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Supplement of

Hydroxy nitrate production in the OH-initiated oxidation of alkenes

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1 Reanalysis of hydroxy nitrate yields of O'Brien et al. (1998).

In response to comments made by Anonymous Referee #3 (<http://www.atmos-chem-phys-discuss.net/14/C2149/2014/acpd-14-C2149-2014.pdf>), the results from a reanalysis of the experiments of O'Brien et al. (1998) are reported here to provide a possible explanation for the differences in the yields of β -hydroxy-nitrates formed in the OH oxidation of alkenes between these two studies.

Using a kinetic model with recommended photochemical reaction rate constants of JPL and IUPAC, and literature values for reaction rates constants that do not have recommendations, simulations of the experiments reported by O'Brien et al. (1998) have been conducted.

The following assumptions regarding the experiments of O'Brien et al. (1998) have been made:

1. Experimental temperature of 296 K.
2. Experimental O₂ mixing ratio of 0.21.
3. Experimental relative humidity of 5%.
4. UV emission spectra of GE F40BL lights (peak emission wavelength = 370 nm, (see Chen et al. (1998))). Light flux during lights on periods such that $J_{\text{NO}_2} = 3.9 \times 10^{-4} \text{ s}^{-1}$ (personal communication, Paul Shepson).
5. Initial 1 hr dark mixing period.
6. Lights on period of 16 minutes, lights off period of 30 minutes, repeated 10 times (total lights on period (160 minutes) constrained by light flux and amount of propene oxidized in the experiments).

1.1 Rapid conversion of NO to NO₂.

At the very high initial NO concentrations (200-500 ppmv) used in the bulk of the O'Brien et al. (1998) experiments in 1 atm of air (21% O₂), NO is rapidly converted to NO₂. Given the IUPAC recommended rate constant for this reaction, we estimate that after the 1 hr of dark mixing, more than 75% of the initial NO is converted to NO₂ (see Figure S1).

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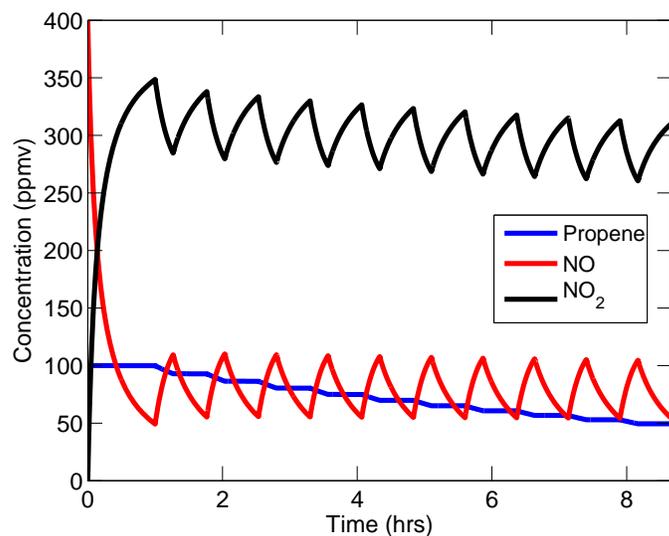


Figure S1 – Modeled timeline traces of propene, NO, and NO₂ for O'Brien et al. (1998) propene experiment 2.

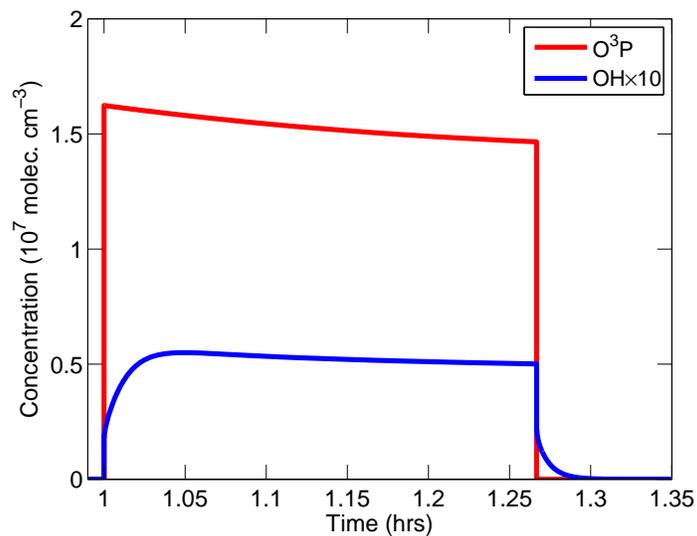


Figure S2 – Modeled timeline traces for OH and O³P concentrations within O'Brien et al. (1998) propene experiment 2. X-axis magnified to display the first 16-minute photolysis period.

1.2 Isopropyl nitrite photolysis, and the fate of 2-propoxy.

The absorption cross-section for isopropyl-nitrite (IPN), the HO_x precursor in the O'Brien experiments, is taken from Raff and Finlayson-Pitts (2010). We assume that the quantum yield to form NO and 2-propoxy is 1 for the wavelengths of concern (310 nm - 400 nm). Under the very high NO_x levels used by O'Brien et al. (1998) it is possible for alkoxy + NO₂ and alkoxy + NO termination reactions to be important, in addition to alkoxy reactions with O₂ and unimolecular decomposition. For these simulation results, we assume the experimental rate constants of 2-propoxy with NO₂, NO, O₂, and the unimolecular decomposition rate of 2-propoxy reported by Mund et al. (1998), Fittschen et al. (1999), Fittschen et al. (1999), and Devolder et al. (1999), respectively. The simulations suggest that the high levels of NO_x limit the efficiency with which OH is produced from the photolysis of IPN due to the fast termination reactions of 2-propoxy with both NO₂ and NO. For example, during experiment 2 (Figure S1), the simulations predict NO₂ and NO mixing ratios of 300 and 75 ppmv, respectively. Thus, from the rates constants referenced above, the fate 2-propoxy under these conditions is predicted to be 71% reaction with NO₂, 19% reaction with NO, 10% reaction with O₂, and 0.2% decomposition. The terminating reactions of 2-propoxy with NO_x are predicted to consume ~90% of the 2-propoxy formed in this experiment, severely limiting this primary HO_x source.

1.3 O³P chemistry of alkenes.

O'Brien et al. (1998) do not include a discussion of the role of O³P chemistry within their experiments. However, kinetic simulations of the subset of O'Brien experiments with >100 ppmv initial NO_x, indicate that the bulk (60-90%, see Figure S2) of the alkene loss was due to reaction of the alkene with O³P. Within these simulations, reaction rate constants of O³P with propene, 1-butene, cis-2-butene, and 1-hexene of 4.0×10^{-12} , 4.2×10^{-12} , 1.8×10^{-11} , 4.7×10^{-12} cm³ molec⁻¹ s⁻¹, respectively, are used (Atkinson and Lloyd (1984); Cvetanovic (1987)). Product channels resulting from O³P + alkene chemistry are modeled as recommended by Atkinson and Lloyd (1984): a high yield (1 atm pressure) for the epoxide/carbonyl (0.6-0.8) channel with the remainder undergoing decomposition to form radical products. The fraction forming radicals is a non-negligible source of HO_x in these simulations.

1.4 NO_x dependence of the propene HN yields.

In addition to the rapid conversion of the NO into NO₂ and thus the high impact of O³P chemistry in the experiments of O'Brien, the simulations also predict the fraction of alkene loss attributable to OH chemistry should be strongly dependent on the ratio of IPN:NO_x in the system. The three propene experiments of O'Brien provide a factor of 2 range in this ratio for the initial conditions. Fitting the data displayed in O'Brien et al. Figure 3, on an experiment-by-experiment basis, and not constraining the fit to pass through the 0,0 datum, suggests that there may indeed be a significant dependence on the observed HN yield as a function of initial NO_x level (Figure S3).

Figure S4 shows the re-fitted O'Brien propene HN yield data versus the fraction of the propene loss attributable to OH chemistry as predicted by the simulations. The reasonable correlation ($R^2=0.98$) gives plausibility to the modeling effort. In addition, the extrapolated HN yield for propene corresponding to 100% propene loss by OH ($x=1$) is consistent with the HN yield of propene reported here. Given the large uncertainties in the data of O'Brien and in the modeling results presented here, this close agreement is likely fortuitous (cf. the non-zero intercept of this

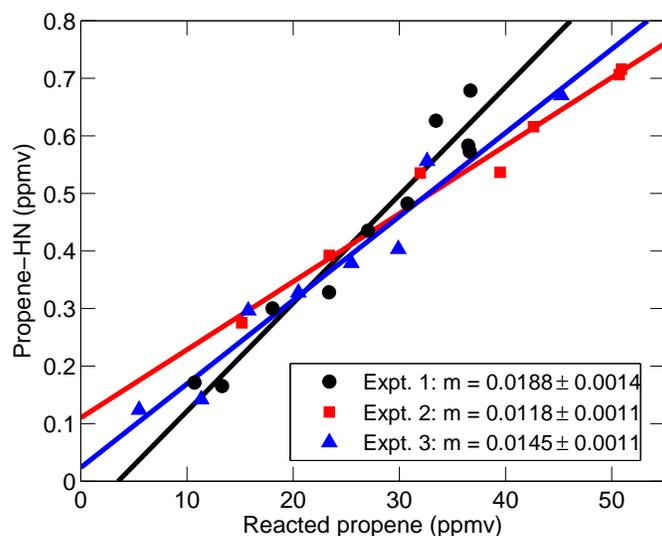


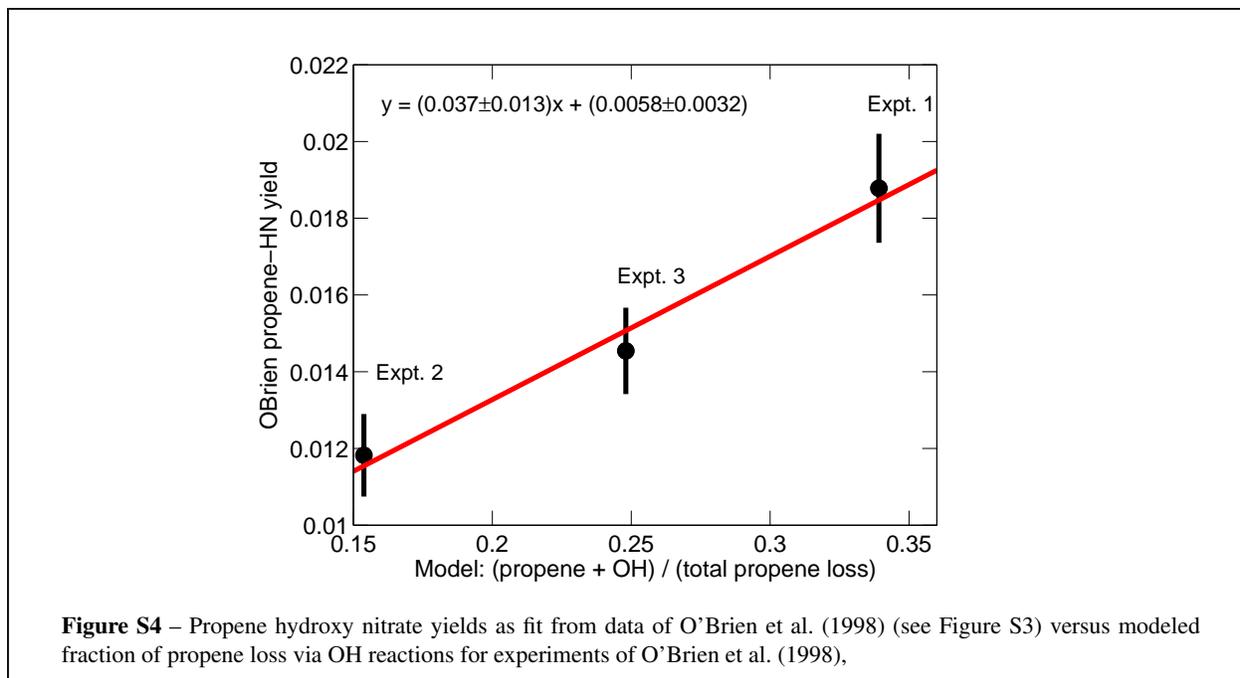
Figure S3 – Data taken from O’Brien et al. (1998) Figure 3, for propene hydroxy-nitrate formation from oxidation of propene. Individual experiments have been fit here using an orthogonal least squares York-type fit, considering errors in both dimensions. The resulting slopes and associated 1-sigma errors are shown above.

regression). The intercept is likely due to missing HO_x sources in the kinetic model, additional RONO_2 sources in the experiment (see below), or a combination of these factors.

1.5 1-butene, cis-2-butene and 1-hexene hydroxy nitrate yields.

Similar simulations for the 1-butene experiments of O’Brien et al. (1998) predict that only about 0.16 of the consumed 1-butene was due to OH oxidation chemistry. Correction of the O’Brien 1-butene hydroxy nitrate yield by the fraction of 1-butene predicted to have reacted with OH yields a result in nominal agreement (within uncertainties) with the 1-butene hydroxy nitrate yield reported in this work. However, similar analysis for the cis-2-butene and 1-hexene experiments fails to explain the differences. The corrected O’Brien yields are larger than those reported here by factors of 2.7, and 2.9, respectively. Perhaps the alkoxy radicals formed from reaction of OH, O_2 , and NO with the initial alkene undergo further reactions with NO_2 to form the same RONO_2 as those formed from reactions of RO_2 with NO. To achieve adequate RONO_2 formation from this alkoxy chemistry would, however, require a rather slow alkoxy decomposition rate ($\sim 3 \times 10^5 \text{ s}^{-1}$) assuming a reaction rate constant with NO_2 of $3.4 \times 10^{-11} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$. Alternatively, the epoxides formed through reactions of O^3P with the alkenes may undergo heterogeneous reactions with HNO_3 in the GC-trap to form the same hydroxy-nitrates.

Finally, we are unable to explain the nominal agreement between the 1-hexene hydroxy nitrate yields under 500 and 2.5 ppmv initial NO_x . The influence of O^3P chemistry on the lower NO_x experiment is predicted to be negligible. Thus, to explain the agreement with high NO_x experiments (where simulations predict ~90% of the 1-hexene loss was due to O^3P reactions), one must hypothesize that the charcoal filter sampling method contains additional, unaccounted for, loss processes. The O’Brien isomeric distribution for the 1-hexene hydroxy nitrates is highly variable across the three experiments, potentially indicating additional hydroxy nitrate formation and/or loss processes



across these experiments.

1.6 Uncertainties in the modeling.

The simulation results presented here are insensitive to the dark mixing times in excess of 1 hr. Additionally, the results do not significantly vary with scaling the total light flux by a factor of 5 in each direction. However, the results are sensitive to the ratio of $J_{\text{NO}_2}/J_{\text{IPN}}$. The ratio of the J-values used here (calculated from the lamp spectra and known absorption cross-sections) is: $J_{\text{NO}_2}/J_{\text{IPN}} = 4.2$. Uncertainties in the $\text{O}^3\text{P} + \text{alkene}$ rates are estimated to be $\pm 20\%$. Uncertainties in the $\text{O}^3\text{P} + \text{alkene}$ product channel branching ratios are likely greater than 20%.

1.7 Conclusion

The results reported by O’Brien et al. (1998) are difficult to compare to those reported here due to likely complications arising from O^3P -related chemistry and differences in analytical approach.

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