Interference from alkenes in chemiluminescent NOx measurements

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Supporting Information

Kinetic Interference Potential (KIP)

Kinetic interference potentials were calculated using the reaction rate constants for the selected alkenes with ozone. The calculated KIP (shown in Table 4 of the manuscript) are a percentage of a given alkene's potential chemiluminescent signal which would not be subtracted in the standard background cycle, under the assumption that the background cycle conditions (O_3 mixing ratio, residence time) would be sufficient to remove 99% of the NO present.

For example, if 99% of NO reacts with excess O_3 in the reaction chamber then the pseudo first order rate conditions are given by:

$$\frac{[NO]}{[NO]_0} = exp^{(-k't)} \quad \text{Eq. S1}$$

where $k' = k[O_3]t$ and $\frac{[NO]}{[NO]_0} = 0.01$ (*i.e.* 1% of NO left after reaction with excess O_3), then

$$exp^{(-k't)} = 0.01 \quad \text{Eq. S2}$$

$$k't = -\ln(0.01) \quad \text{Eq. S3}$$

where *k* is the rate constant for the reaction of NO with O_3.

$$k't \times \frac{k_{(Alkene+O_3)}}{k_{(NO+O_3)}} = k_{(Alkene+O_3)}[O_3]t \quad \text{Eq. S4}$$

Substituting Eq. S3 into Eq. S4 and rearranging gives:

$$exp^{(-k_{(Alkene+O_3)}[O_3]t)} = \frac{[Alk]}{[Alk]_0} \quad \text{Eq. S5}$$

which gives the fraction of alkene left after the background cycle. The percentage of alkene contributing to the signal interference would therefore be given by:

$$100 \times \left(1 - \frac{[Alk]}{[Alk]_0}\right) \quad \text{Eq. S6}$$