Direct Measurement of OH and HO$_2$ Formation in R + O$_2$ Reactions of Cyclohexane and Tetrahydropyran: Influence of Oxygenation in Cyclic Hydrocarbons

Supplementary Materials

Ming-Wei Chen[a*], Brandon Rotavera[b,c], Wen Chao[d,e], Judit Zádor[a], Craig A. Taatjes[a*]

a Combustion Research Facility, Sandia National Laboratories, Livermore, California 94550, USA

b College of Engineering, University of Georgia, Athens, Georgia 30602, USA

c Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA

d Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

e Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

A. Rate coefficients from ME calculations

Table S1. Theoretical rate coefficients (cm^3 s^{-1}) at 20 Torr of cyclohexyl + O$_2$ obtained from ME calculations based on the previous study[1] at temperatures relevant to the present work.

T (K)	R+O$_2$ → ROO	QOOH1	QOOH2	QOOH3	HO$_2$	OH[a]	OH[b]	OH[c]
500	7.90E-12	8.60E-18	6.00E-14	4.18E-15	1.89E-13	1.21E-14	3.08E-14	1.03E-14
550	6.65E-12	1.53E-17	6.64E-14	4.56E-15	3.22E-13	2.05E-14	6.02E-14	1.97E-14
600	5.43E-12	8.30E-17	7.27E-14	4.63E-15	4.92E-13	3.13E-14	1.01E-13	3.22E-14
650	4.35E-12	4.78E-17	6.09E-14	3.95E-15	6.39E-13	4.05E-14	1.39E-13	4.36E-14
700	3.34E-12	2.90E-17	5.48E-14	3.37E-15	7.85E-13	4.98E-14	1.78E-13	5.51E-14
750	2.47E-12	2.35E-17	4.68E-14	2.73E-15	8.98E-13	5.68E-14	2.09E-13	6.42E-14

[a] OH produced from the pathway along QOOH1.

[b] OH produced from the pathway along QOOH2.

[c] OH produced from the pathway along QOOH3.

Table S2. Theoretical rate coefficients (s^{-1}) at 20 Torr of cyclohexyl peroxy decomposition and isomerization obtained from ME calculations based on the previous study[1] at temperatures relevant to the present work.

	ROO →							
T (K)	R+O_2	QOOH1	QOOH2	QOOH3	HO_2	OH[a]	OH[b]	OH[c]
500	1.28E-1	1.09E-2	3.81	5.21E-2	4.77E-1	2.93E-2	2.43E-2	6.32E-3
550	3.153	0.1402	34.15	0.6195	7.419	0.4077	0.5329	0.1575
600	42.48	3.482	226.4	4.806	71.4	1.455	6.207	1.999
650	350.5	1.66E-03	1219	27.25	462.1	30.78	40.78	14.62
700	1904	1.74E-02	5782	123.2	2110	138	126.5	64.77
750	6711	0.1973	2.62E4	467.3	6629	429.7	-403.1	136.9

[a] OH produced from the pathway along QOOH1.

[b] OH produced from the pathway along QOOH2.

[c] OH produced from the pathway along QOOH3.

Table S3. Theoretical rate coefficients (cm^3 s^{-1}) at 20 Torr of tetrahydropyranyl + O_2 obtained from ME calculations based on adjusting the ROO well depth (+2 kcal/mol) and QOOH1→HO_2 transition state (-2 kcal/mol) to the PES of cyclohexyl + O_2 at temperatures relevant to the present work.

	R+O_2 →							
T (K)	ROO	QOOH1	QOOH2	QOOH3	HO_2	OH[a]	OH[b]	OH[c]
500	6.65E-12	2.34E-17	1.25E-13	8.30E-15	1.26E-12	1.94E-14	4.53E-14	1.52E-14
550	5.07E-12	3.50E-17	1.24E-13	8.17E-15	1.72E-12	2.79E-14	7.62E-14	2.51E-14
600	3.68E-12	1.26E-16	1.18E-13	7.37E-15	2.14E-12	3.64E-14	1.11E-13	3.58E-14
650	2.74E-12	7.91E-17	8.63E-14	5.61E-15	2.28E-12	4.16E-14	1.37E-13	4.33E-14
700	1.90E-12	3.57E-17	6.91E-14	4.30E-15	2.42E-12	4.63E-14	1.62E-13	5.01E-14
750	1.28E-12	2.37E-17	5.32E-14	3.17E-15	2.45E-12	4.91E-14	1.78E-13	5.46E-14

[a] OH produced from the pathway along QOOH1.

[b] OH produced from the pathway along QOOH2.

[c] OH produced from the pathway along QOOH3.

Table S4. Theoretical rate coefficients (s^{-1}) at 20 Torr of tetrahydropyranyl peroxy decomposition and isomerization obtained from ME calculations based on adjusting the ROO well depth (+2 kcal/mol) and QOOH1→HO$_2$ transition state (-2 kcal/mol) to the PES of cyclohexyl + O$_2$ at temperatures relevant to the present work.

	ROO →							
T (K)	R+O$_2$	QOOH1	QOOH2	QOOH3	HO$_2$	OH^a	OH^b	OH^c
500	7.93E-1	7.84E-2	2.82E+1	3.81E-1	2.61E+1	2.11E-1	1.63E-1	4.08E-2
550	14.79	0.791	206.2	3.673	272	2.314	2.719	0.7773
600	151.9	13.26	1128	23.47	1830	8.824	23.84	7.524
650	963.8	9.13E-3	4971	109.9	8532	108.6	113.8	41.52
700	4101	6.41E-2	1.86E+4	407.1	2.90E+4	387.8	224.2	136.6
750	1.23E+4	0.4252	6.07E+4	1256	7.41E+4	1030	-777.7	225

^{a} OH produced from the pathway along QOOH1.

^{b} OH produced from the pathway along QOOH2.

^{c} OH produced from the pathway along QOOH3.

B. Data

HO$_2$ and OH data files are supplied as ASCII format, and collection of traces are also shown in this section.

Figure S1. HO$_2$ data observed from the Cl-initiated cyclohexane oxidation reaction. Symbols are representing every 25th data point.
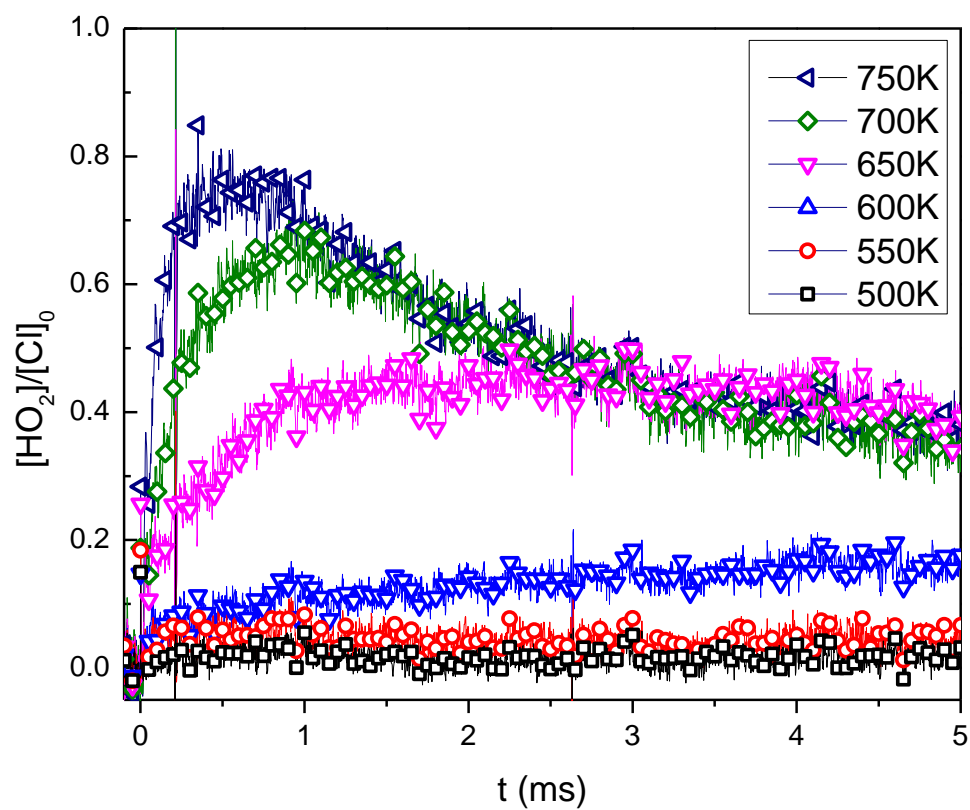
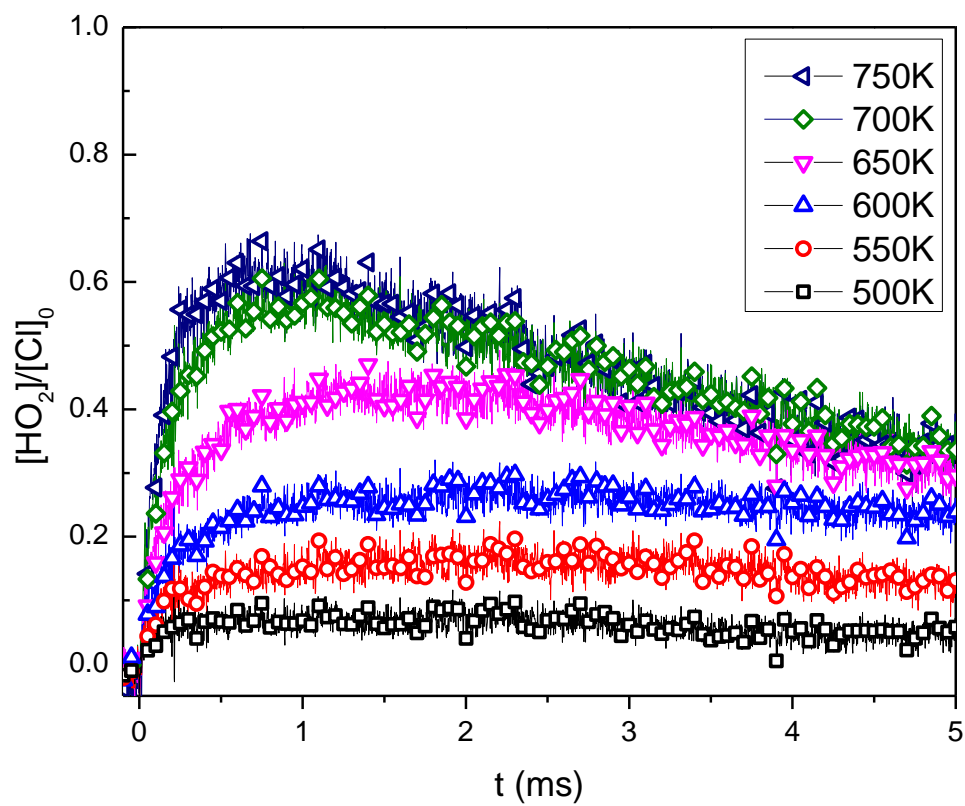**Figure S2.** HO$_2$ data observed from the Cl-initiated tetrahydropyran oxidation reaction. Symbols are representing every 25th data point.

Figure S3. OH data observed from the Cl-initiated cyclohexane oxidation reaction.
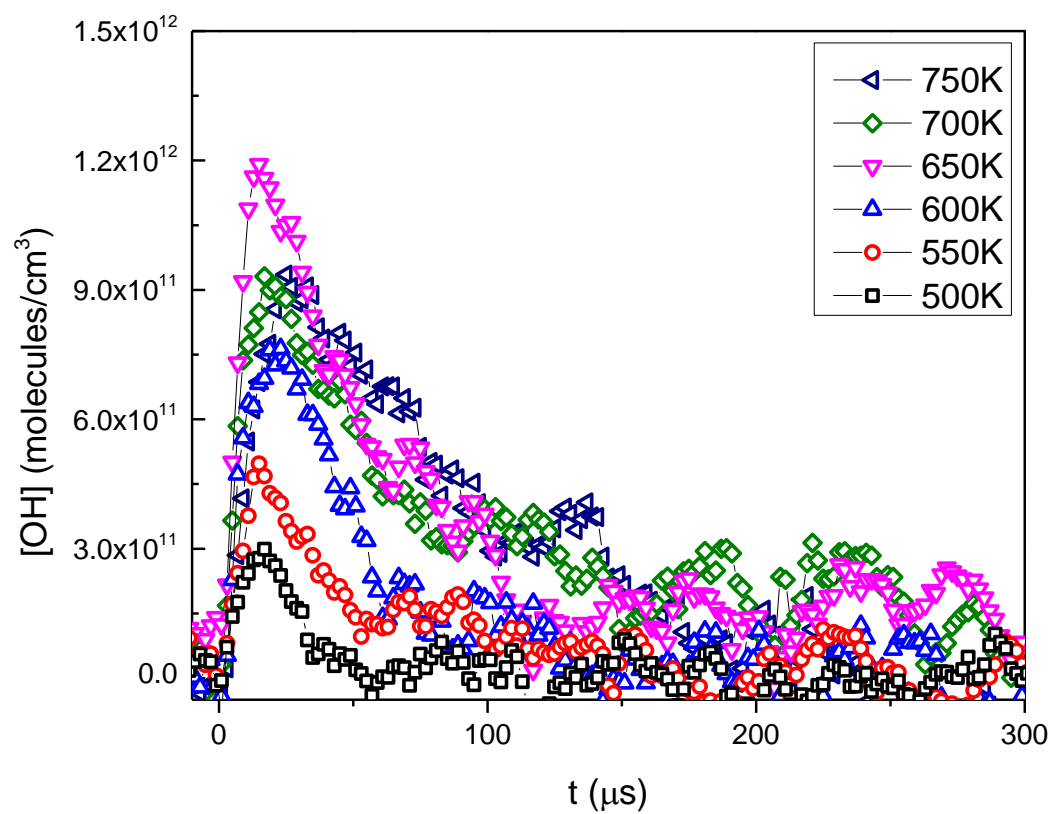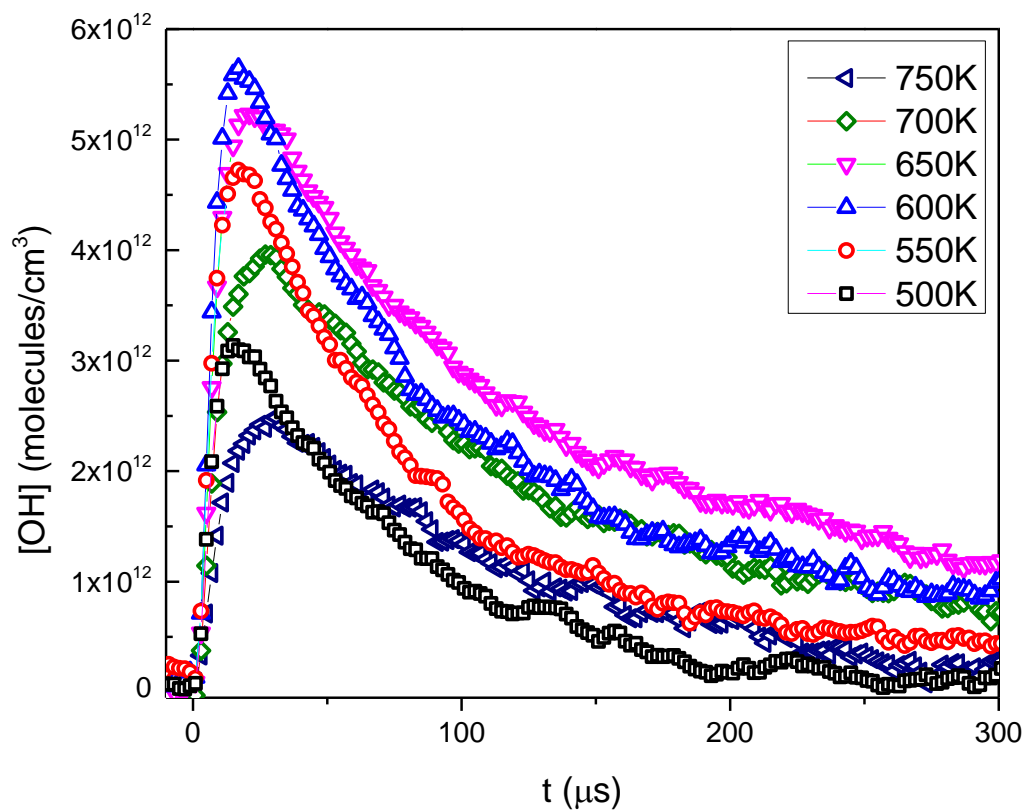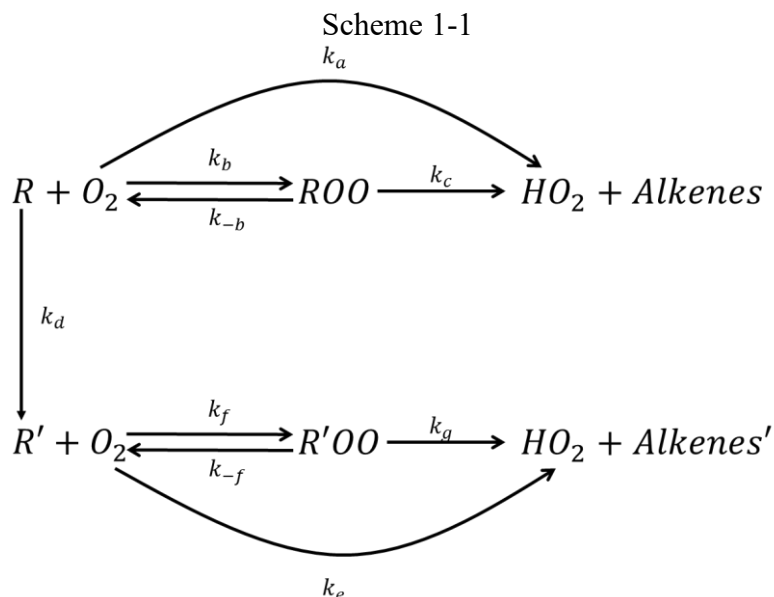
Figure S4. OH data observed from the Cl-initiated tetrahydropyran oxidation reaction.
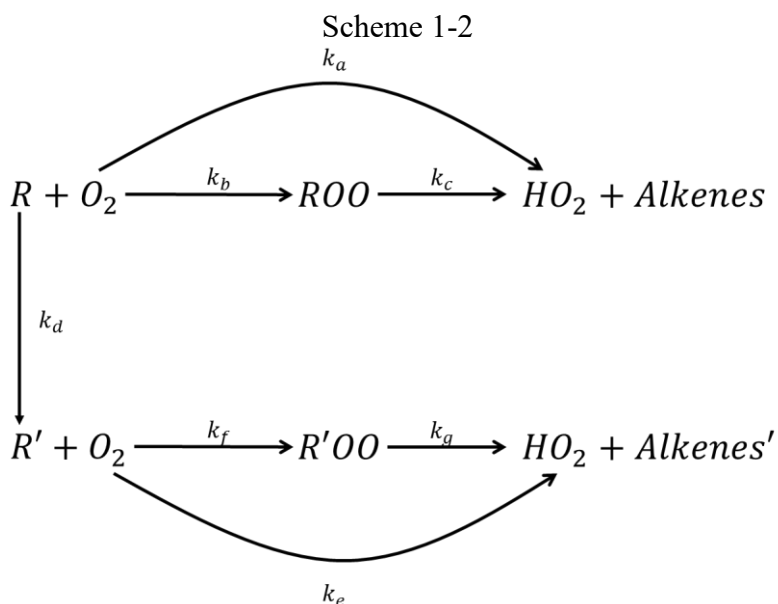
C. Simple and skeletal kinetic models for tetrahydropyran oxidation.

Scheme I: Simple scheme.
Considering the THP-yl (R) decomposition branching from the regular R + O₂ skeleton, the complete scheme of the reduced model for THP oxidation should be:

Scheme 1-1

$$R + O_2 \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} ROO \xrightarrow{k_c} HO_2 + Alkenes$$

with k_a arrow from $R + O_2$ to $HO_2 + Alkenes$, k_d arrow down from $R + O_2$ to $R' + O_2$.

$$R' + O_2 \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} R'OO \xrightarrow{k_g} HO_2 + Alkenes'$$

with k_e arrow from $R' + O_2$ to $HO_2 + Alkenes'$.

However, the solution of $[HO_2]_t$ is still very complex even when ignoring the equilibrium between $R + O_2$ and ROO:

Scheme 1-2

$$R + O_2 \xrightarrow{k_b} ROO \xrightarrow{k_c} HO_2 + Alkenes$$

with k_a arrow from $R + O_2$ to $HO_2 + Alkenes$, k_d arrow down from $R + O_2$ to $R' + O_2$.

$$R' + O_2 \xrightarrow{k_f} R'OO \xrightarrow{k_g} HO_2 + Alkenes'$$

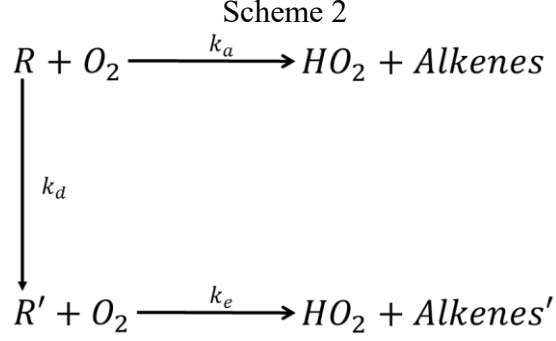with k_e arrow from $R' + O_2$ to $HO_2 + Alkenes'$.

Because it is not reasonable to resolve more than two timescales from the experimental trace, and the two fitted timescales are showing no sequential behavior, an even simpler reaction scheme is illustrative.

Scheme II: Skeletal scheme.
A scheme ignoring alkyl peroxy intermediates can simplify the solution of $[HO_2]_t$, because we know the two timescales in the HO_2 time profile of THP-yl $+O_2$ do not show the behavior expected from a

"sequential" mechanism via thermal isomerization and dissociation of QOOH:

Scheme 2

$$R + O_2 \xrightarrow{k_a} HO_2 + Alkenes$$

$$\Big\downarrow k_d$$

$$R' + O_2 \xrightarrow{k_e} HO_2 + Alkenes'$$

The ordinary differential equations of this simplified scheme are:

$$\frac{d[R]}{dt} = -k_a[O_2][R] - k_d[R] \tag{S1}$$

$$\frac{d[R']}{dt} = -k_a[O_2][R'] + k_d[R'] \tag{S2}$$

$$\frac{d[HO_2]}{dt} = k_a[O_2][R] + k_a[O_2][R'] \tag{S3}$$

Then the solutions are:

$$[R]_t = [R]_0 e^{-(k_a[O_2]+k_d)t} \tag{S4}$$

$$[R']_t = \frac{[R]_0 k_d}{-k_a[O_2] + k_e[O_2] - k_d}\left(e^{-(k_a[O_2]+k_d)t} - e^{-k_e[O_2]t}\right) \tag{S5}$$

$$[HO_2]_t = \frac{[R]_0}{k_a[O_2] - k_e[O_2] + k_d}\Big((k_a[O_2] - k_e[O_2])\big(1 - e^{-(k_a[O_2]+k_d)t}\big) + k_d\big(1 - e^{-k_e[O_2]t}\big)\Big) \tag{S6}$$

By collecting terms in equation (6), we can obtain:

$$[HO_2]_t = \frac{[R]_0(k_a[O_2] - k_e[O_2])}{k_a[O_2] - k_e[O_2] + k_d}\left(1 - e^{-(k_a[O_2]+k_d)t}\right) + \frac{[R]_0 k_d}{k_a[O_2] - k_e[O_2] + k_d}\left(1 - e^{-k_e[O_2]t}\right) \tag{S7}$$

which has the same analytical form as the fitting model in the manuscript:

$$[HO_2]_t = A_1(1 - e^{-k_1 t}) + A_2(1 - e^{-k_2 t}) \tag{S8}$$

Where

$$A_1 = \frac{[R]_0(k_a[O_2] - k_e[O_2])}{k_a[O_2] - k_e[O_2] + k_d} \tag{S9}$$

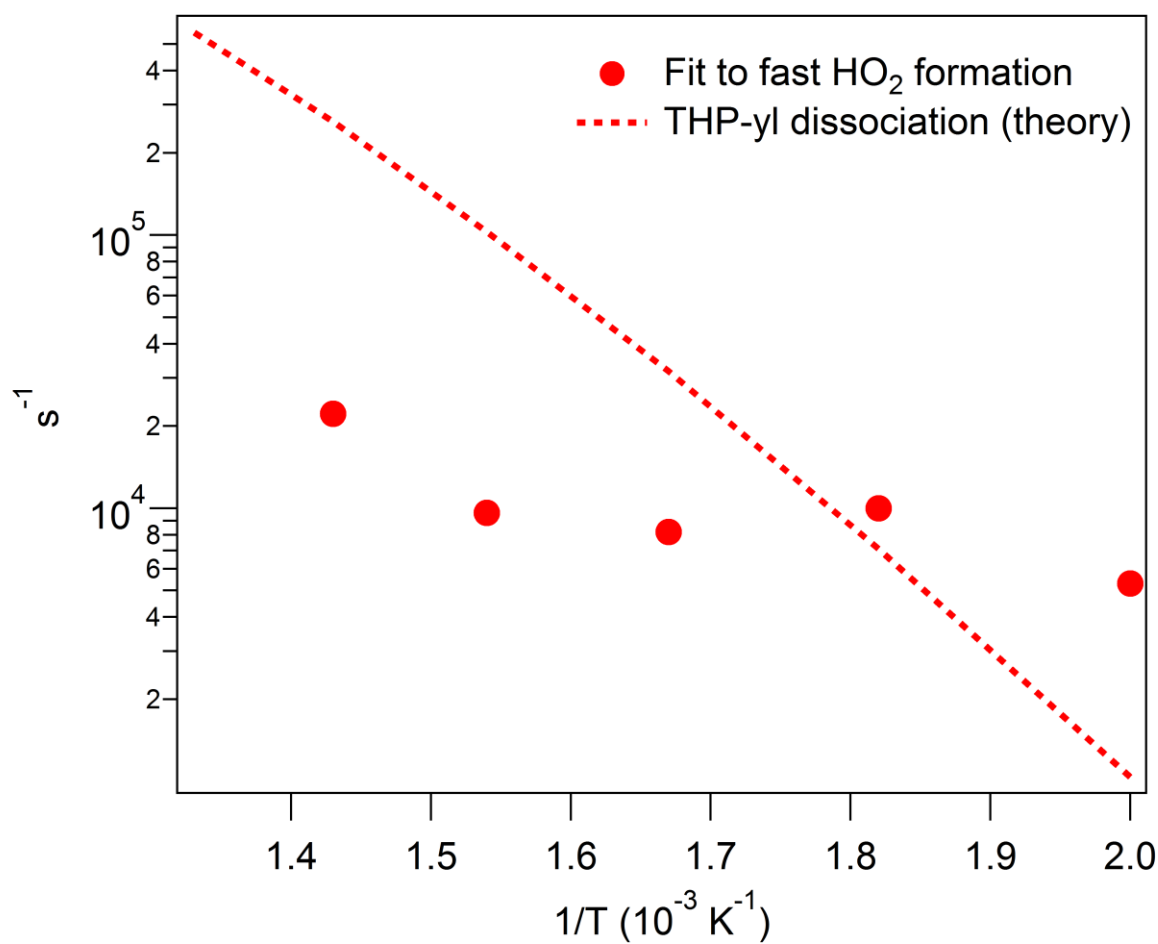$$A_2 = \frac{[R]_0 k_d}{k_a[O_2] - k_e[O_2] + k_d} \tag{S10}$$

$$k_1 = k_a[O_2] + k_d \tag{S11}$$

$$k_2 = k_e[O_2] \tag{S12}$$

The fitted parameters can be interpreted in different models for the two fuels because the kinetic behavior of the oxidation is different between cyclohexane and tetrahydropyran. In this skeletal model with decomposition of the initial radical, the relative amplitudes of the two components would show a dramatic temperature dependence. The component arising from the ring-opened product would increase with increasing temperature with approximately the activation energy of the radical dissociation; the ratio of A_2 to A_1 is the dissociation rate coefficient divided by the sum of the two pseudo-first order rate coefficients for reaction of the radicals with O_2. However, only while that component was negligible would the timescales reflect only the "formally direct" HO_2 formation from the initial and from the ring-opened radicals; once k_d becomes a significant fraction of the pseudo-first order rate coefficients for the oxygen reactions, k_1 should also show the temperature dependence of the radical dissociation. This skeletal scheme therefore does not reproduce the observed behavior and the difference between tetrahydropyran oxidation and cyclohexane oxidation is not simply described by dissociation of the unstable initial radical.

D. THP-yl dissociation

Figure S5. Comparison of theoretical THP-yl dissociation rate coefficient reported in Rotavera et al.[2] to the fitted experimental inverse time constant for fast HO_2 formation

E. References

1. A. M. Knepp, G. Meloni, L. E. Jusinski, C. A. Taatjes, C. Cavallotti and S. J. Klippenstein, *PCCP*, 2007, **9**, 4315-4331.
2. B. Rotavera, J. D. Savee, I. O. Antonov, R. L. Caravan, L. Sheps, D. L. Osborn, J. Zádor and C. A. Taatjes, *Proc. Combust. Inst.*, 2017, **36**, 597-606.