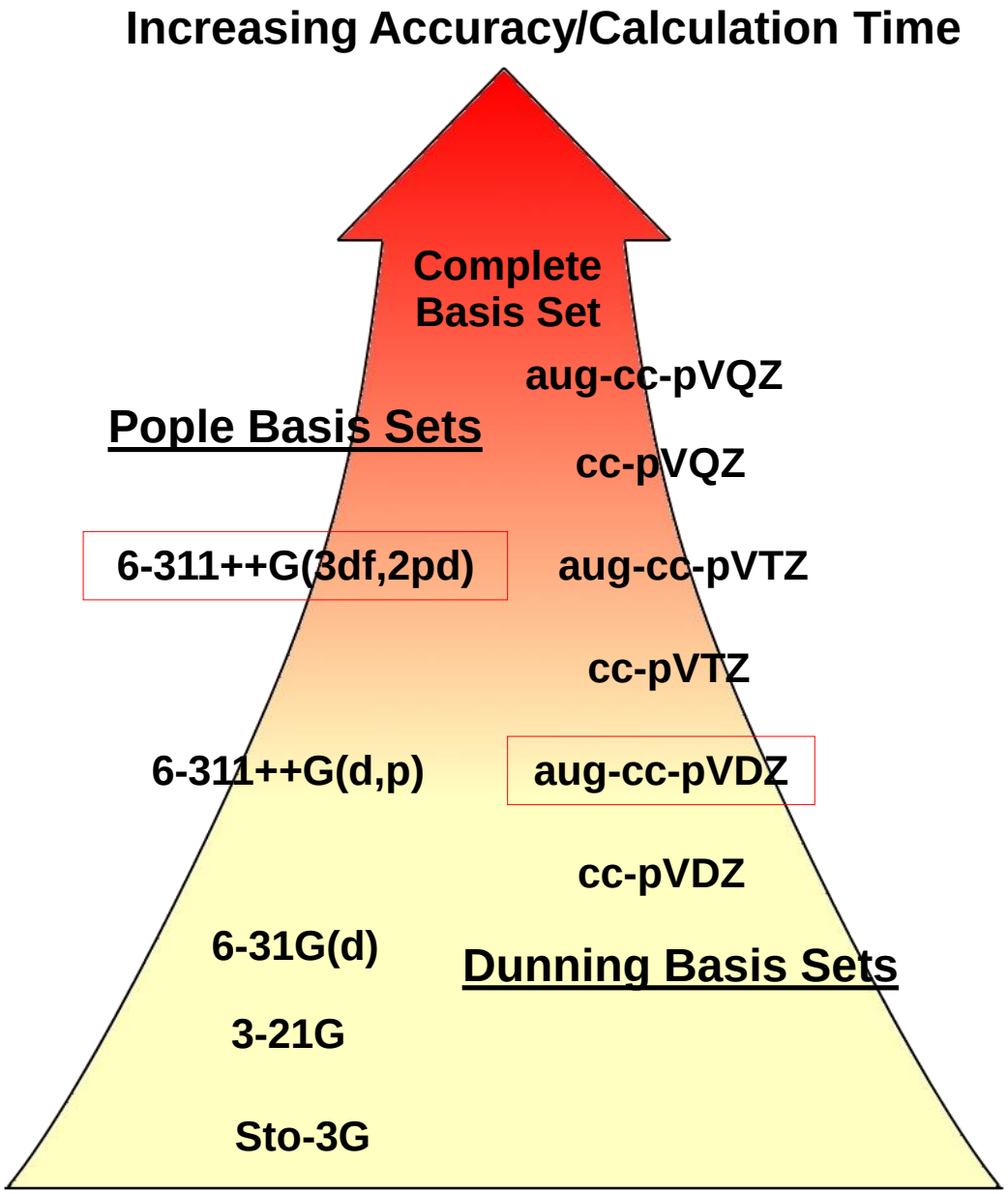
- Computational demands scale strongly with the number of atoms in the system. The feasible accuracy must be determined.
- Coupled Cluster methods may provide energetics and barriers within 2 kJ/mol.

(cf. Klippenstein, *Ab Initio* Theoretical Chemical Kinetics, CEFRC Summer School; Zador et al. 2011)



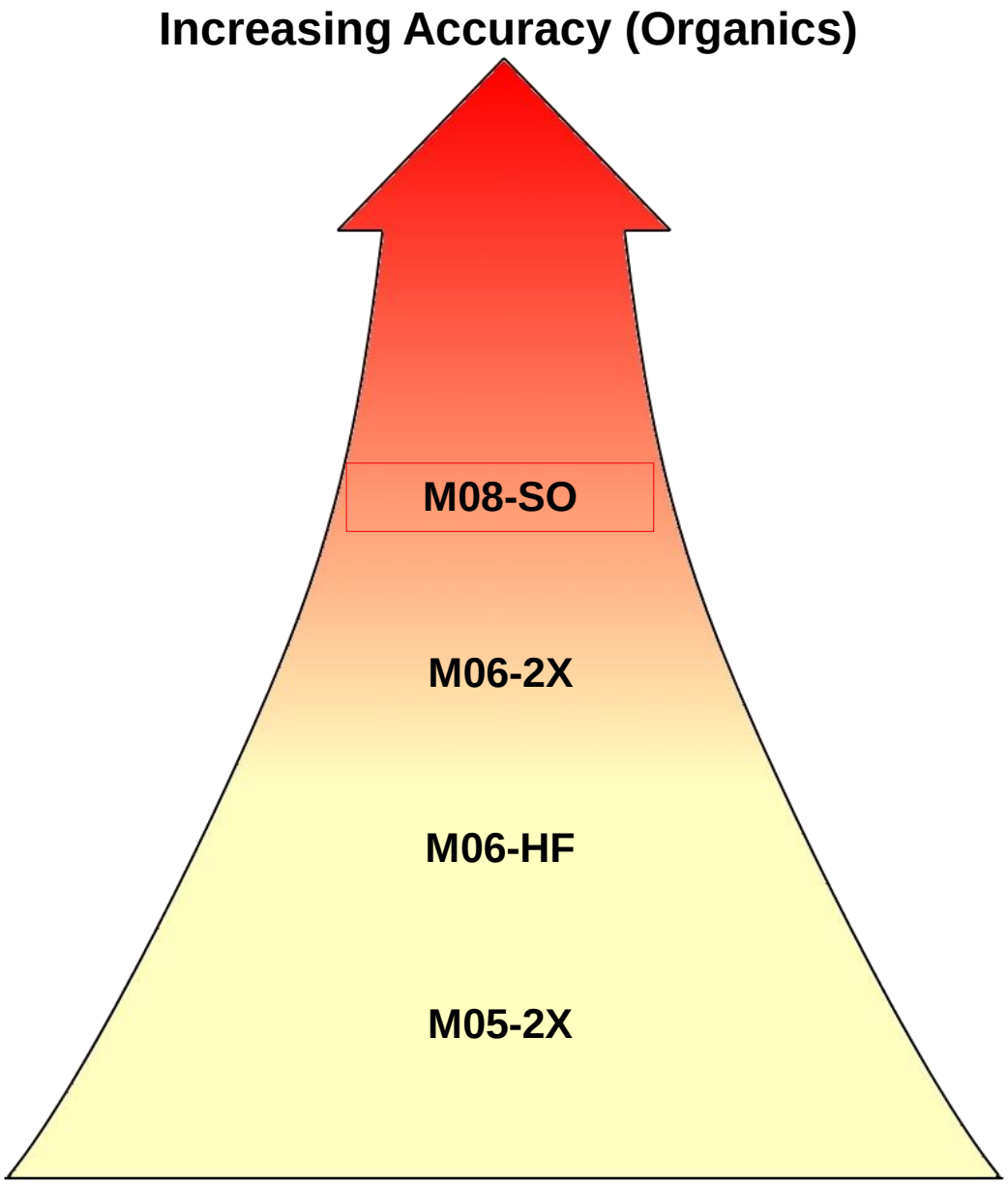
Basis Set Accuracy

- The basis set size is increased by adding polarization functions (d/p), which effect geometries and energies.
- Diffuse functions (++ or aug) are important for hydrogen bonding.
- The Dunning basis sets are correlation-consistent (cc), V stands for valence only and DZ for double-zeta.
- The 6-31g(d) basis set is the smallest to give reasonable approximations of energies.



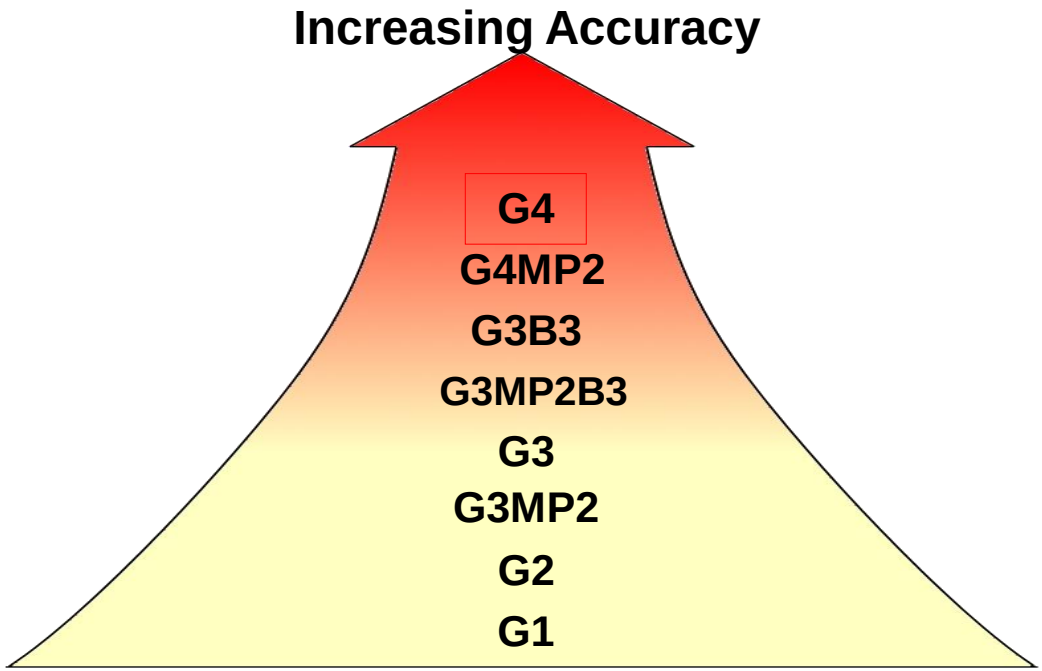
Minnesota DFT Functionals

- The Minnesota series of DFT functionals (cf. Truhlar and co-workers) provide improved reaction barrier heights and hence rate determinations.
- Developed using genetic algorithms to minimise the error via a series of training sets (e.g. based on barriers for hydrogen extractions).
- For each generation the training and test sets increase in size.



Composite Methods (e.g. Gaussian)

- Composite methods combine high levels of accuracy with efficiency by utilising the strongest aspects of several different methodologies.
- The aim is to be accurate within 4 kJ/mol for properties of stable species and radicals.
- Less accurate for calculating transition states and barrier heights.
- Particularly suitable for quickly building up large databases of thermodynamic data needed in kinetics models.



Average Absolute Deviation of Enthalpy from Experiment (kcal mol^{-1})

Type	No.	G3	G4
Nonhydrogens	79	2.10	1.13
Hydrocarbons	38	0.69	0.48
Subst. Hydrocarbons	100	0.82	0.68
Inorganic Hydrides	19	0.95	0.92
Radicals	34	0.83	0.66
All	270	1.19	0.80

Transition State Theory

- The reactions studied were pressure independent with clear transition states - only TST and VTST of interest and applied through POLYRATE 2010-A (Zheng et al. 2010).

- The structures and properties (including vibrational frequencies) need to be known for reactants, products and transition states. For standard TST the reaction rate is given by:

$$k_R = \sigma_{symm} \frac{kT}{h} \frac{Q^{\#}}{Q_A Q_B} \exp(-\Delta E_0 / kT)$$

Where,

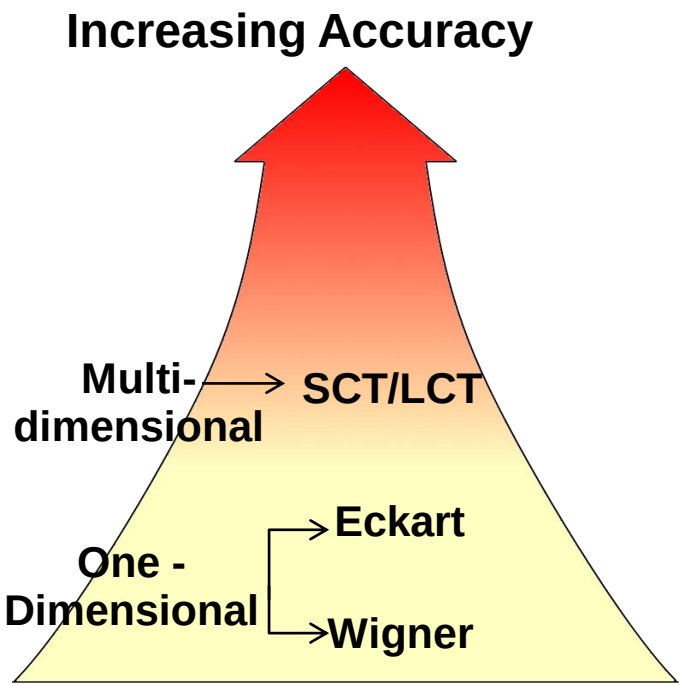
k	Boltzmann constant.
h	Plancks constant.
$Q^{\#}$	Product of vibrational, translation and rotational partition functions for the transition state.
$Q_A Q_B$	Product of vibrational, translation and rotational partition functions for the reactants.
ΔE_o	Activation energy.

Tunnelling Corrections

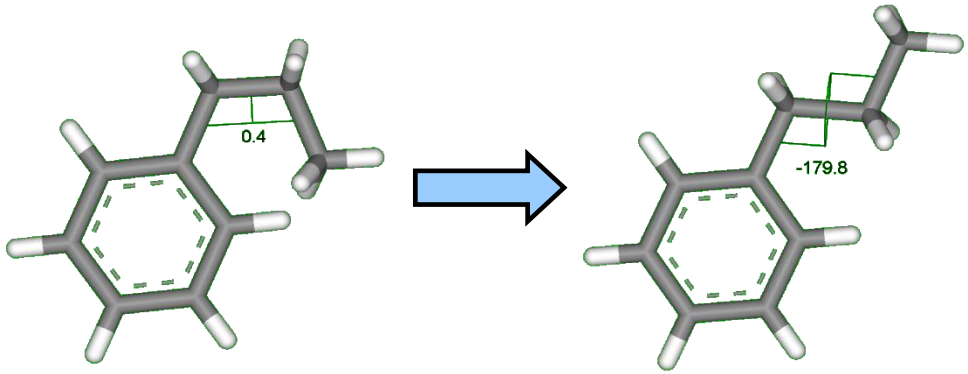
- One dimensional methods only require data on the stationary points. Allows simple ad-hoc corrections to be made to known rate constants.
- Wigner correction requires accurate imaginary frequencies $|V_{TS}|$.

$$\kappa(T) = 1 + \frac{1}{24}\left(\frac{h/|V_{TS}|}{k_b T}\right)^2$$

- Eckart corrections require energetics from reactants and transition states (symmetric) and from the products (asymmetric).
- Multi-dimensional methods require data on the curvature of the energy barrier.
- Calculations need to be carried either side of the barrier leading to increased computational expense.

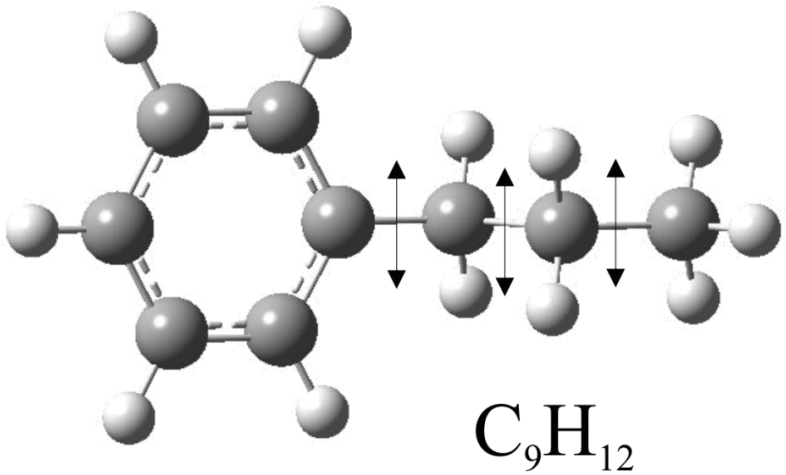


Geometries

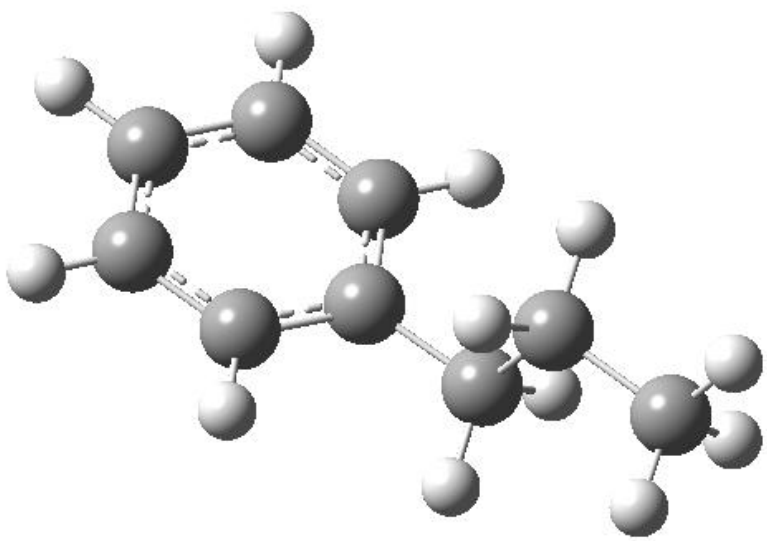


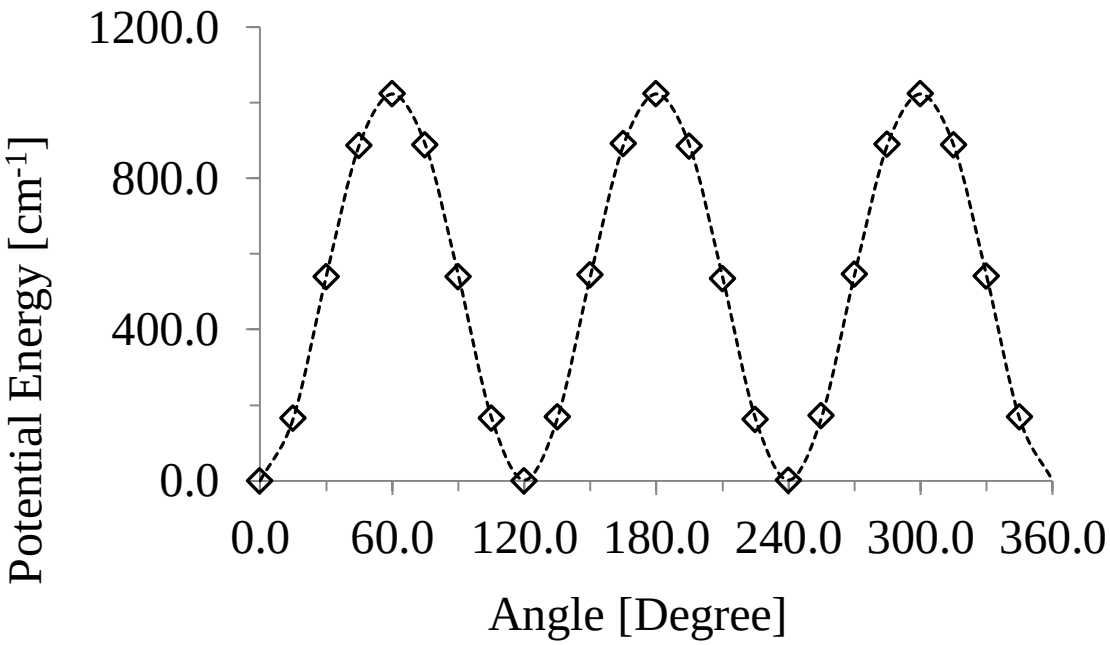
- The global minimum conformer has to be found to correctly establish the reaction energies.
- The optimised geometry is important for determining vibrational frequencies.
- Vibrational frequencies are used to both determine the ZPE and to calculate the partition functions of reactants/products/transition states.
- Geometries were here optimised using DFT methods. For the CCSD(T) calculations M06-2X/6-31++G(3df,3pd) geometries were used and for composite methods B3LYP/6-31(2df,p) geometries.

Internal Rotors: Potential Energy Scans



- Three hindered internal rotors identified for nPB.
- Rotors studied at the B3LYP/6-31g(d,p) level by rotating the dihedral angle through 360˚ in steps of 15 ˚ and optimising.
- The resulting energies were then fitted to the six term expansion $V=\frac{1}{2}\Sigma V_n(1-\cos(n\Theta))$.
- Methyl rotor shown with diamonds the calculated energies and the line the fitted function.





Summary of Explored Methods

Quantum Mechanical Methods

- Coupled Cluster: CCSD(T).
- DFT: M08-SO, M062X and M06.
- Composite: G4, G4MP2, CBS-QB3 and CBS-4M.

Basis Sets

- aug-cc-VDZ, 6-311++G(3df,3pd) and 6-31G(2df,p).

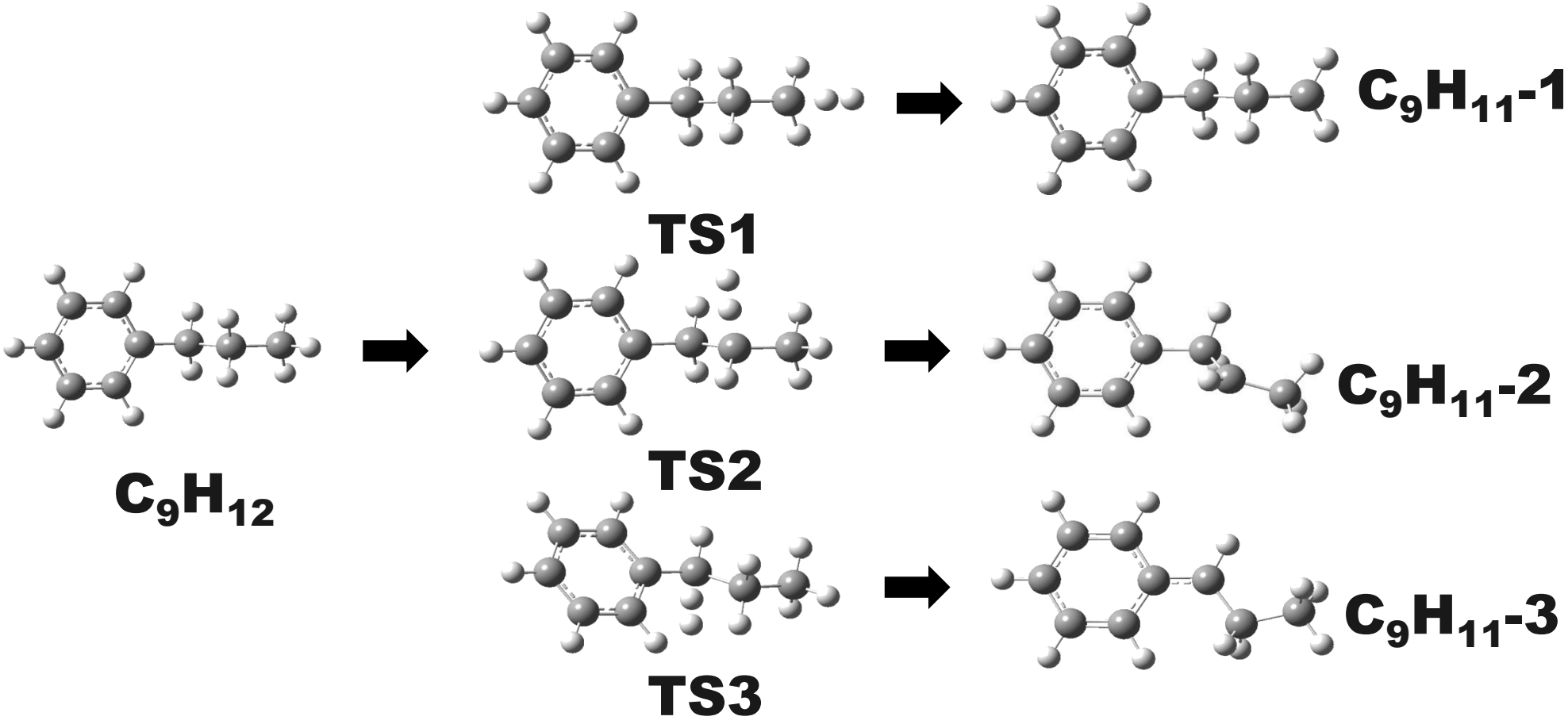
Tunnelling

- One-dimensional tunneling via Wigner, symmetric Eckart (forward barrier) and asymmetric Eckart (forward and reverse barriers).
- Multi-dimensional tunneling via SCT.

CCSD(T) coupled with aug-cc-pVDZ was the maximum practical level at which the calculations could be performed for the nPB system.

H Extractions from nPB

- The three hydrogen extraction via the H radical are shown below. The same process was also studied for the CH_3 radical.



H Extractions from nPB

Reaction	Reactant	Reactant	Product	Product
Number	1	2	1	2
1	C_9H_{12}	H	C_9H_{11}-1	H_2
2	C_9H_{12}	H	C_9H_{11}-2	H_2
3	C_9H_{12}	H	C_9H_{11}-3	H_2
4	C_9H_{12}	CH_3	C_9H_{11}-1	CH_4
5	C_9H_{12}	CH_3	C_9H_{11}-2	CH_4
6	C_9H_{12}	CH_3	C_9H_{11}-3	CH_4

QM Methods

- CCSD(T)/aug-cc-VDZ//M062X/6-311++G(3df,3pd)
- M08-SO/6-31G(2df,p)
- M062X/6-311++G(3df,3pd)
- M062X/6-31G(2df,p)
- M06/6-31G(2df,p)
- B3LYP/6-31G(2df,p)
- G4
- G4MP2
- CBS-QB3
- CBS-4M

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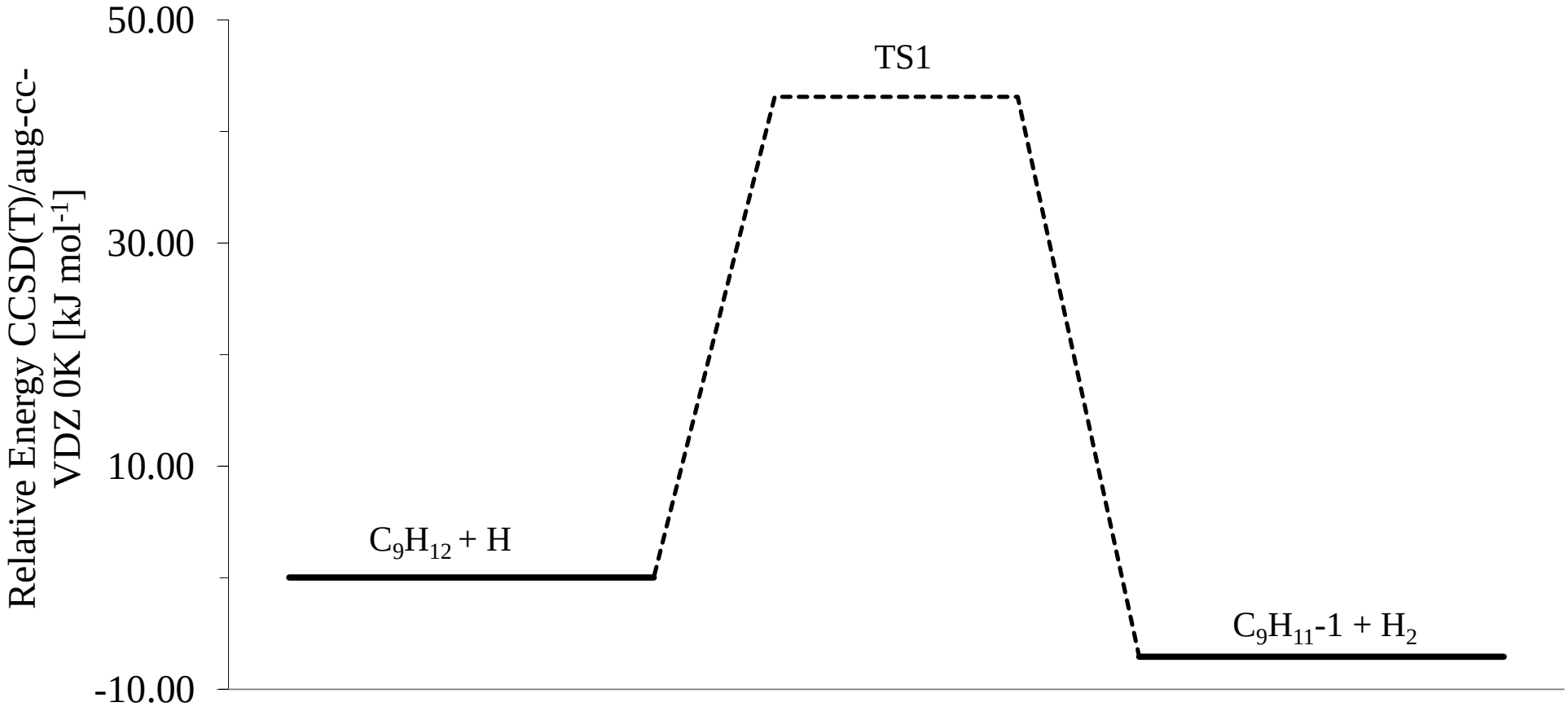
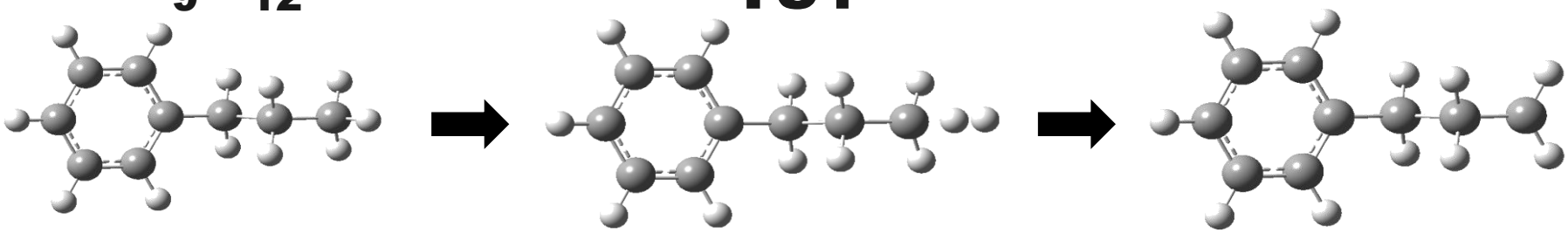
1- C_9H_{12} + H = C_9H_{11}-1 + H_2 – Potential Energy Surface



C_9H_{12} **TS1** **C_9H_{11}-1**



(R1) $C_9H_{12} + H = C_9H_{11}\text{-}1 + H_2$

- Comparison of methods for (R1) with forward and reverse barriers for $C_9H_{12}+H=C_9H_{11}\text{-}1+H_2$ calculated. Data in kJ/mol.
- Values compared to the coupled cluster calculation.
- M06-2X/6-31G(2df,p) was found to give a good match with CCSD(T) for extractions via the H radical.

Method and Basis Set	$V_f^{\#}$	$V_r^{\#}$	$\Delta V_f^{\#}$	$\Delta V_r^{\#}$	$\lvert\Delta\rvert$
CCSD(T)/aug-cc-VDZ//M06-2X/6-311++G(3df,3pd)	43.1	50.2	0.0	0.0	0.0
M06-2X/6-31G(2df,p)	45.1	52.4	2.0	2.2	2.1
M06/6-31G(2df,p)	39.6	51.5	-3.5	1.3	2.4
M08-SO/6-31g(2df,p)	46.9	55.1	3.8	4.9	4.3
CBS-QB3	42.7	59.4	-0.4	9.2	4.8
M06-2X/6-311++G(3df,3pd)	46.7	58.5	3.6	8.3	5.9
CBS-4M	46.8	60.8	3.7	10.5	7.1
G4	36.2	61.0	-6.9	10.8	8.9
G4MP2	19.2	37.3	-14.9	-9.6	12.3
B3LYP/6-31G(2df,p)	20.0	45.9	-23.1	-4.4	13.7

(R2) $C_9H_{12} + H = C_9H_{11}\text{-}2 + H_2$

- Comparison of methods for (R2) with forward and reverse barriers calculated for $C_9H_{12}+H=C_9H_{11}\text{-}2+H_2$. Values compared to the coupled cluster calculation.
- M06-2X/6-31G(2df,p) was again found to give a relatively good match for extractions via the H radical.

Method and Basis Set	$V_f^{\#}$	$V_r^{\#}$	$\Delta V_f^{\#}$	$\Delta V_r^{\#}$	$\lvert\Delta\rvert$
CCSD(T)/aug-cc-VDZ//M06-2X/6-311++G(3df,3pd)	34.0	47.0	0.0	0.0	0.0
M06-2X/6-31G(2df,p)	33.9	55.8	-0.1	8.8	4.5
M06-2X/6-311++G(3df,3pd)	34.5	59.7	0.5	12.7	6.6
M08-SO/6-31G(2df,p)	35.9	58.9	1.8	11.9	6.9
CBS-4M	35.8	59.3	1.8	12.3	7.1
CBS-QB3	31.9	59.9	-2.1	12.9	7.5
M06/6-31G(2df,p)	29.4	58.7	-4.6	11.7	8.2
G4	25.1	59.9	-8.9	12.9	10.9
G4MP2	17.7	56.6	-16.3	9.6	12.9
B3LYP/6-31G(2df,p)	11.9	54.5	-22.1	7.6	14.8

(R4) $C_9H_{12} + CH_3 = C_9H_{11}\text{-}2 + CH_4$

- Comparison of methods for (R4) with forward and reverse barriers calculated for $C_9H_{12}+CH_3=C_9H_{11}$-2+CH_4. Values compared to the coupled cluster calculation.
- A range of methods were found to give a relatively good forward barrier match for extractions via the CH_3 radical.
- Overall reduced accuracy compared to extraction with the H radical for the reverse barrier.

Method and Basis Set	$V_f^{\#}$	$V_r^{\#}$	$\Delta V_f^{\#}$	$\Delta V_r^{\#}$	$\lvert\Delta\rvert$
CCSD(T)/aug-cc-VDZ//M06-2X/6-311++G(3df,3pd)	44.2	58.5	0.0	0.0	0.0
M06-2X/6-31G(2df,p)	40.4	68.7	-3.8	10.2	7.0
CBS-4M	47.1	70.0	2.9	11.5	7.2
CBS-QB3	46.7	71.8	2.5	13.3	7.9
M06-2X/6-311++G(3df,3pd)	46.9	71.9	2.7	13.4	8.0
G4	41.6	73.1	-2.6	14.6	8.6
B3LYP/6-31G(2df,p)	40.4	75.5	-3.8	17.0	10.4
M08-SO/6-31G(2df,p)	45.7	78.5	1.5	20.0	10.7
G4MP2	34.4	71.4	-9.8	12.9	11.3

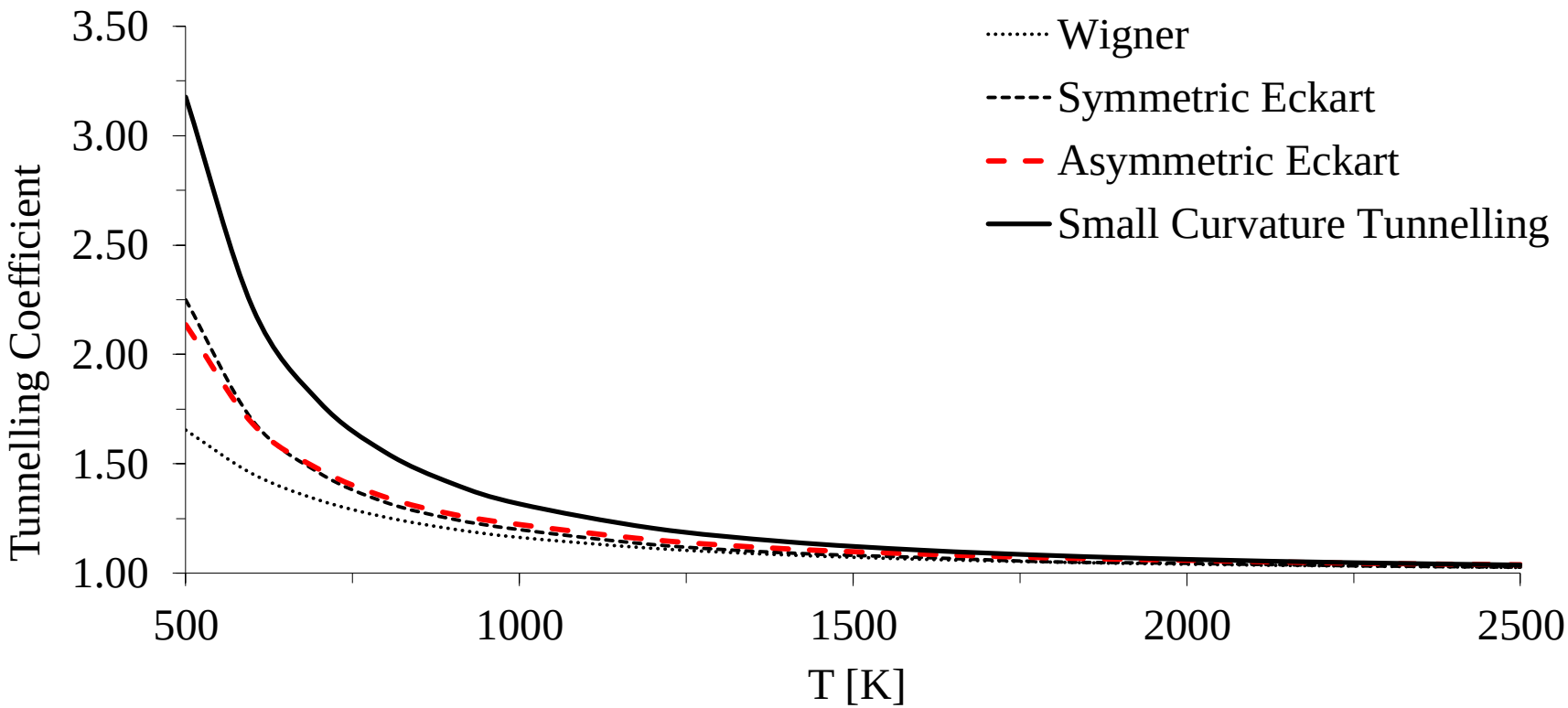
nPB Hydrogen Extraction Energies

- CCSD(T)/aug-cc-pVDZ and M06-2X/6-31g(2df,p) identified as suitable levels of theory to study the nPB system.
- CCSD(T)/aug-cc-pVDZ was the highest level of theory at which we could usefully study molecules the size of nPB with reasonable computing times.
- The M06-2X functional allowed VTST/SCT and TST/SCT calculations to study of the effect of quantum tunnelling and the variational character of the reactions while maintaining reasonably accurate energetics.

	CCSD(T)/aug-cc-pVDZ		M06-2X/6-31G(2df,p)		Δ	
	$V_f^{\#}$	$V_r^{\#}$	$V_f^{\#}$	$V_r^{\#}$	$V_f^{\#}$	$V_r^{\#}$
R1	43.1	50.2	45.1	52.4	2.0	2.2
R2	34.0	47.0	33.9	55.8	-0.1	8.8
R3	30.8	80.1	26.3	89.3	-4.6	9.2
R4	58.3	66.8	52.0	65.6	-6.3	-1.2
R5	44.2	58.5	41.1	68.7	-3.8	10.0
R6	40.0	90.6	33.1	102.9	-6.9	12.2

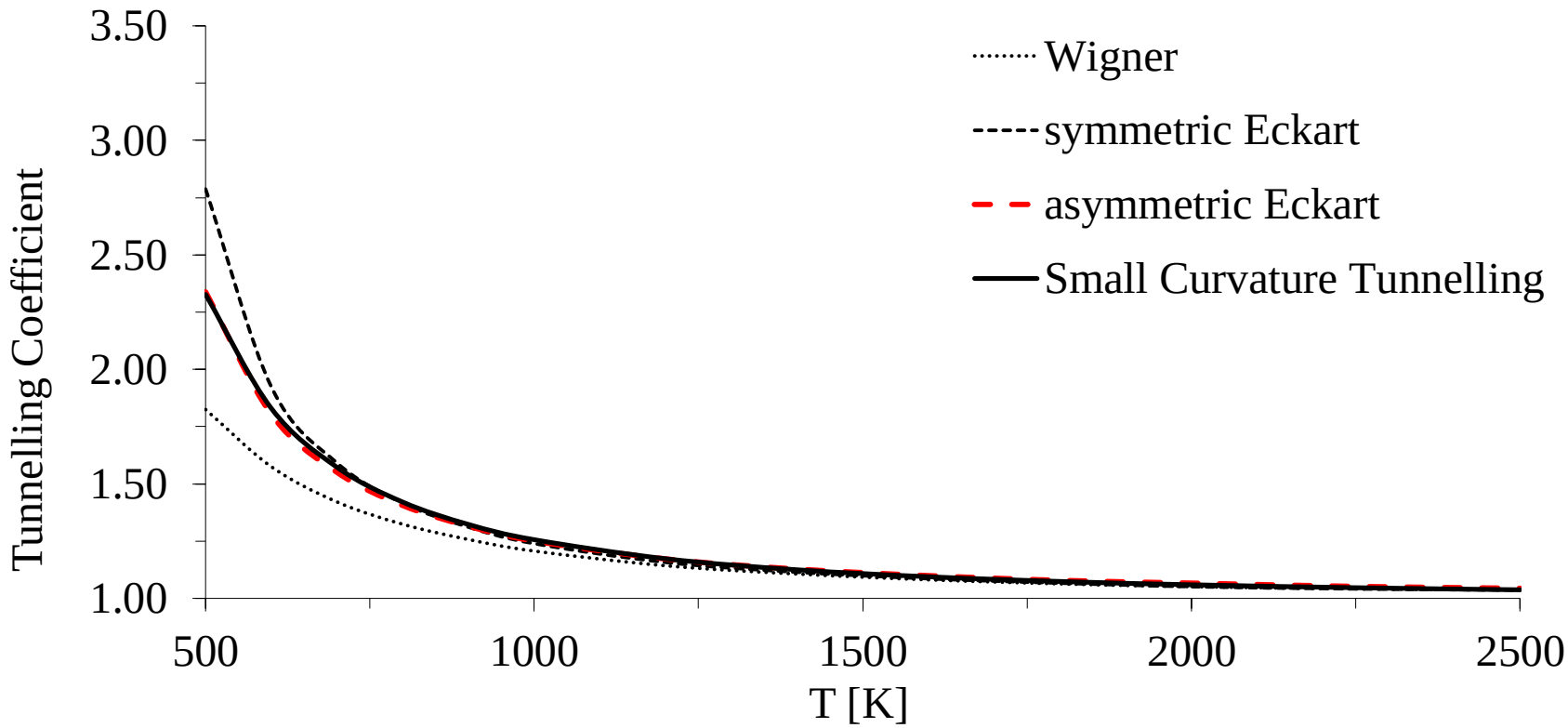
Tunnelling: (R1) $C_9H_{12} + H = C_9H_{11}\text{-}1 + H_2$

- Predicting tunnelling effects using multi-dimensional methods such as SCT is very costly for nPB at the CCSD(T) level.
- Methods compared at the M06-2X level to choose an appropriate alternative.
- Reaction (R1) has a forward barrier of 45 kJ/mol with Wigner and Eckart corrections failing to fully account for tunnelling. Eckart coefficients provide a closer match.

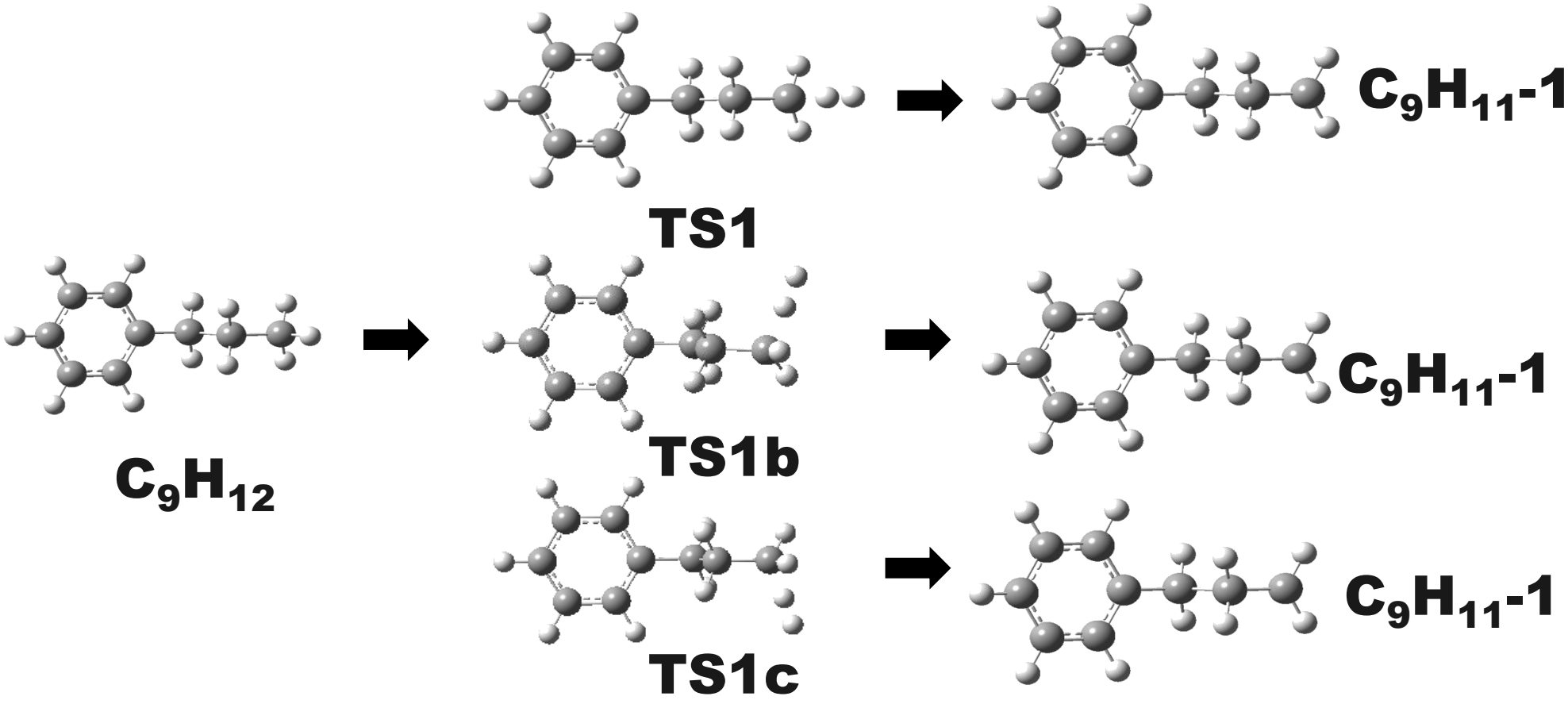


Tunnelling: (R3) $C_9H_{12} + H = C_9H_{11}\text{-}3 + H_2$

- Reaction (R3) has a smaller barrier (26.3 kJ/mol) with tunnelling effects less prominent.
- The Wigner method underestimates the tunnelling correction. The symmetric Eckart method inaccurate due to a reverse barrier of 89.3 kJ/mol.
- The asymmetric Eckart values provide a very close match to the SCT result.



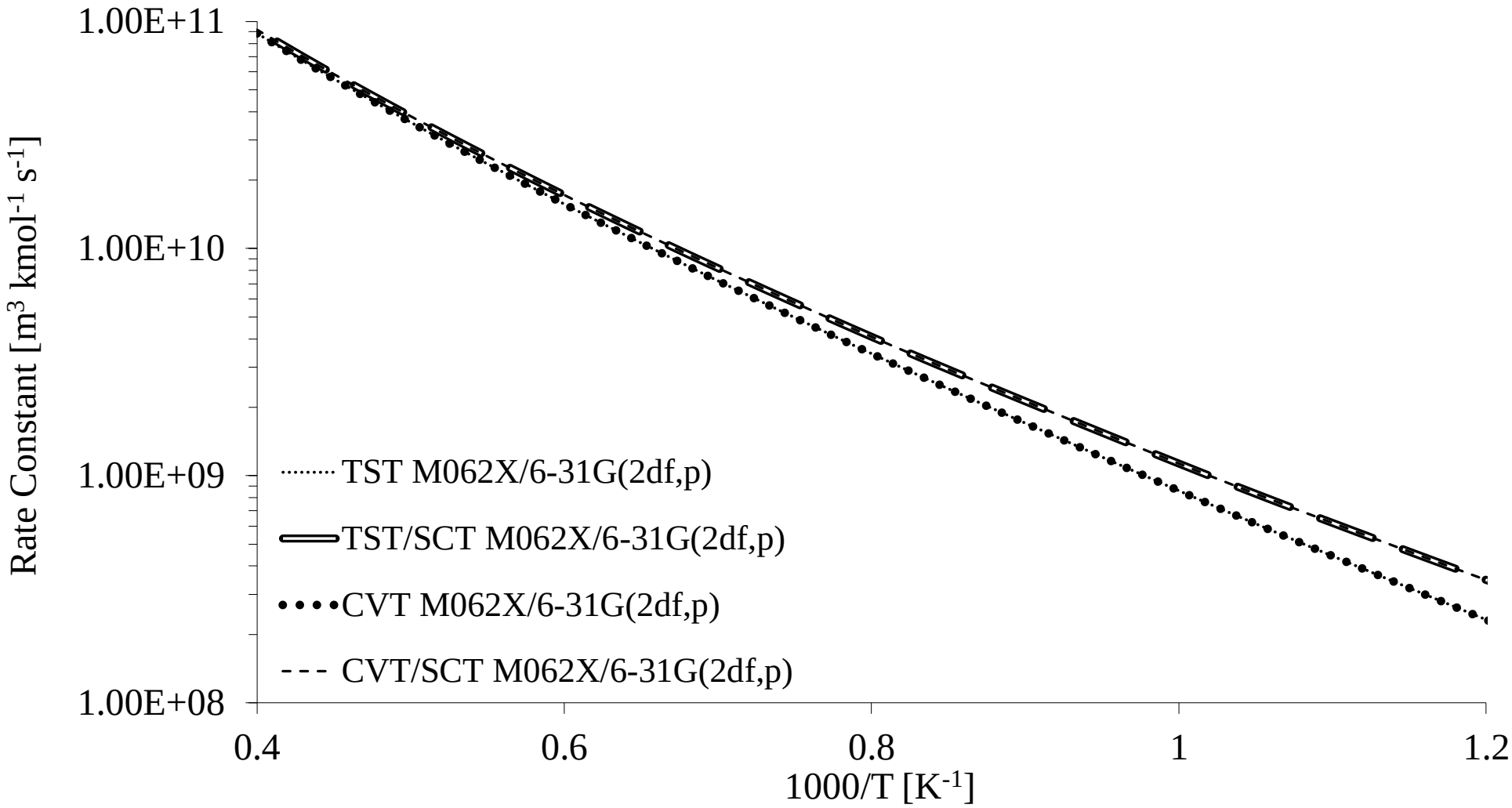
Reaction Degeneracies: (R1) $C_9H_{12} + H = C_9H_{11}\text{-}1 + H_2$



- Three energetically equivalent transition states were found for (R1) and a reaction degeneracy of 3 was used.
- The process was also applied to the other reactions while also taking into account the symmetry number of the methyl radical.

TST/CVT (R1) $C_9H_{12} + H = C_9H_{11}\text{-}1 + H_2$

- VTST calculations were carried out using the M06-2X functional - the reactions showed little variational character. This allowed the use of the more accurate CCSD(T) energies with standard TST.



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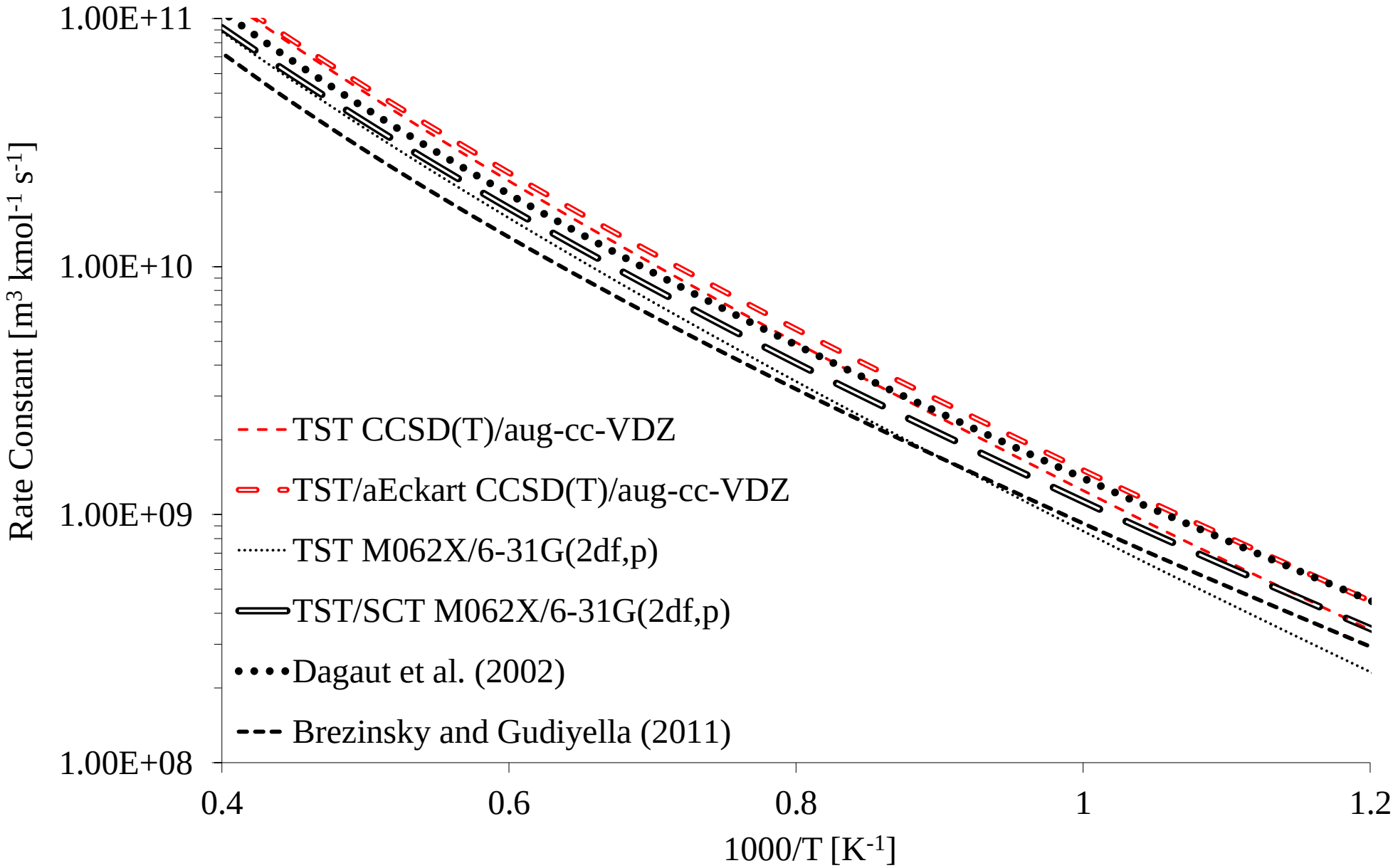
(R1) $C_9H_{12} + H = C_9H_{11}\text{-}1 + H_2$



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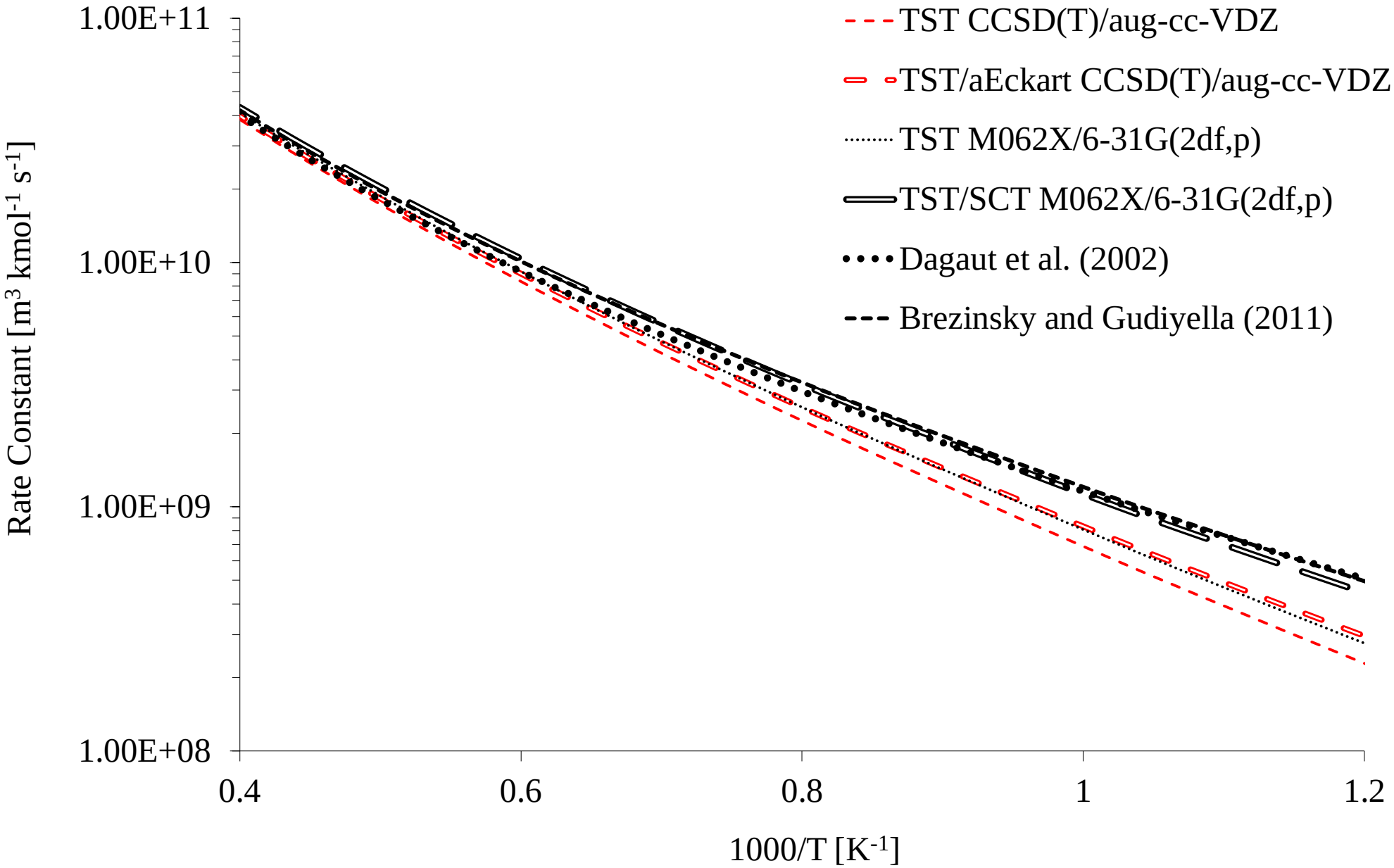
(R2) $C_9H_{12} + H = C_9H_{11}\text{-}2 + H_2$



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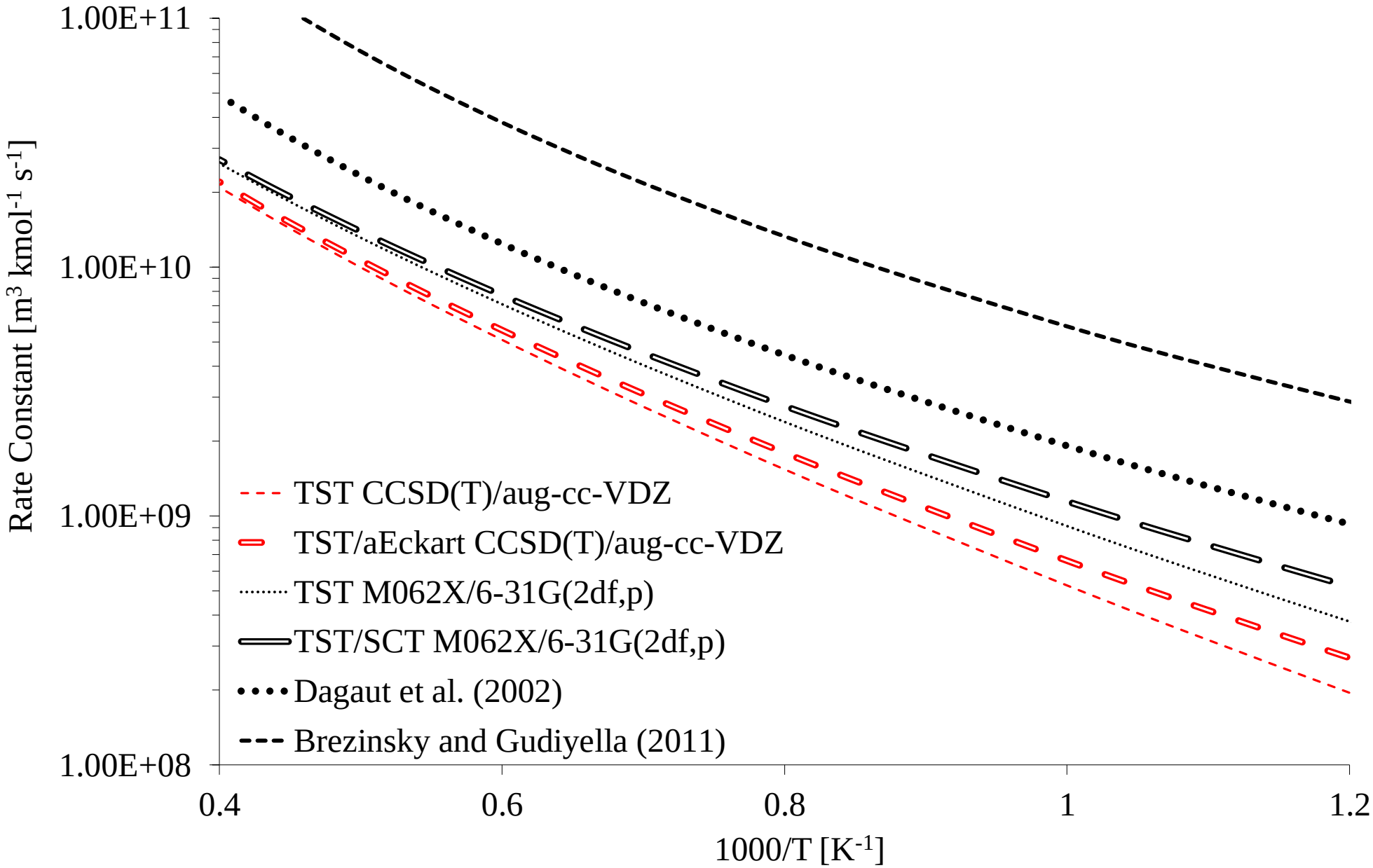
(R3) $C_9H_{12} + H = C_9H_{11}\text{-}3 + H_2$



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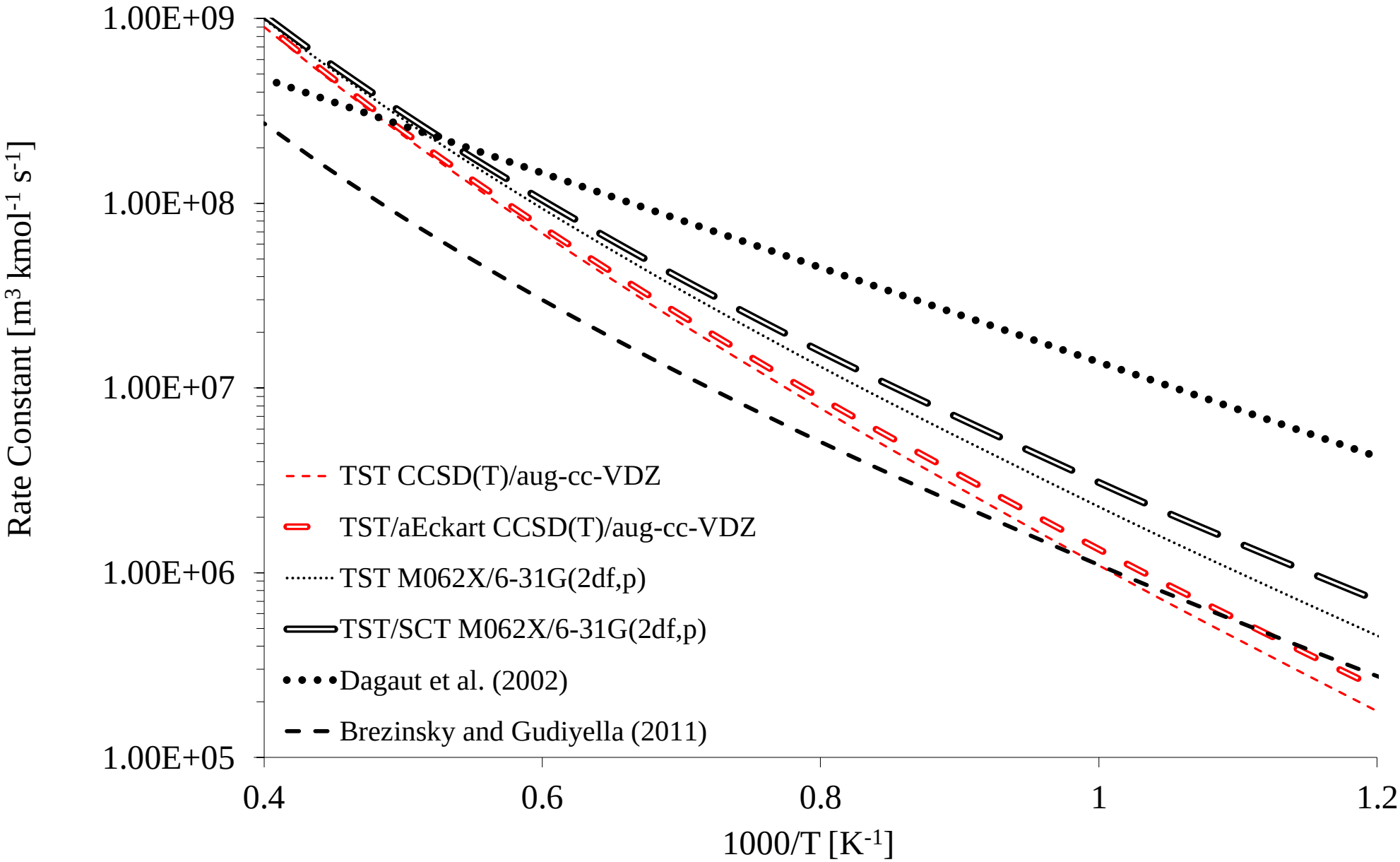
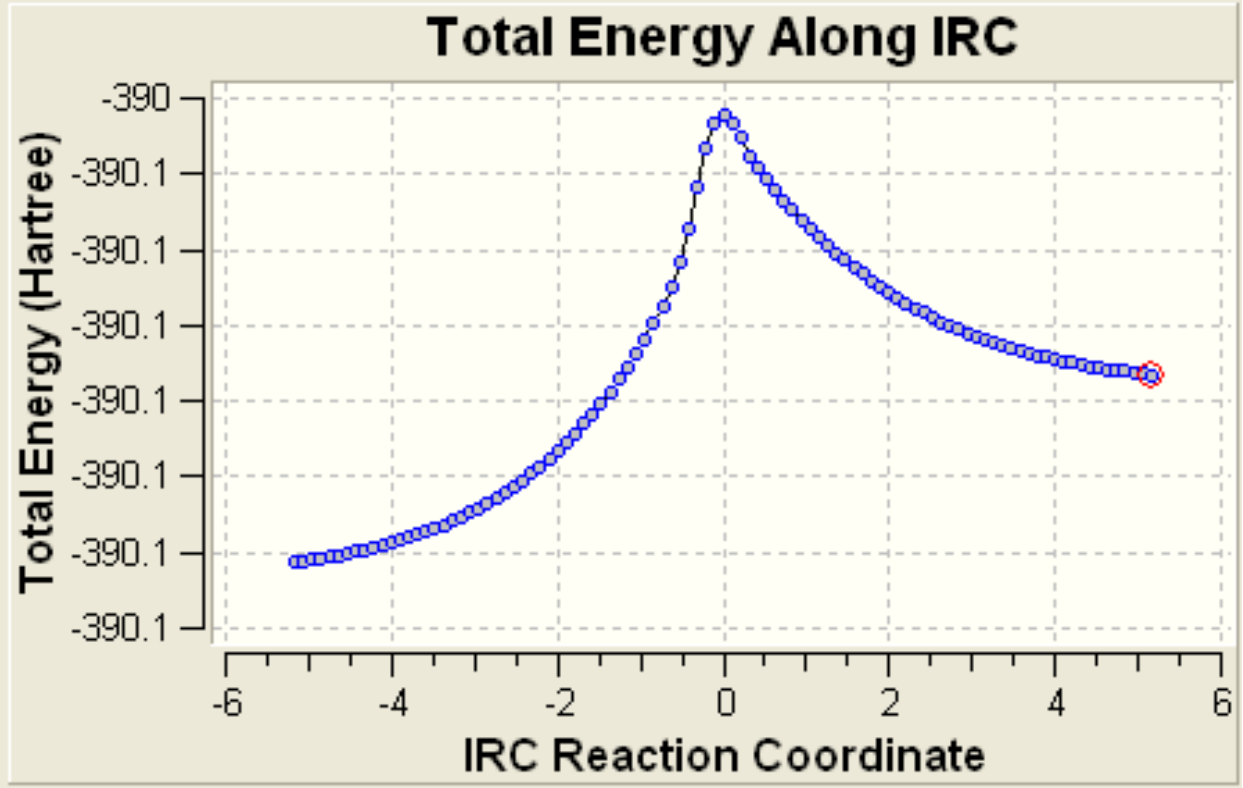
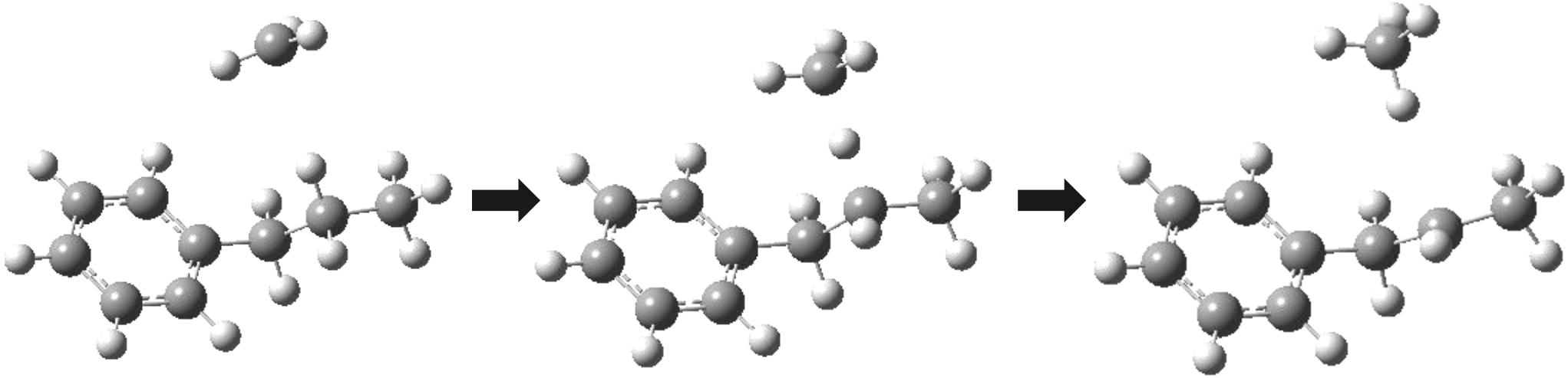
(R4) $C_9H_{12} + CH_3 = C_9H_{11}\text{-}1 + CH_4$



(R5) $C_9H_{12} + CH_3 = C_9H_{11}\text{-}2 + CH_4$

The graph on the right shows the energy along the intrinsic reaction co-ordinate (IRC).





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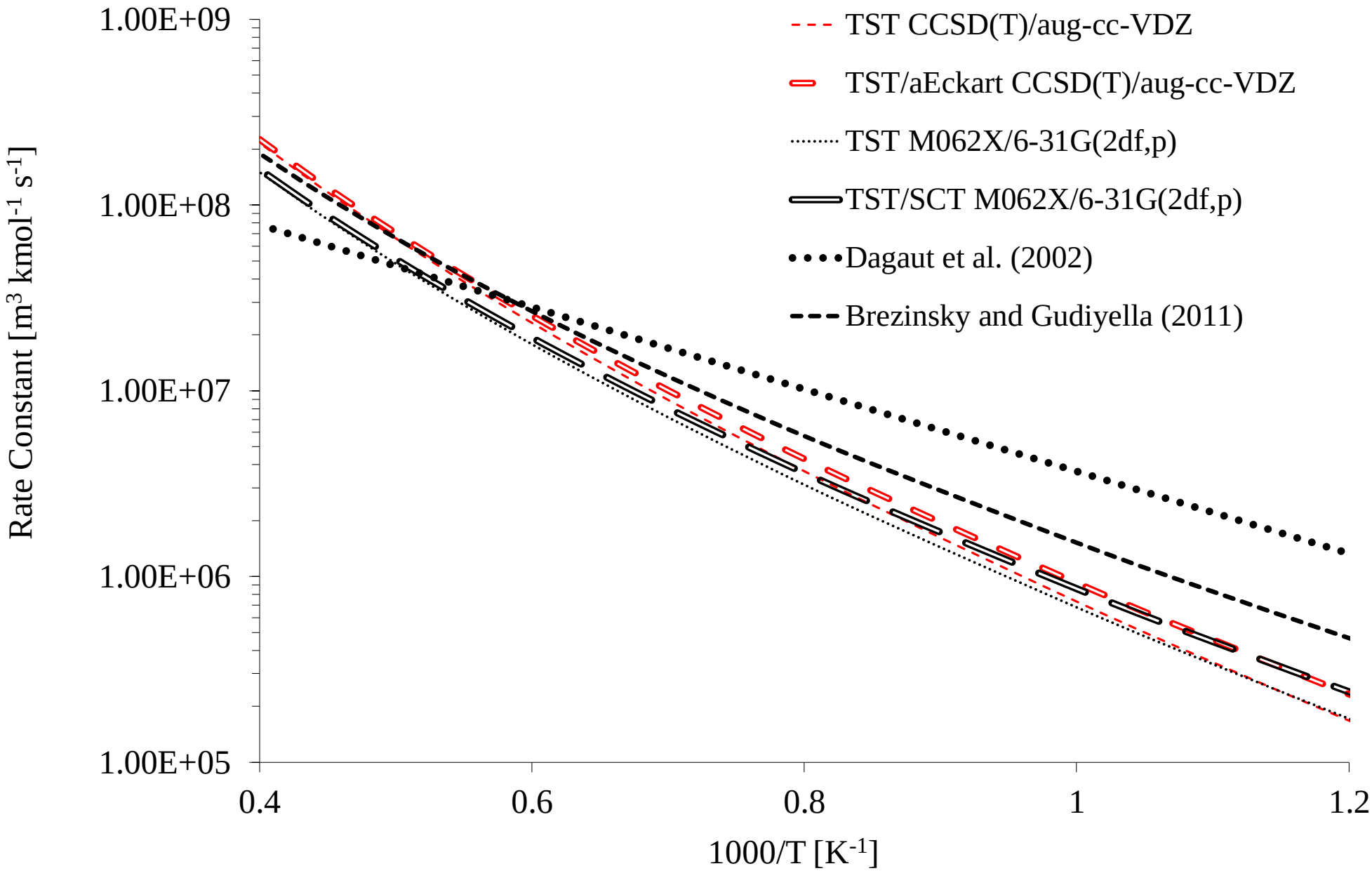
(R5) $C_9H_{12} + CH_3 = C_9H_{11}\text{-}2 + CH_4$



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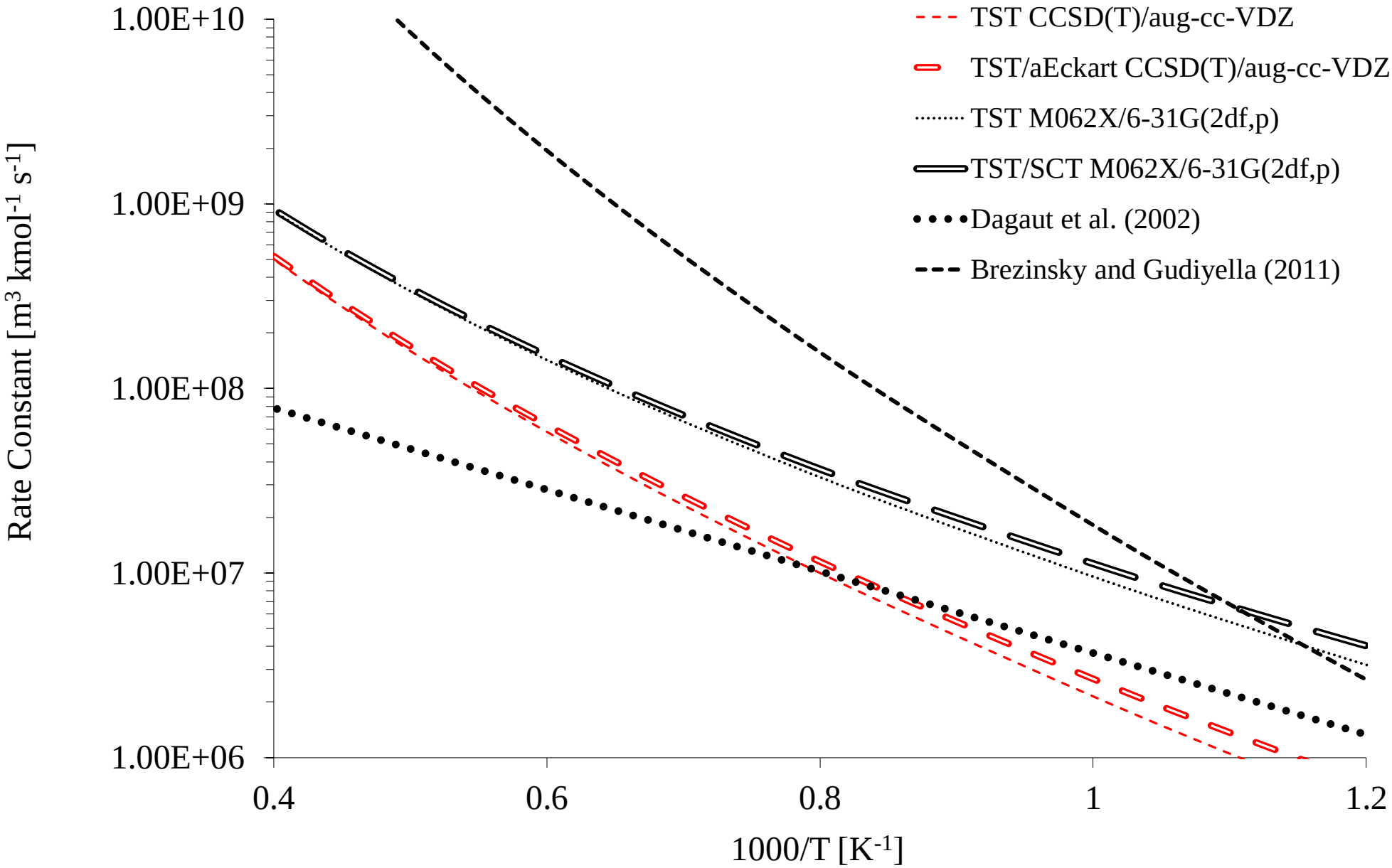
(R6) $C_9H_{12} + CH_3 = C_9H_{11}\text{-}3 + CH_4$



Conclusions

- CCSD(T)/aug-cc-pVDZ arguably the most accurate method applicable for calculating energetics of molecules within the nPB system in a timely manner.
- The M06-2X functional can provide accurate energies for the nPB system - larger differences for some CH_3 reactions.
- The M06-2X functional allows calculation of accurate tunneling corrections and variational (VTST) kinetics for molecules within the nPB system.
- The variational character is, however, minimal for the current bimolecular exchange reactions which have clear transition states.
- Asymmetric Eckart tunneling corrections can be readily applied to CC calculations. Provide a relatively accurate description of quantum tunneling effect.
- The applied methodology can be expected to significantly reduce the empiricism associated with mechanism construction at reasonable expense and the application to more complex sub-systems is possible.

Acknowledgement

Peter Lindstedt and Roger Robinson wish to thank Dr Chiping Li, Dr Julian Tishkoff (AFOSR) and Dr Gregg Abate (EOARD) for supporting this work via Award FA8655-09-1-3089.