Hydroxy nitrate production in the OH-initiated oxidation of alkenes

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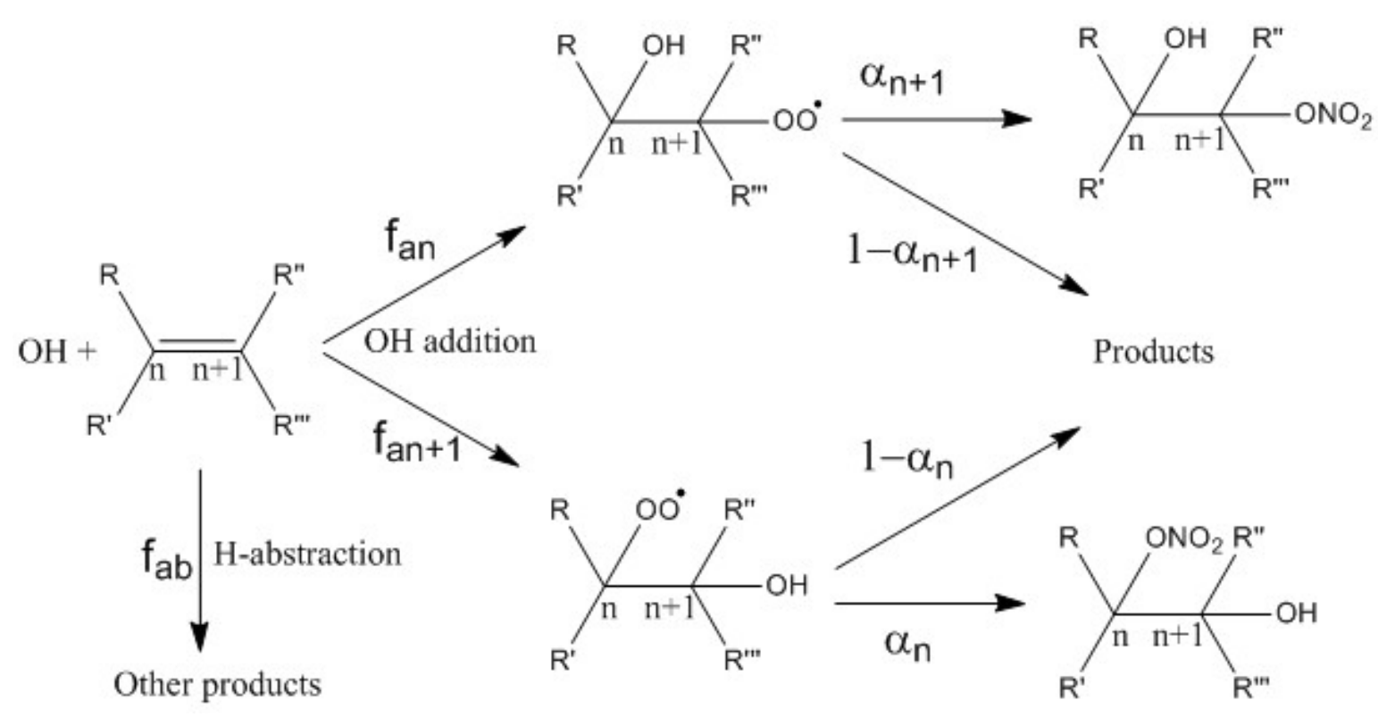
INTRODUCTION

Knowledge of the branching ratio (α) of RO_2 + NO to form alkyl nitrates from from specific volatile organic compounds is important for diagnosing in ozone formation. This knowledge can guide specific control strategies to mitigate pollution. The branching ratio, α, for alkenes is particularly important in the atmosphere. To the right is a figure describing how OH reacts with alkenes and subsequently forms alkyl nitrates.



The goals of this study are to:
•quantify α for alkenes in the laboratory.
•evaluate the role of alkene chemistry in the Houston region using the results presented here.

Methods

Laboratory measurements

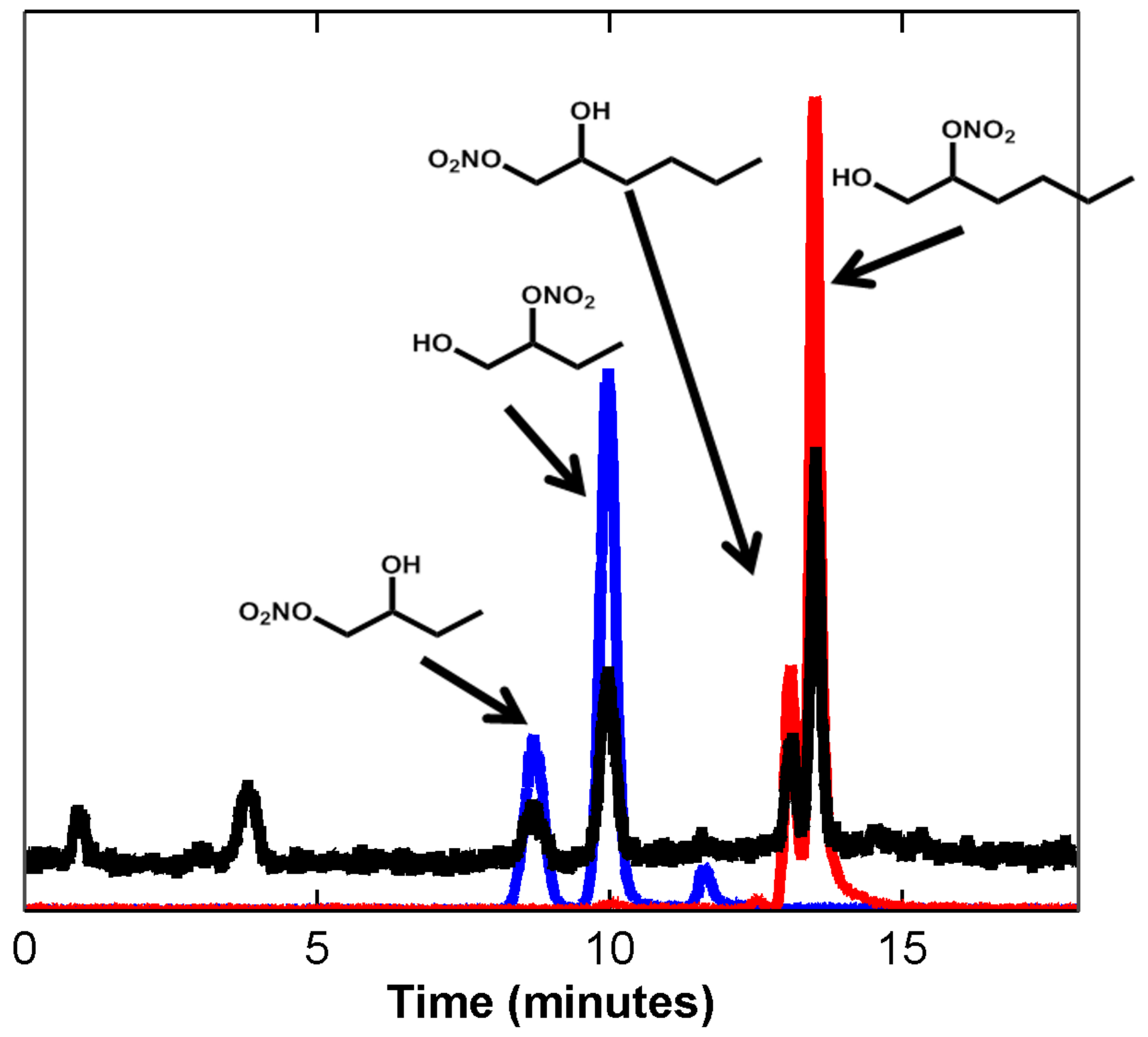
A $1 m^3$ FEP reaction chamber is used to oxidize alkenes by OH in the presence of NO or HO_2 to quantify alkyl nitrate branching ratios for a suite of alkenes ranging from C_2 to C_8.

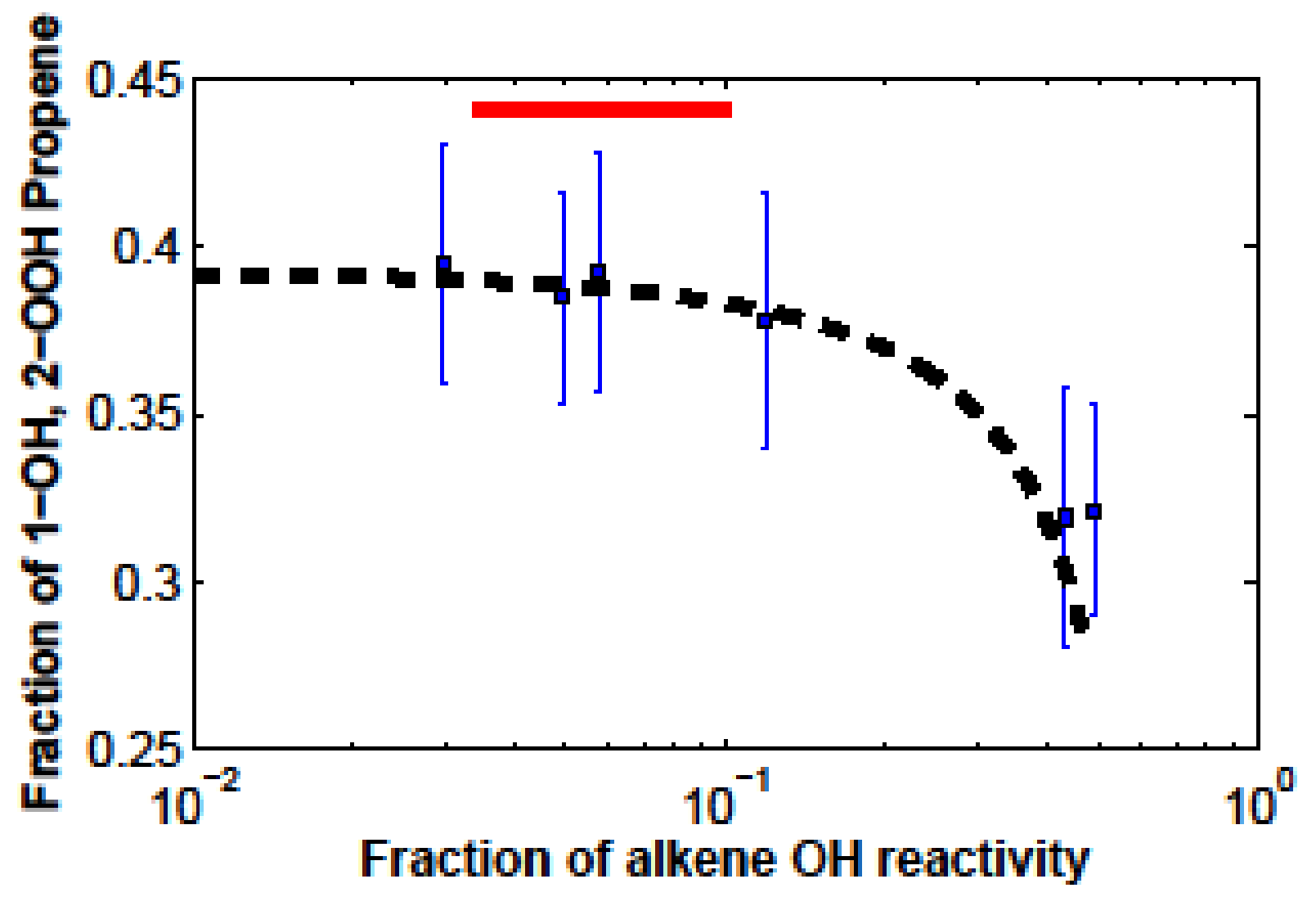
Absolute and relative branching ratios

By placing multiple alkenes in one oxidation experiment, we are able to determine an absolute α for each compound, as well as α relative to each compound in the experiment. This allows us to more directly determine the dependence on α by structure.

$RONO_2$ isomers

The Caltech CF_3O^- CIMS and Berkeley TD-LIF are coupled at the end of a gas chromatograph to provide isomer-specific information and secondary calibration of the CIMS for specific hydroxynitrates by the Berkeley TD-LIF instrument. An example GC chromatogram is shown to the right.



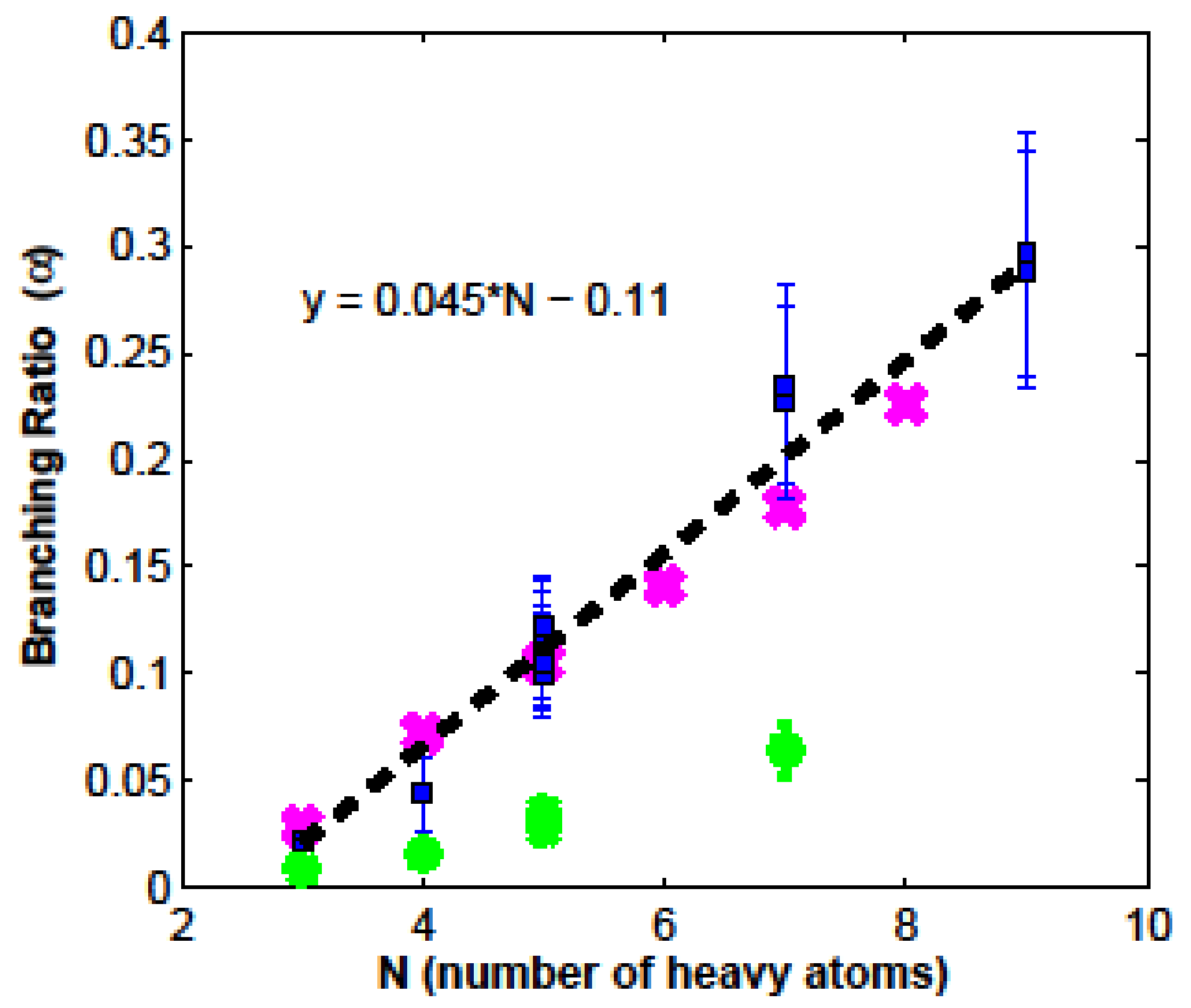


ROOH isomer

We quantify isomer distributions of hydroxy hydroperoxides under HO_2 dominated conditions. Results presented here (red line) are confirmed to be unaffected by $RO_2 + RO_2$ chemistry.

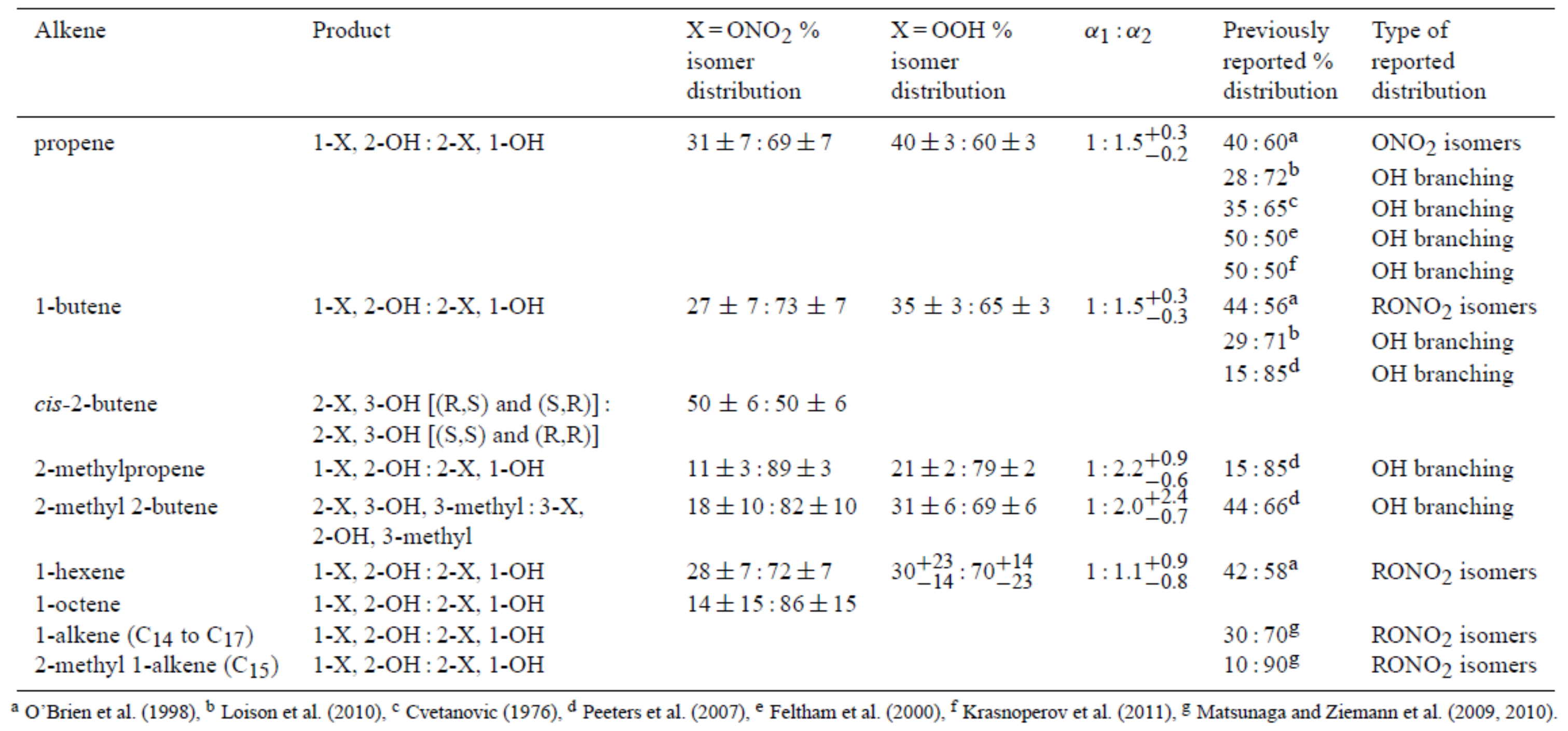
Branching ratio for alkenes

We find that α for alkenes (blue boxes) are similar to those for n-alkanes[1] (pink exes) on a per-heavy atom basis. α for alkenes from this study are higher than previously published values (C_2-C_6 alkenes[2], green stars).



Isomer-specific branching ratios

Assuming unity yield of ROOH from $RO_2 + HO_2$ implies that α increases with the substitution of the peroxy radical:

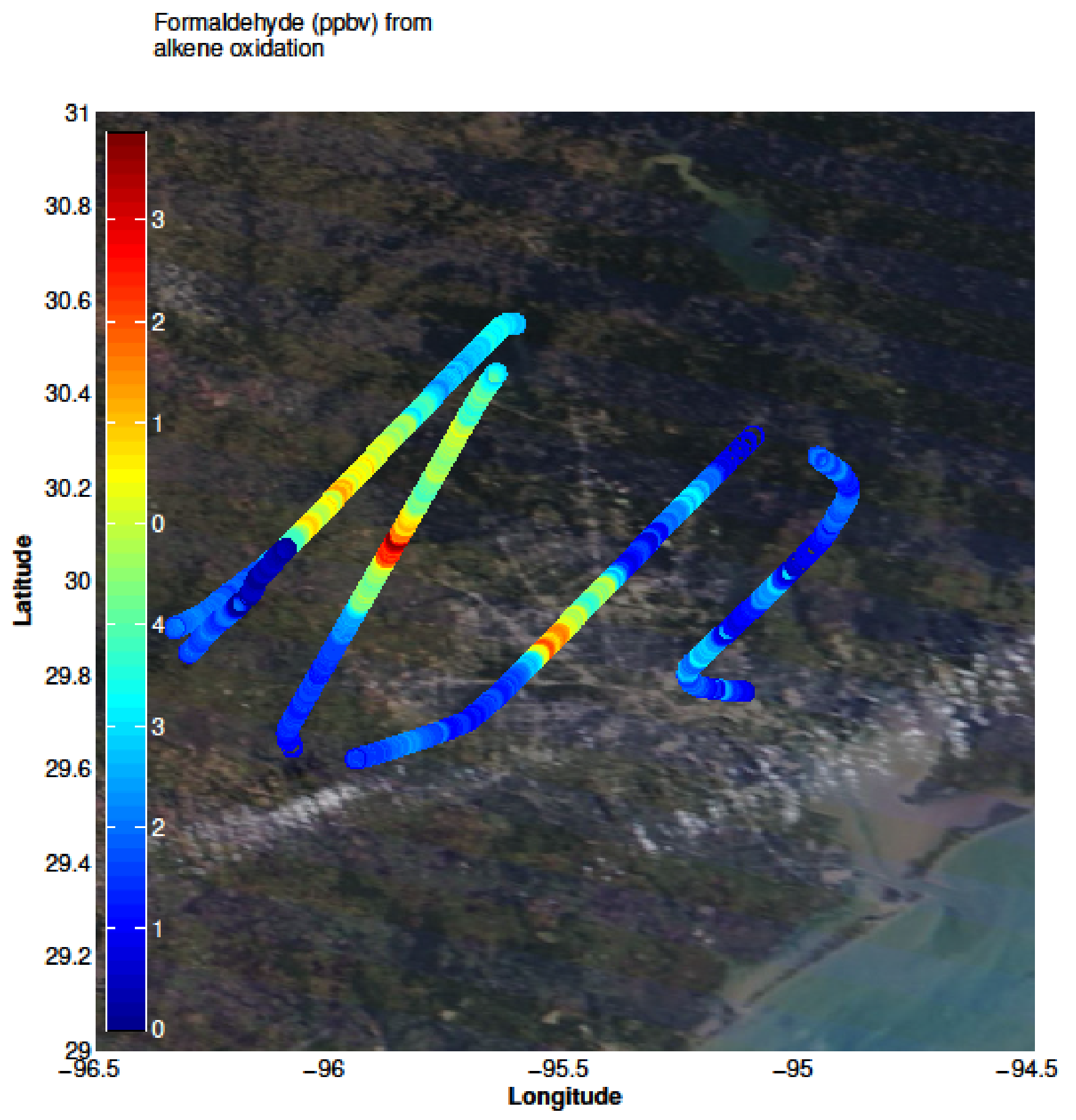


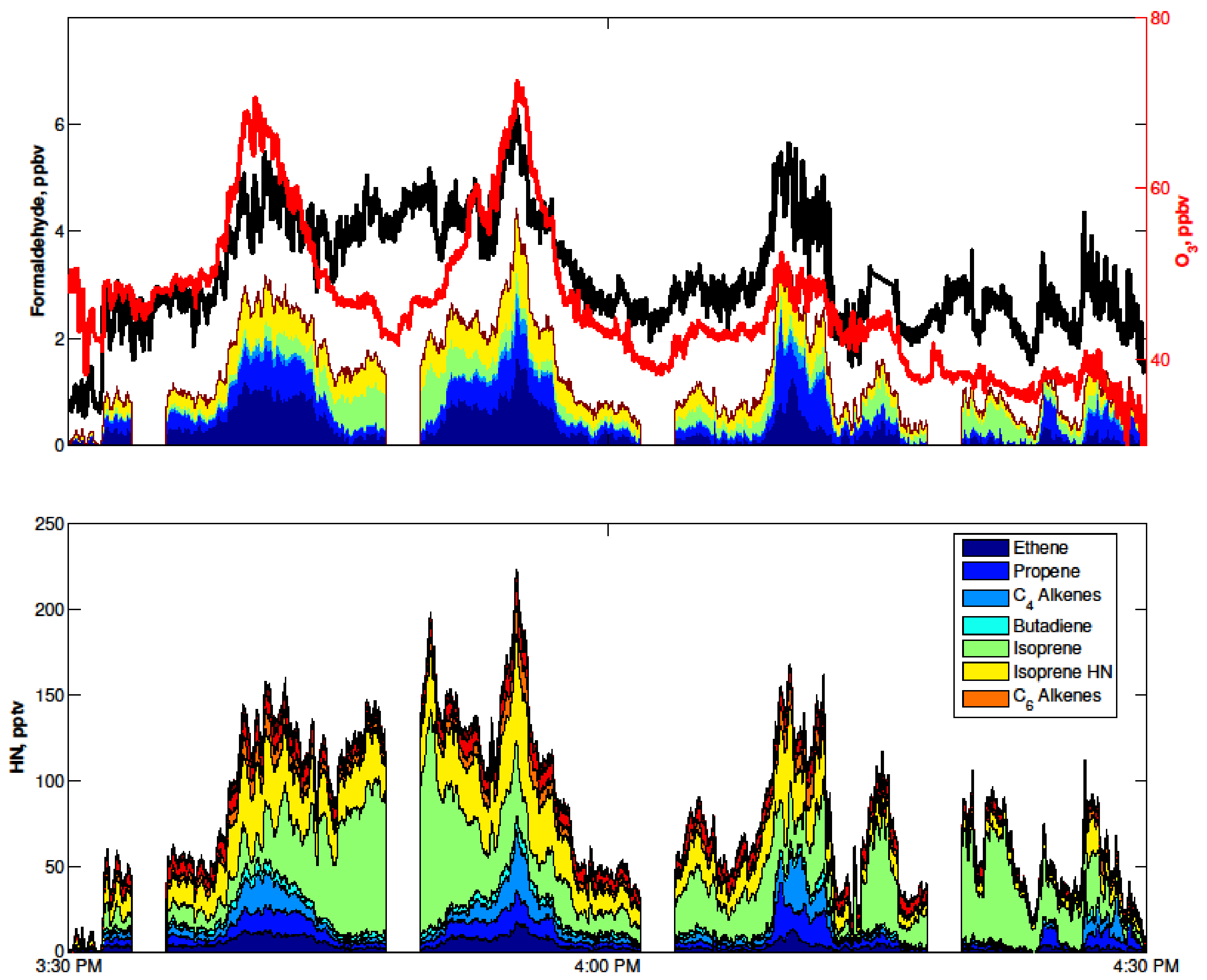
Alkene	Product	X = ONO_2 % isomer distribution	X = OOH % isomer distribution	$\alpha_1 : \alpha_2$	Previously reported % distribution	Type of reported distribution
propene	1-X, 2-OH : 2-X, 1-OH	31 ± 7 : 69 ± 7	40 ± 3 : 60 ± 3	$1:1.5^{+0.3}_{-0.2}$	40 : 60[a]	ONO_2 isomers
					28 : 72[b]	OH branching
					35 : 65[c]	OH branching
					50 : 50[e]	OH branching
					50 : 50[f]	OH branching
1-butene	1-X, 2-OH : 2-X, 1-OH	27 ± 7 : 73 ± 7	35 ± 3 : 65 ± 3	$1:1.5^{+0.3}_{-0.3}$	44 : 56[a]	$RONO_2$ isomers
					29 : 71[b]	OH branching
					15 : 85[d]	OH branching
cis-2-butene	2-X, 3-OH [(R,S) and (S,R)] : 2-X, 3-OH [(S,S) and (R,R)]	50 ± 6 : 50 ± 6				
2-methylpropene	1-X, 2-OH : 2-X, 1-OH	11 ± 3 : 89 ± 3	21 ± 2 : 79 ± 2	$1:2.2^{+0.9}_{-0.6}$	15 : 85[d]	OH branching
2-methyl 2-butene	2-X, 3-OH, 3-methyl : 3-X, 2-OH, 3-methyl	18 ± 10 : 82 ± 10	31 ± 6 : 69 ± 6	$1:2.0^{+2.4}_{-0.7}$	44 : 66[d]	OH branching
1-hexene	1-X, 2-OH : 2-X, 1-OH	28 ± 7 : 72 ± 7	$30^{+23}_{-14} : 70^{+14}_{-23}$	$1:1.1^{+0.9}_{-0.8}$	42 : 58[a]	$RONO_2$ isomers
1-octene	1-X, 2-OH : 2-X, 1-OH	14 ± 15 : 86 ± 15				
1-alkene (C_{14} to C_{17})	1-X, 2-OH : 2-X, 1-OH				30 : 70[g]	$RONO_2$ isomers
2-methyl 1-alkene (C_{15})	1-X, 2-OH : 2-X, 1-OH				10 : 90[g]	$RONO_2$ isomers

[a] O'Brien et al. (1998), [b] Loison et al. (2010), [c] Cvetanovic (1976), [d] Peeters et al. (2007), [e] Feltham et al. (2000), [f] Krasnoperov et al. (2011), [g] Matsunaga and Ziemann et al. (2009, 2010).

Attributing elevated CH_2O and O_3 to alkene oxidation over Houston

Previous field studies in the Houston–Galveston airshed have yielded contradictory conclusions on the causes of high ozone episodes Houston. TexAQS I (2000) indicated that the direct emission of alkenes were associated with rapid ozone production.[3] Subsequently, however, data from TexAQS II (2005-6) indicated that primary or secondary emissions of formaldehyde and nitrous acid might contribute significantly to ozone production.[4] Using Caltech CIMS measurements of hydroxy nitrates, we can derive a lower limit contribution to measured CH_2O by alkenes in the Houston plume, as shown to the right.





CONCLUSIONS

- The branching ratio for C_2-C_8 monoalkenes can be expressed as: α = (0.045 ± 0.016) x N – (0.11 ± 0.05), where N is the number of heavy atoms excluding the peroxy moiety. This is similar to the α found for n-alkanes.
- Isomer specific α increases with increasing substitution of the peroxy radical
- Small alkenes are found to play a significant role in present-day oxidant formation more than a decade (2013) after the 2000 Texas Air Quality Study identified these compounds as major contributors to photochemical smog in Houston.

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