What are the implications from uncertainties in the kinetics we rely on?

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Why do we care about uncertainty?

Back up our claims

Quantify our current knowledge

Find where we need more research
Arrhenius equation

Rate constants define our chemistry. Their relationship with temperature is given by the Arrhenius equation

\[ k = A \exp\left( \frac{E_a}{R} / T \right) \]

\[ k = \text{Rate constant}, \quad A = \text{Arrhenius A factor} \]

\[ E_a = \text{“Activation energy”} \]

The parameters are determined experimentally.

JPL and IUPAC provide us with temperature varying uncertainties.
What we did

For each reaction in turn (50+, not complicated organics): increased rate constant by $1\sigma$ (temperature dependent).

Increased photolysis reactions increased by 10% in turn.

Run a year for spin up, then a year for results.

Errors added together in quadrature - Root of the Sum of the Squares (assumed linearity and errors are independent).
Fractional change in species burden due to increasing rate of $\text{O}_3 + \text{NO}$ reaction by 1 $\sigma$
Fractional change in species burden due to increasing rate of $O_3 + NO$ reaction by 1 $\sigma$
Total annual mean fractional difference of tropospheric O₃

Fractional difference of surface O₃ (%) vs. Latitude (°N)
Tropospheric Ozone radiative forcing error

Repeated experiment with preindustrial conditions and compared to present day

\[ \Delta RF = 0.024 (O_{3}^{\text{present}} - O_{3}^{\text{preind}}) \]

\[ \Delta RF = \text{Radiative forcing (} W m^{-2} \) \]
\[ O_{3}^{\text{present}} = \text{Mean present annual tropospheric Ozone (DU)} \]
\[ O_{3}^{\text{preind}} = \text{Mean preindustrial annual tropospheric Ozone (DU)} \]

Inter-model spread used as the uncertainty in the O3 radiative forcing.
Uncertainty in tropospheric Ozone radiative forcing

- But models use the same kinetics
- Inter model range (17%)
Uncertainty in tropospheric Ozone radiative forcing

- But models use the same kinetics
- Inter model range (17%)
- Chemical Kinetics > 12%
- Total > 21%
- Uncertainty increased by at least 25%

No stratospheric perturbation
No change to isoprene chemistry
Conclusion

- Impact on concentration from kinetic uncertainty has been evaluated.
- Tropospheric Ozone burden uncertainty of at least 8%.
- Tropospheric Ozone radiative forcing uncertainty due to kinetics is greater than 12%.
- Impacts on model / measurement comparisons.

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Thanks for listening...
References

Stevenson et al (2013)
Tropospheric ozone changes, radiative forcing and attribution to emissions in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP)

Shine et al (1990)
IPCC Report Chapter 2 - Radiative Forcing of Climate
Proof that upper perturbation is opposite lower perturbation

Annual mean Tropospheric OH levels with various reaction perturbations

Default OH = 12.9603522256 (Tg)
Radiative forcing equation proof

Original equation shown as an estimate in 1988 - Shine et al (1988)

Updated with 2013 ACCMIP DATA - Stevenson et al (2013)

Tropospheric column O3 provided (DU)
Tropospheric O3 radiative forcing provided (mWm^-2)

DU / mWm^-2 = Conversion factor

Conversion factor mean = 0.0237
Std dev = 0.0012
Proof of Linear system

Tropospheric $O_3$ fractional burden change (%)
Tropospheric O$_3$ fractional burden change (%)
Fractional difference in tropospheric O$_3$ radiative forcing (%)