

Supporting Information for:

**Time-resolved measurements of product formation in the low-
temperature (550 – 675 K) oxidation of neopentane: a probe to investigate
chain-branching mechanism**

Arkke J. Eskola,^{1,2} Ivan O. Antonov,¹ Leonid Sheps,¹ John D. Savee,¹ David L.
Osborn,¹ Craig A. Taatjes^{1,*}*

¹*Combustion Research Facility, Sandia National Laboratories, 7011 East Avenue, MS 9055,
Livermore, California 94551, USA*

²*University of Helsinki, Department of Chemistry, A.I. Virtasen Aukio 1, FI-00560 Helsinki,
Finland*

**corresponding authors: arkke.eskola@helsinki.fi, cataatj@sandia.gov*

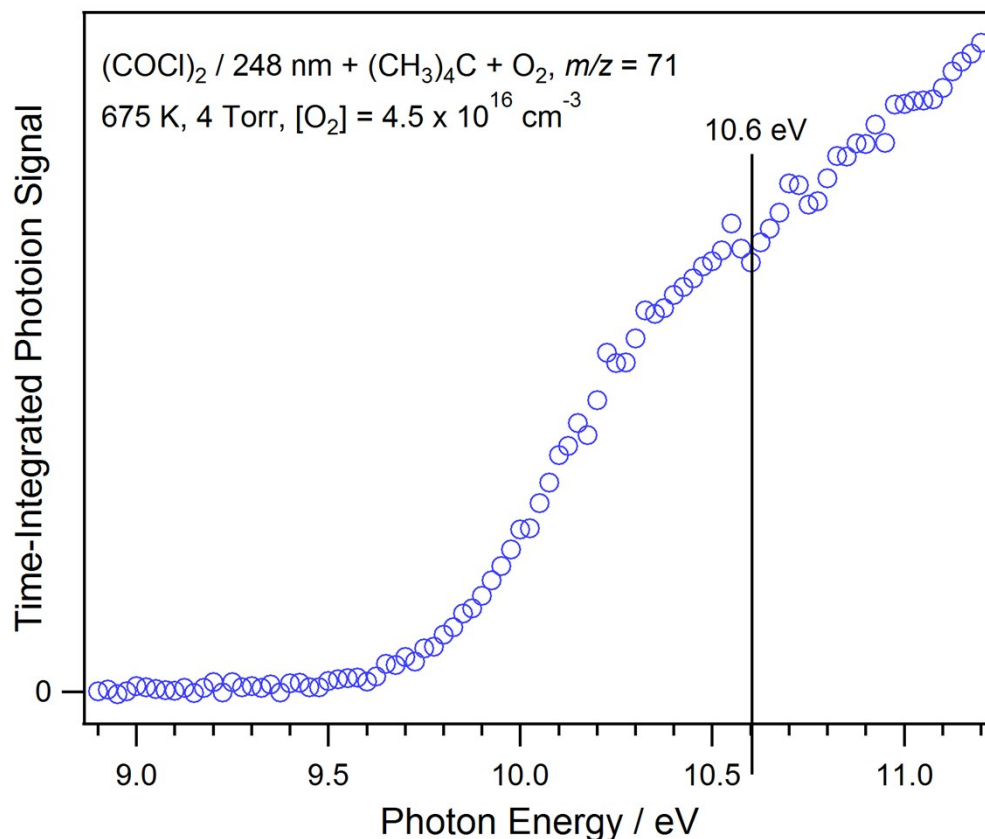


Figure S1. Photoionization spectrum (integrated over 0 – 40 ms after initiation) from Cl-atom initiated neopentane oxidation experiments, which were performed at 4 Torr and 675 K. At this highest experimental temperature, a potential contribution of RO_2 decomposition back to $\text{R} + \text{O}_2$ is strongest. Radical R, neo- C_5H_{11} , has experimental adiabatic ionization energy $IE(\text{ad.}) \approx 7.9$ eV and vertical ionization energy $IE(\text{ver.}) \approx 8.3$ eV. Radical R, if present in any significant extent, should be clearly observed at energies $\sim 9 - 11$ eV. However, no signal is observed in spectrum at energies below about 9.5 eV. At this energy (9.5 eV) dissociative ionization of RO_2^+ on $m/z = 71$ (neo- $\text{C}_5\text{H}_{11}\text{OO}^+ \rightarrow \text{neo-C}_5\text{H}_{11}^+ + \text{O}_2$) is expected to appear. In figure 2a of the manuscript are shown $m/z = 71$ signals at different temperatures measured using a photon energy of 10.6 eV. It is clear from figure above that signal at $m/z = 71$ using 10.6 eV photon energy originates virtually entirely from the dissociative ionization of RO_2^+ and not from R.

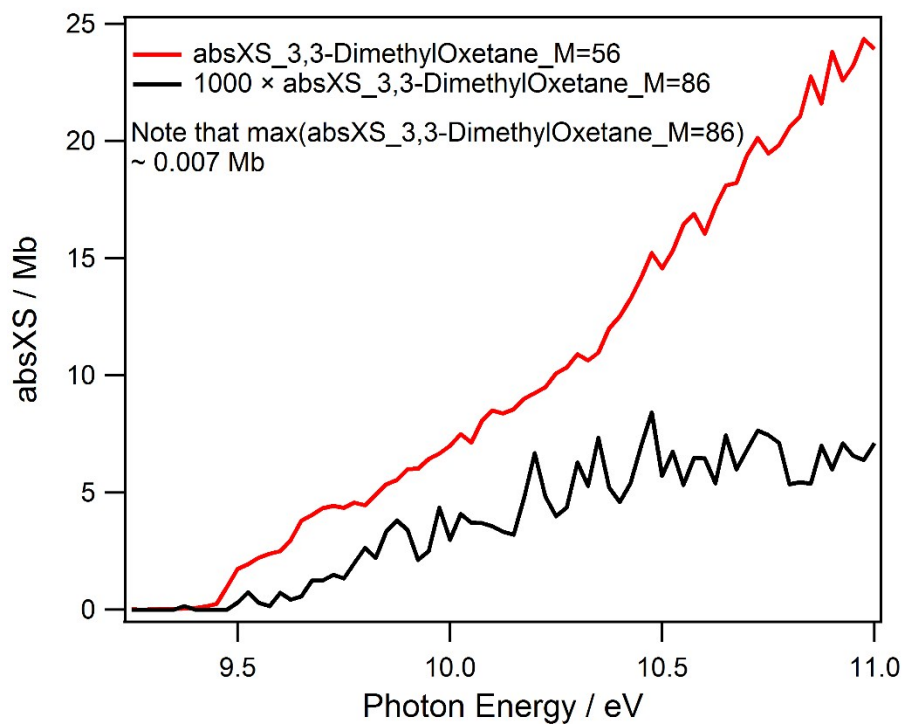


Figure S2. Absolute photoionization spectrum of 3,3-dimethyl oxetane (molecular mass = 86 u) measured in this work. Note that 3,3-dimethyl oxetane has very small photoionization cross section at the parent $m/z = 86$. Due to its practically negligible photoionization cross section at the parent mass, 3,3-dimethyl oxetane is detected in the current work using its daughter ion signal at $m/z = 56$, which has relatively strong photoionization cross section.

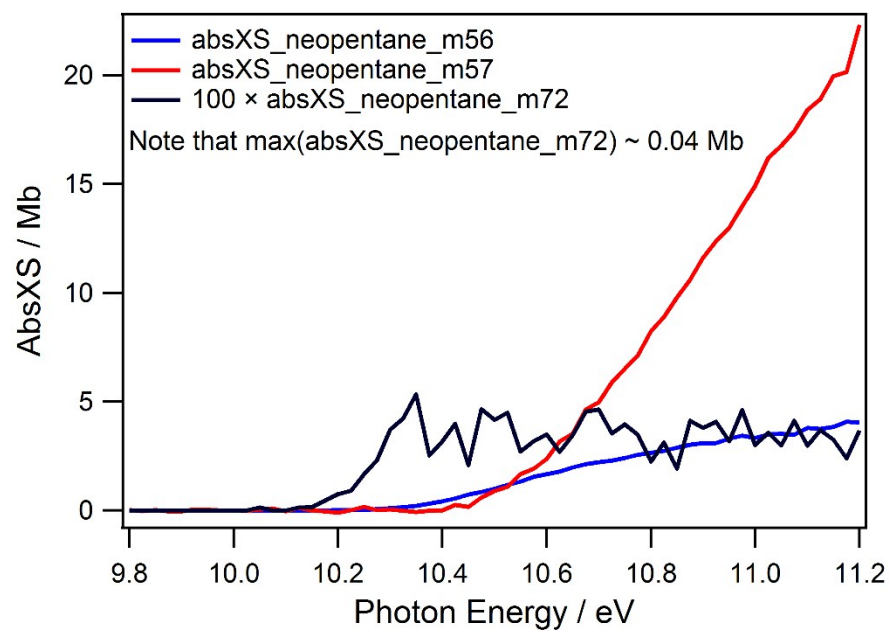


Figure S3. Absolute photoionization spectrum of neopentane (molecular mass = 72 u) measured in this work. Neopentane has very small photoionization cross section at the parent $m/z = 72$. Instead, it has daughter ions at $m/z = 56$ and $m/z = 57$.

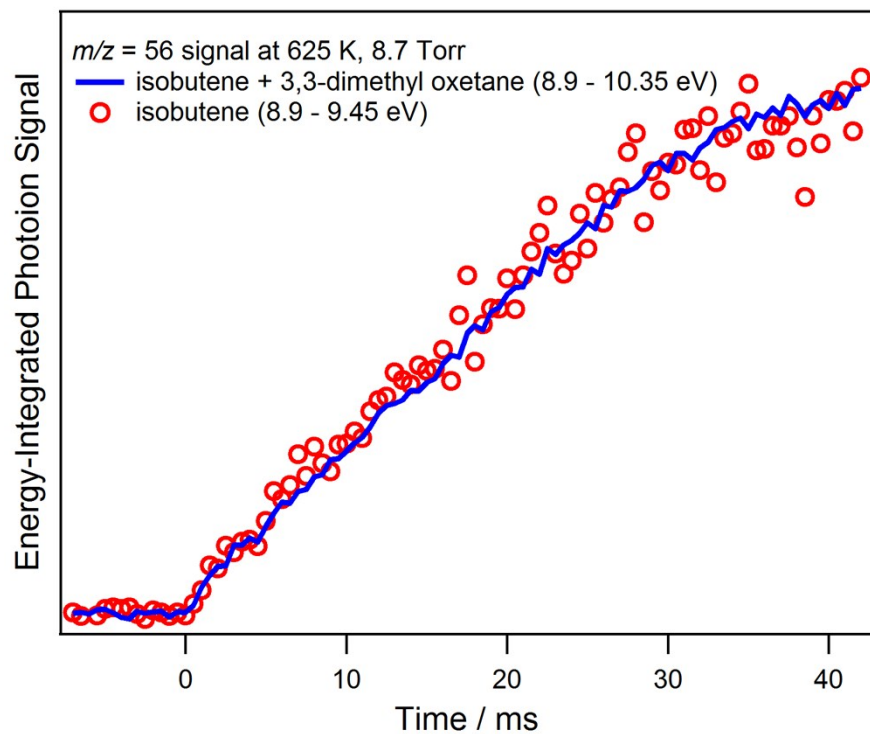


Figure S4. Time trace of signal at $m/z = 56$ from Cl-atom initiated neopentane oxidation experiments at 625 K, 8.7 Torr using the low-pressure reactor ($[O_2] = 5 \times 10^{16} \text{ cm}^{-3}$). Signal that is integrated from 8.9 to 9.45 eV originates only from isobutene, see figure 3a, whereas integrated signal from 8.9 to 10.35 eV contains contributions both from isobutene and 3,3-dimethyl oxetane, see figure S2.

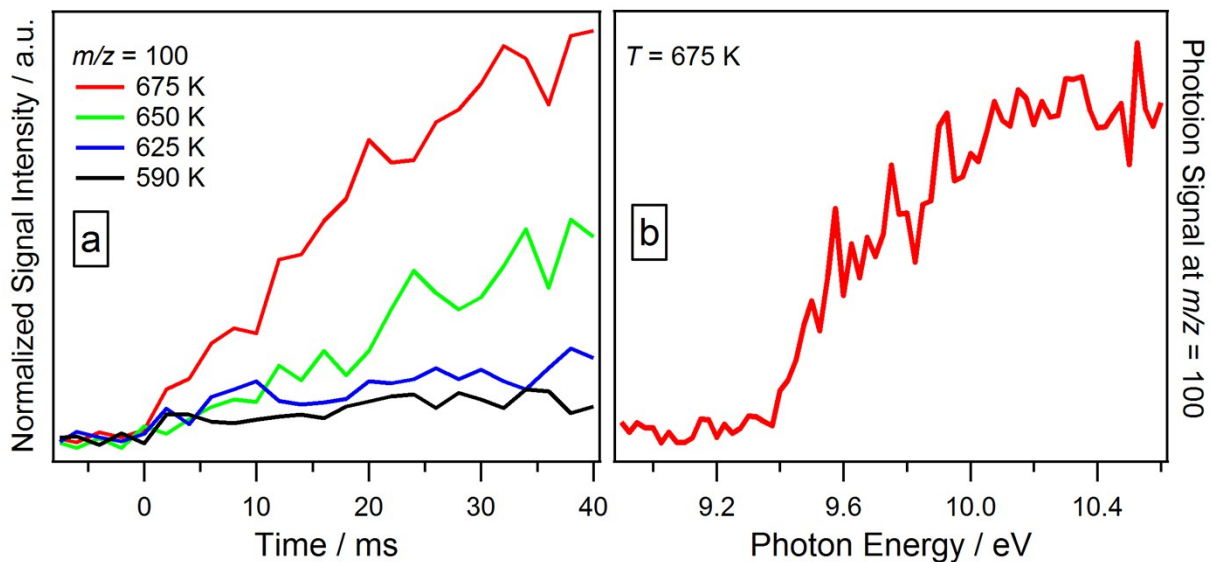


Figure S5. a) Comparison of the $m/z = 100$ signal time behavior at different temperatures ($p = 10$ Torr). **b)** the $m/z = 100$ signal photo-ionization spectrum measured at 675 K, 10 Torr. It is suggested that the $m/z = 100$ signal originates from dimethyl propanedial, $(\text{CH}_3)_2\text{C}(\text{CHO})_2$, which is produced in formally direct $\text{QOOH} + \text{O}_2 \rightarrow \text{OOQOOH}^* \rightarrow \text{HOOPOOH}^* \rightarrow \text{OH} + \text{HOOP}=\text{O}^* \rightarrow \text{OH} + \text{O}=\text{P}_{-\text{H}}=\text{O} + \text{H}_2\text{O}$ water elimination reaction. Also $\dot{\text{O}}\text{P}=\text{O} + \text{O}_2 \rightarrow \text{O}=\text{P}_{-\text{H}}=\text{O} + \text{HO}_2$ reaction might play some role.

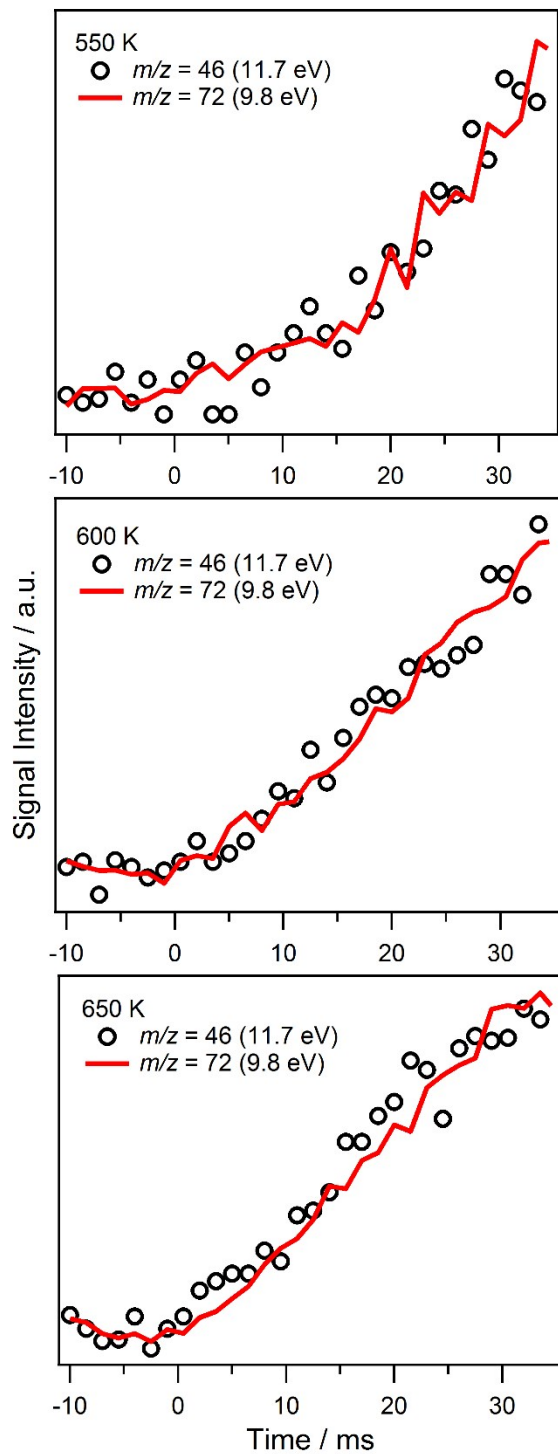


Figure S6. Time traces of formic acid ($m/z = 46$, 11.7 eV) and methyl propanal ($m/z = 72$, 9.8 eV) formation in neopentane oxidation experiments performed at 1 atm pressure ($[\text{O}_2] = 2.85 \times 10^{18} \text{ cm}^{-3}$) and 550, 600, and 650 K temperature to investigate their origin as decomposition products of γ -KHP.

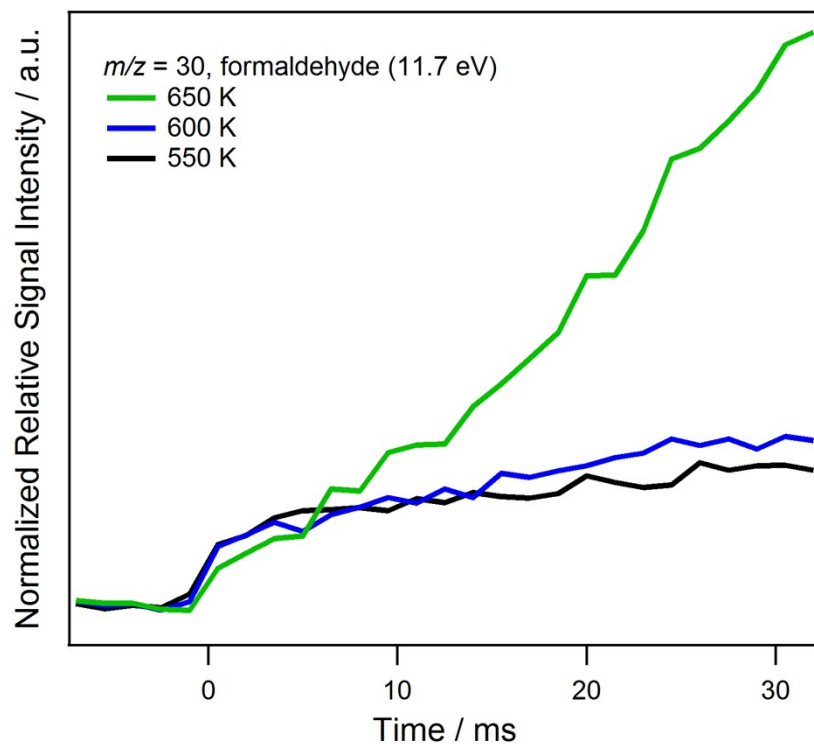


Figure S7. Comparison of formaldehyde ($m/z = 30$, measured using 11.7 eV photon energy) time traces from a same set of Cl-atom initiated neopentane oxidation experiments as those shown in figure 4. Measurements were performed under constant density conditions ($[\text{O}_2] = 2.85 \times 10^{18} \text{ cm}^{-3}$) at about 1 atm pressure to investigate kinetics and mechanism of γ -KHP formation and subsequent reactions under conditions close to autoignition temperature.

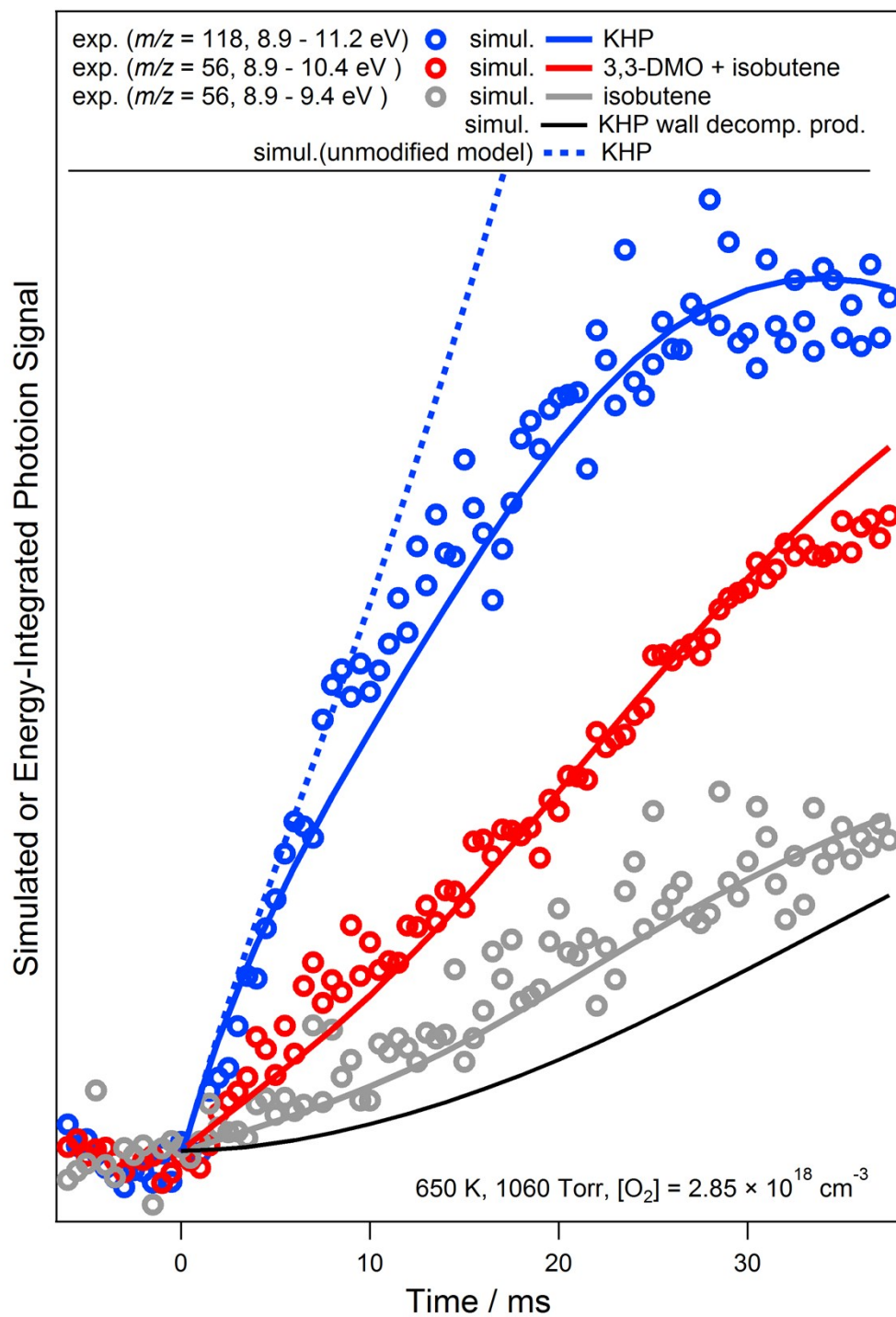


Figure S8. Simulation of experimental Cl-atom initiated neopentane oxidation signals at 650 K, 1060 Torr using a modified (that is KHP volume-averaged, surface reaction rate 58 s^{-1} on reactor wall added) and unmodified NUIGMech_C5_July2015-model.

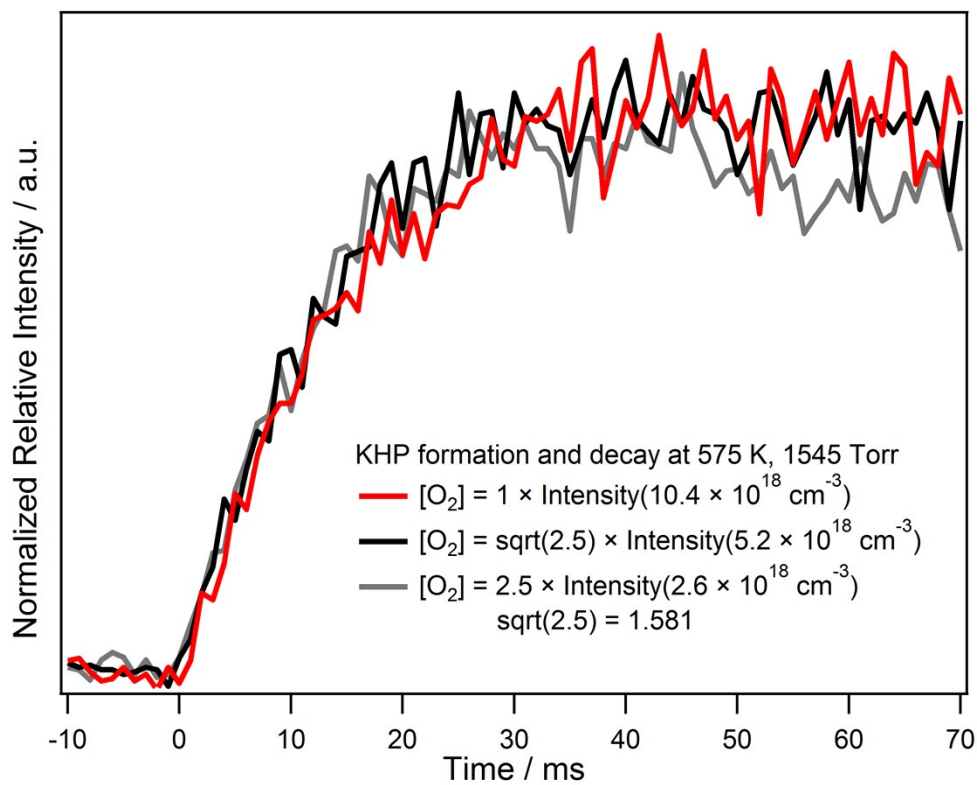


Figure S9. Experimental KHP formation and decay signals at 575 K, 1545 Torr pressure from a same set of neopentane oxidation experiments at three different oxygen concentrations. Signal intensities are first normalized using oxygen signals. Then intensities of signals with $[O_2] = 5.2$ and $2.6 \times 10^{18} \text{ cm}^{-3}$ are multiplied with factors q and q^2 to obtain best possible overlap of signals as shown in figure. As a result of this exercise, KHP signal intensity increases approximately with a factor of 1.6 as $[O_2]$ is doubled. A hydrogen discharge (Lyman- α) radiation at 10.2 eV was used for ionization.

Table S1. Observed products in the current experiments.

Product	Product parent mass (<i>m/z</i>)	Mass (<i>m/z</i>) product detected
Ethene	28	28
Formaldehyde	30	30
Propene	42	42
Acetaldehyde	44	44
Formic acid	46	46
Isobutene	56	56
Acetone	58	58
Propanal	58	58
1,1-dimethyl cyclopropane ¹	70	70
Methacrolein	70	70
Methylpropanal	72	72
2,2-Dimethyloxirane	72	72
2-Methyl-2-Propen-1-ol	72	72
2,2-Dimethylpropanal	86	86
3,3-Dimethyloxetane	86	56
2,2-dimethylpropanedial ¹	100	100
KHP	118	118

¹Tentative assignment