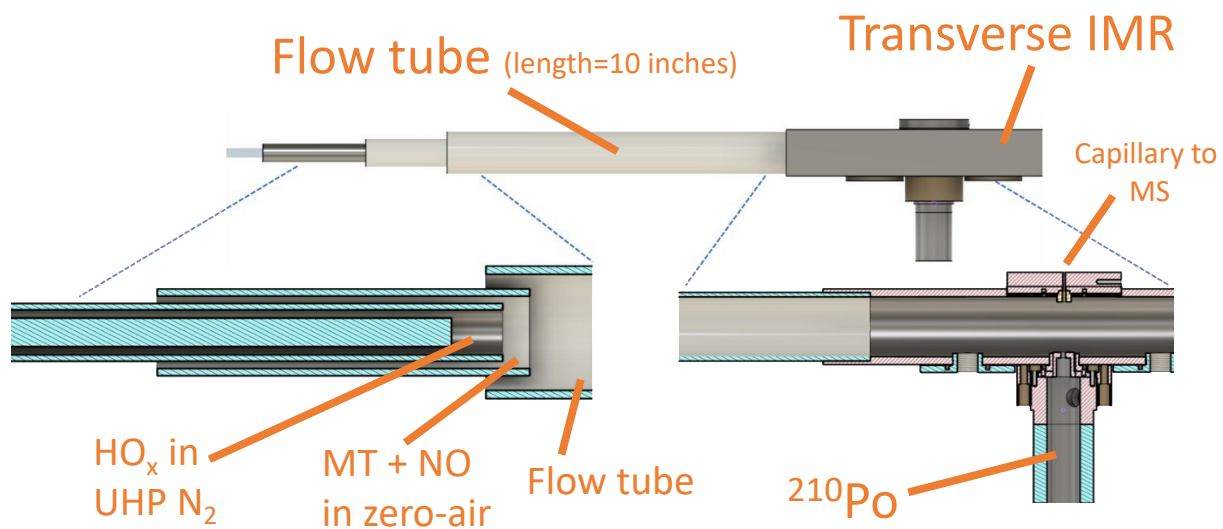


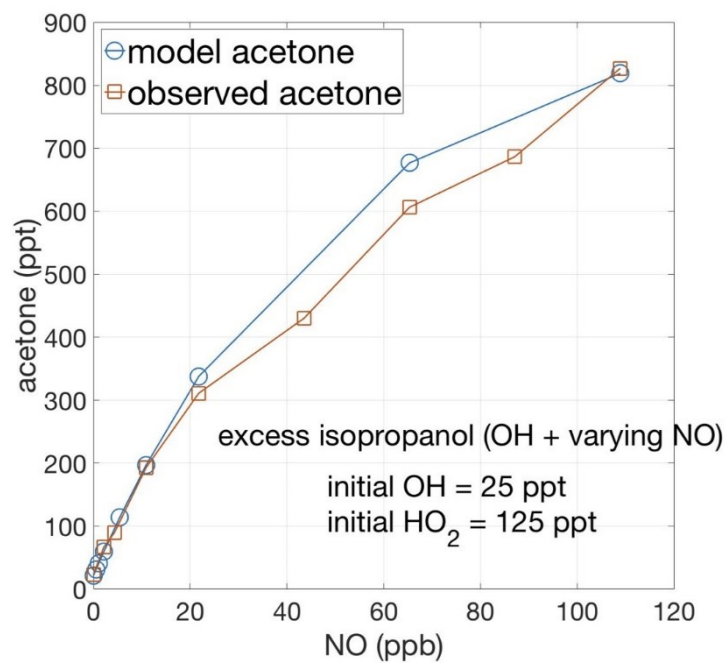
### **Custom-built permeation device**

A permeation device was built using a 5 mm OD 10 cm long perfluoroalkoxy tube filled with acetone and capped at both ends with 1/8" OD polytetrafluoroethylene rods. The device was maintained at 40°C with a constant ~100 sccm flow of zero-air, and weighed weekly with a micro balance to quantify the permeation rate.

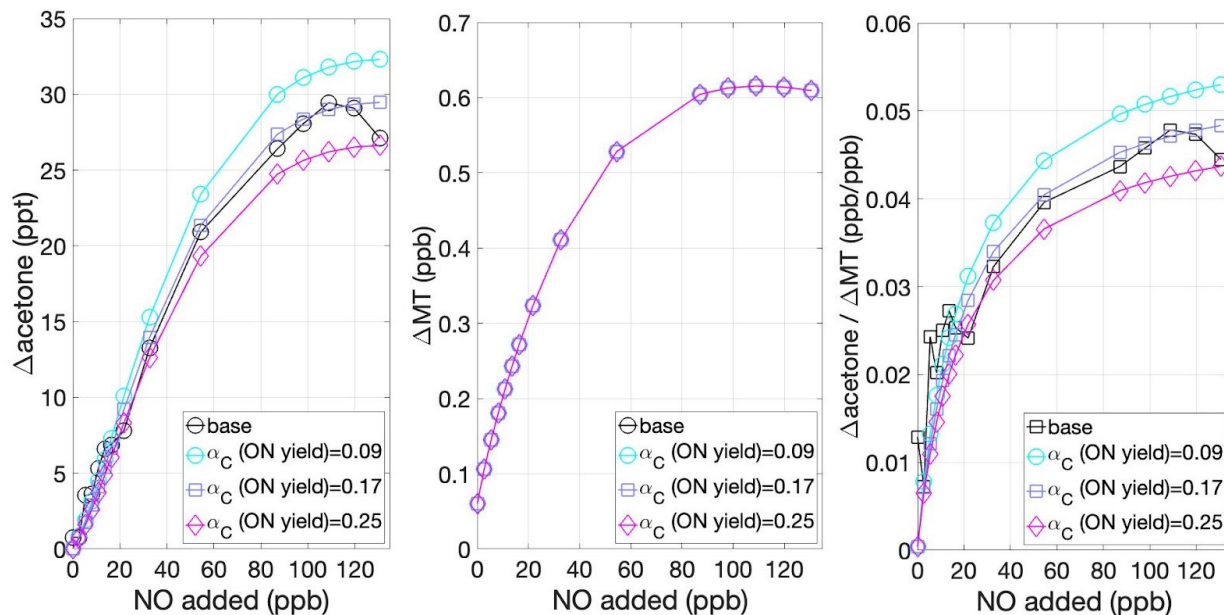
## SI Figures



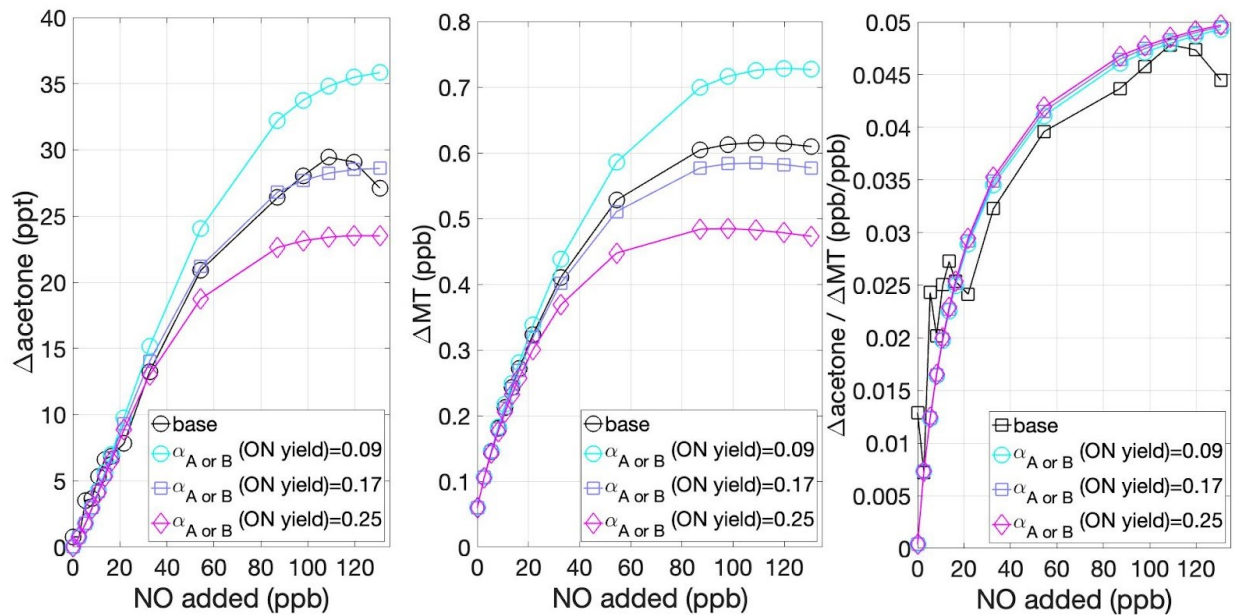
**Figure S1.** Schematic of the transverse atmospheric pressure IMR, utilized for this work. (Top) Side view. Insets are cross-sectional views.



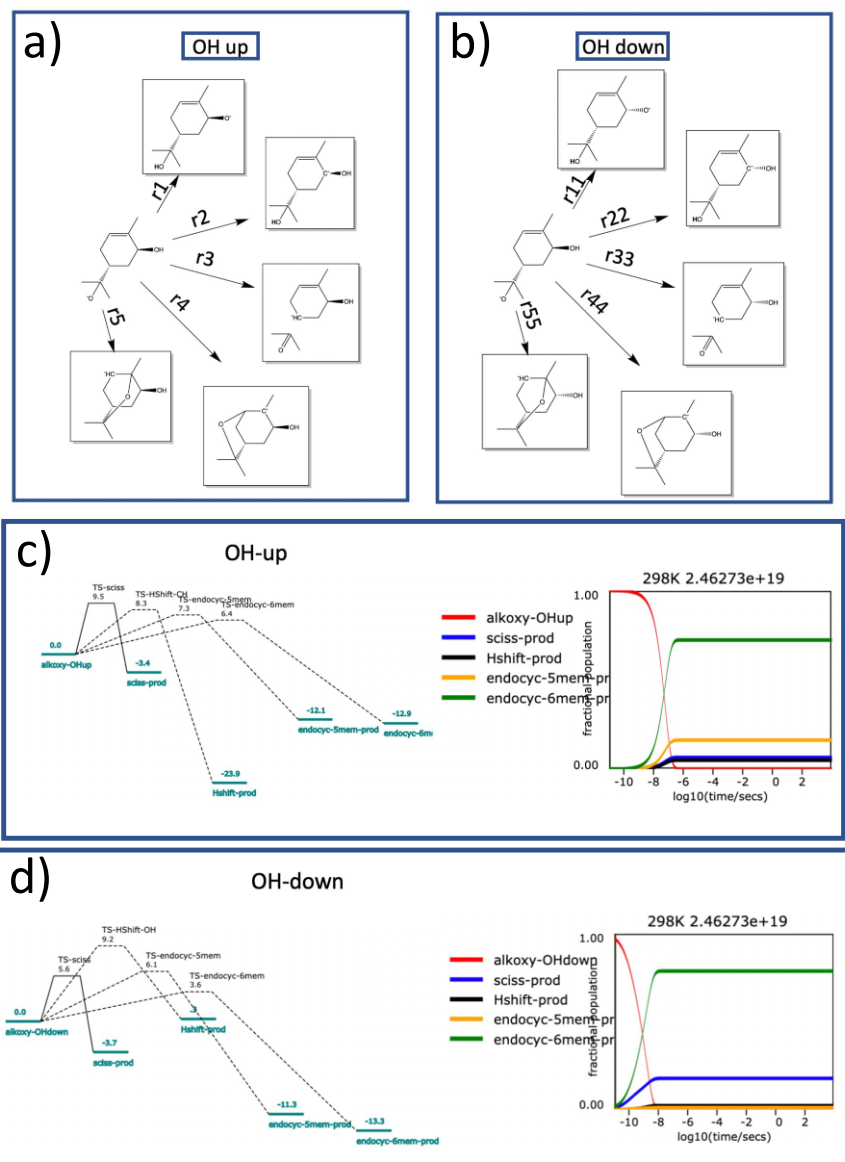
**Figure S2.** Observed and modeled production of acetone as a function of NO added.



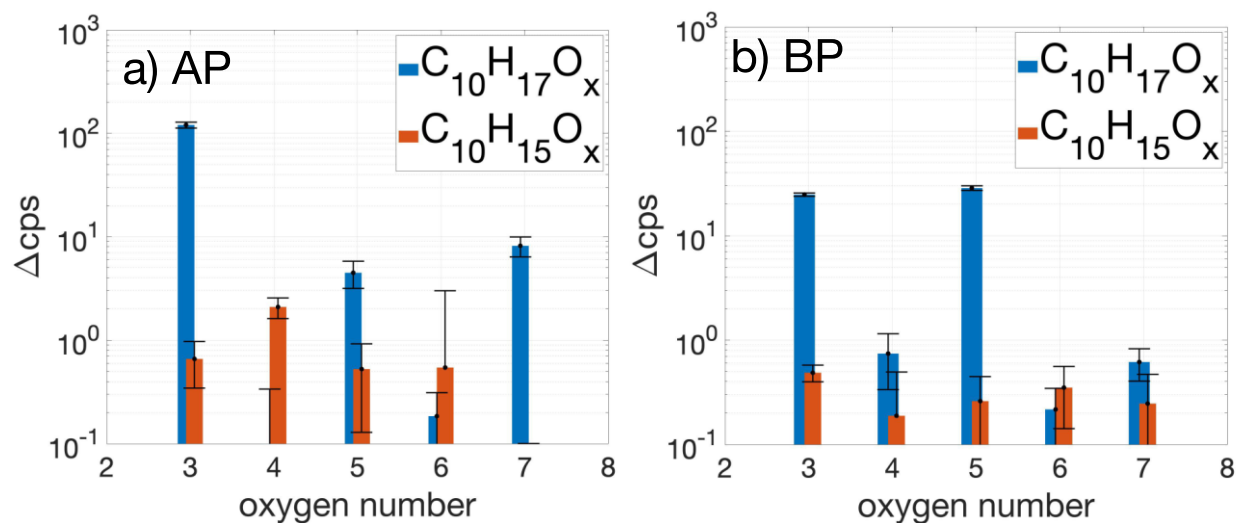
**Figure S3.** Production relative to when oxidation is off as a function of NO added are shown for (a) observed acetone production, (b) modeled AP loss, and (c) the ratio of acetone produced per AP reacted. The color traces represent three box model simulations varying  $\alpha_C$  (yield of alkyl nitrate,  $C_{10}H_{17}NO_4$ ) from 0.09 to 0.25 for the reaction between NO and the ring-opening isomer of hydroxy peroxy radical ( $C_{10}H_{17}O_3$ ). The variability in simulated  $\Delta$ acetone/ $\Delta$ AP due to uncertainty in  $\alpha_C$  is within the uncertainty of the non-linear least squares fits to the observed, shown in **Figures 3c and 3d**.



**Figure S4.** Same as **Figure S3** but varying the alkyl nitrate yield for the reaction between NO and the ring-retained isomers. As alkyl nitrate production decreases, production of pinonaldehyde, therefore, HO<sub>2</sub> increases. HO<sub>2</sub> rapidly reacts with NO to form OH, which reacts with the excess monoterpenes. But since acetone and MT are similarly affected, the modeled  $\Delta$ acetone/ $\Delta$ AP versus NO is negligibly affected.



**Figure S5.** Theoretical calculation of the fates of the C-4 ring-opened alkoxy radicals with the hydroxyl (-OH) group pointed (a) up and (b) down. Energy barriers of the corresponding fates and energy levels of the products relative to the parent alkoxy radical, along with their distribution in time are shown for the two (c and d) diastereomers.



**Figure S6.** Logarithmic scale enhancements in the absence of NO of the signal levels of  $\text{C}_{10}\text{H}_{15}\text{O}_x$  and  $\text{C}_{10}\text{H}_{17}\text{O}_x$  peroxy radicals due to OH oxidation of (a) AP and (b) BP. For AP,  $\text{C}_{10}\text{H}_{15}\text{O}_4$  is the only peroxy radical produced presumably from H-abstraction that is detected robustly, that is, the enhancement is at least  $\sim 1$  cps and the standard deviation during oxidation is lower than the enhancement above when oxidation is off. In comparison,  $\text{C}_{10}\text{H}_{17}\text{O}_{3,5,7}$  peroxy radicals produced from OH-addition are all readily observed for both AP and BP.