Supporting Information:

High-Pressure Rate Rules for Alkyl + O_2Reactions: Part 1 - The Dissociation, Concerted Elimination and Isomerization Channels of the Alkyl Peroxy Radical.

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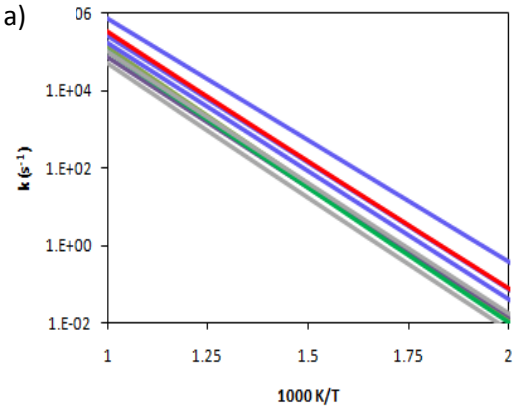
a)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1.E+04
1.E+02
1.E+00
1.E-02
k (s⁻¹)
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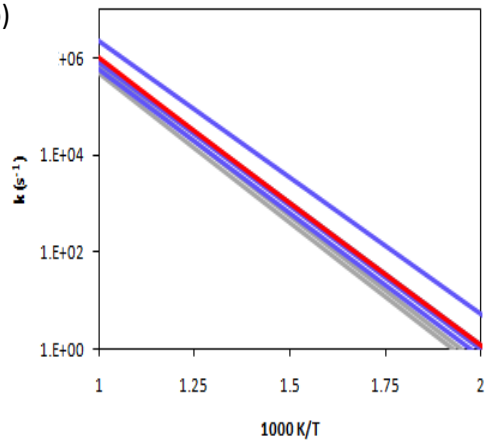
1.25
1.5
1.75
2
1000 K/T

b)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1.E+00
k (s⁻¹)
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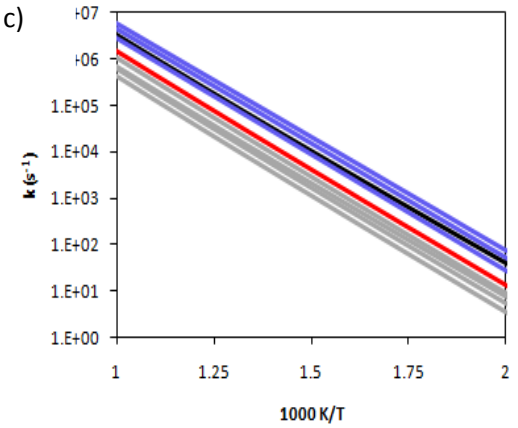
1.5
1.75
2
1000 K/T

c)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+06
1.E+05
1.E+04
1.E+03
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1.E+00
k (s⁻¹)
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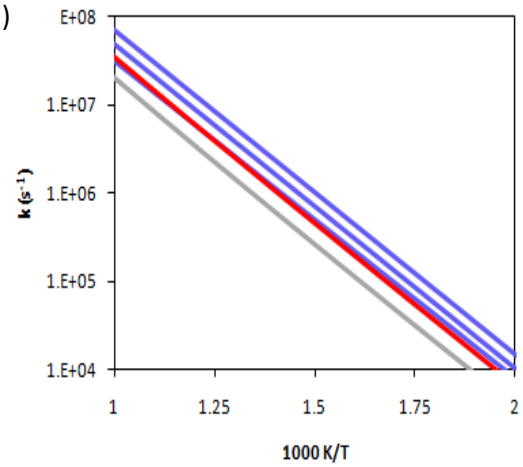
1.25
1.5
1.75
2
1000 K/T

d)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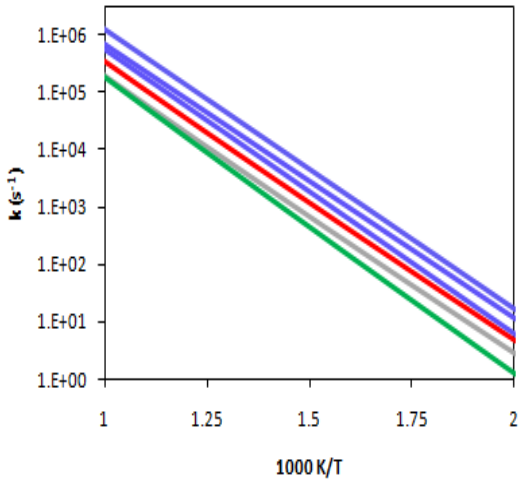
1.E+06
1.E+05
1.E+04
k (s⁻¹)
1
1.25
1.5
1.75
2
1000 K/T

e)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1.E+04
1.E+03
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k (s⁻¹)
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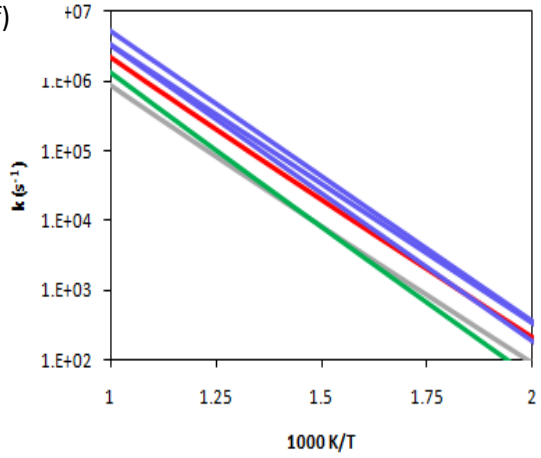
1.25
1.5
1.75
2
1000 K/T

f)


+07
1.E+06
1.E+05
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k (s⁻¹)
1
1.25
1.5
1.75
2
1000 K/T

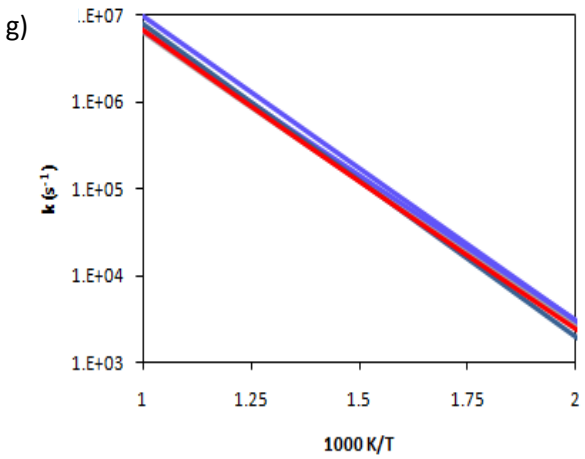

Figure S1: Comparisons of the rate rules derived in this work to previously reported values for the a) the primary 1-4, b) secondary 1-4, c) tertiary 1-4, d) primary 1-5, e) tertiary 1-5, f) primary 1-6, g) secondary 1-6, and h) tertiary 1-6 isomerization reactions. Red lines: Rate rules derived in this work; Blue lines: Ref 1; Green lines: Ref 4; Grey lines: Ref 3; Black lines: Ref 2.

1. Miyoshi, A., *J. Phys. Chem. A* **2011,** 115, (15), 3301-3325.

2. Zhang, F.; Dibble, T. S., *J. Phys. Chem. A* **2011,** 115, (5), 655-663.

3. Sharma, S.; Raman, S.; Green, W. H., *J. Phys. Chem. A* **2010,** 114, (18), 5689-5701.

4. Zhu, L.; Bozzelli, J. W.; Kardos, L. M., *J. Phys. Chem. A* **2007,** 111, (28), 6361-6377.

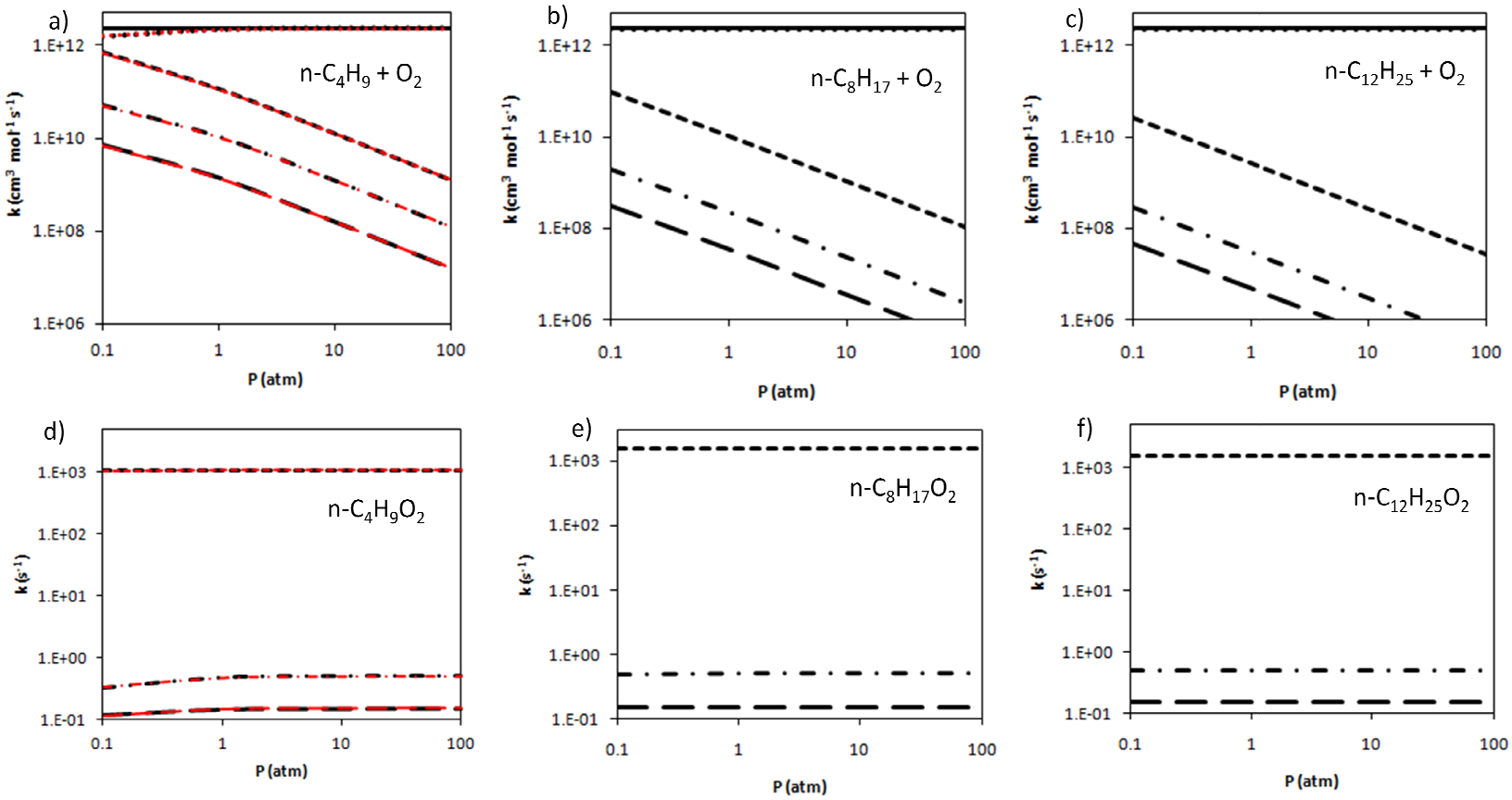

Figure S2: Calculated pressure dependent rate constants at 500 K for the chemically activated reactions of a) $C_4H_9 + O_2$ b) $C_8H_{17} + O_2$ and c) $C_{12}H_{25} + O_2$ and the corresponding thermal dissociation reactions of RO_2 (d, e, and f, respectively). The solid line corresponds to k_∞ for $R + O_2 \rightarrow RO_2$, the dotted line to the stabilization channel, the small dashed lines to the sum of the isomerization channels, the dot-dash lines to the dissociation channel and the large dashed lines to the concerted elimination channel. The black lines correspond to calculations performed using a ΔE_{all} value of -154 cm^{-1} while the red lines are for -80 cm^{-1}.

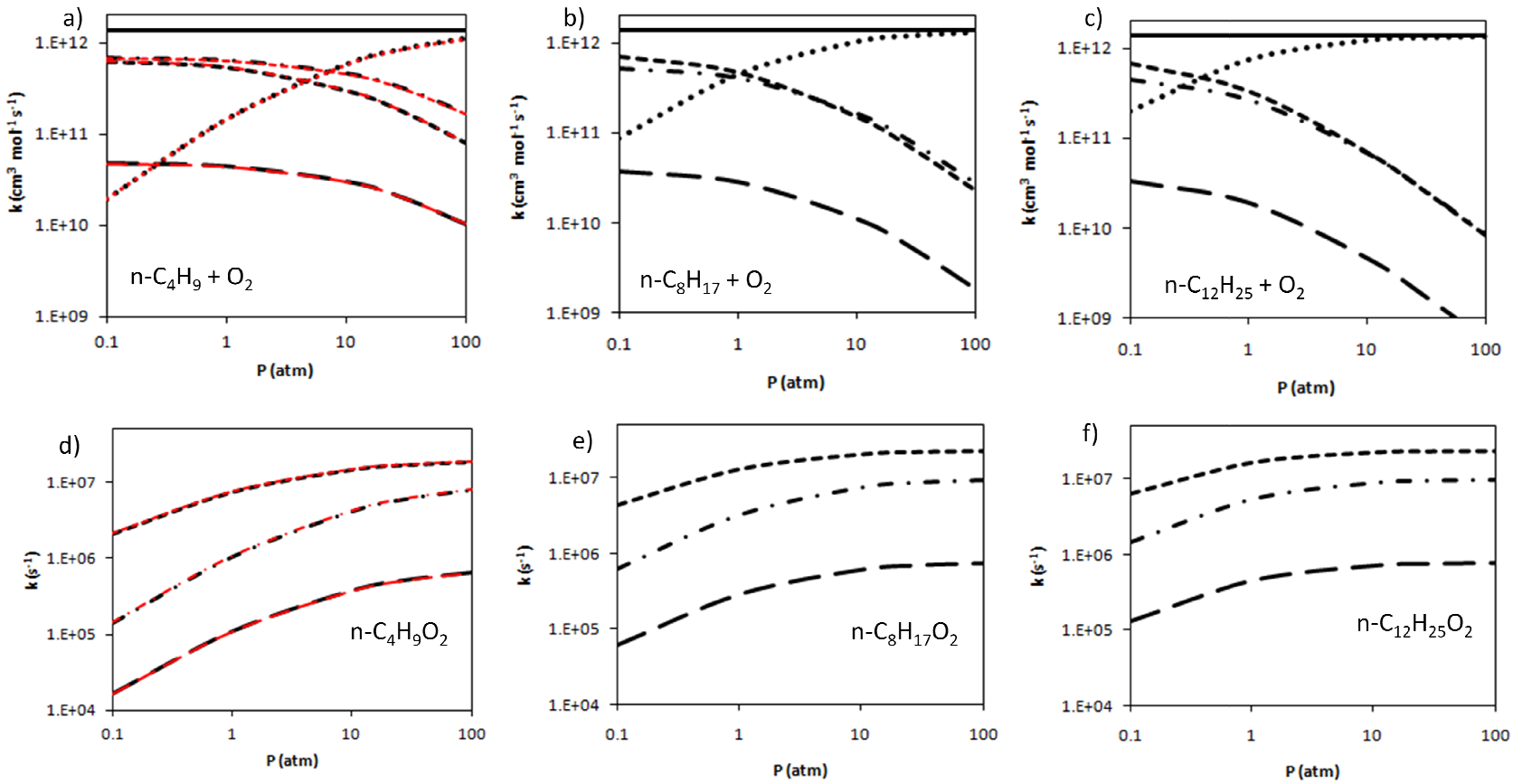

Figure S3: Calculated pressure dependent rate constants at 1000 K for the chemically activated reactions of a) $C_4H_9 + O_2$ b) $C_8H_{17} + O_2$ and c) $C_{12}H_{25} + O_2$ and the corresponding thermal dissociation reactions of RO_2 (d, e, and f, respectively). The solid line corresponds to k_∞ for $R + O_2 \rightarrow RO_2$, the dotted line to the stabilization channel. The black lines correspond to calculations performed using a ΔE_{all} value of -154 cm^{-1} while the red lines are for -80 cm^{-1}.