Computational Modeling of Reactions of Carbonyl Oxides with Sulfur Dioxide in the Troposphere

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Olefin ozonolysis follows different pathways in gas and liquid phase.

- Ozonolysis easily explored in solution; difficult in gas due to short-lived species.
- Computational methods help explore gaseous pathways.
Overview of my project

- Quantum chemistry calculations (B3LYP, QCISD, composite methods)

- (Variational) Transition state theory calculations

- RRKM calculations

- Based on Emily Guinn’s 2008 honor’s thesis work

- This presentation focuses on the SO₂ pathway (middle-right)

- Kurtén, 2007: NO₂ reaction 61x as fast as reaction w/ H₂O; SO₂ reaction 170x as fast as H₂O
Besides reducing the Criegee intermediate, SO₂ can also catalyze rearrangement into carboxylic acids.

- Yield of carboxylic acid falls off at the limit of high SO₂ concentration – why?

- Suggested thiatrioxolane adduct, reactions:

\[
\begin{align*}
\text{CH}_2\text{OO} + \text{SO}_2 & \quad \rightleftharpoons \quad \text{Adduct} \\
\text{Adduct} & \rightarrow \text{CH}_2\text{OOH} + \text{SO}_2 \\
\text{Adduct} + \text{SO}_2 & \rightarrow \text{CH}_2\text{O} + \text{SO}_3 + \text{SO}_2
\end{align*}
\]
Emily Guinn 08’s computational research (Honors thesis 2008)

- Emily did DFT and RRKM calculations on Criegee intermediate reactions with various molecules, including SO₂

- MultiWell: none of the adduct is thermalized, all goes to formic acid

- Bimolecular reactions with vibrationally-excited (~30 kcal mol⁻¹) species are rare, so doubt is cast on Hatakeyama’s hypothesis.
Reaction paths found

- Elaborate reaction paths; search for an answer to Hatakeyama’s question
Adduct formation

- Emily’s results: net $\Delta E_{0K} = -31.99$ kcal mol$^{-1}$

- The transition structure is difficult to find.

- Formation of adduct (thiatrioxolane oxide) nearly barrier-less

- Meaningful TST calculations cannot be performed, because $\Delta E_{-1} > \Delta E_{\text{Barrier}}$, so $k_2 \gg k_{-1}$, and therefore $k \approx k_1$. Barrierless reaction rates are extremely difficult to calculate.
Formic acid and direct cylcoreversion pathways

- Adduct can exist in one of two stable conformations: with syn-hydrogen (to S=O) pseudo-equatorial (lower E) or pseudo-axial (higher E)

- In either case, pseudo-equatorial hydrogen only migrates to the acidic position

- Formic acid formation is thermodynamically favored; formaldehyde formation is kinetically favored
Adduct isomerization pathway

- Adduct can rearrange into far more thermodynamically stable dioxethitetane dioxide (methylene sulfate)

- This rearrangement is a multi-step process

- The opened adduct intermediate can undergo \( \beta \)-scission to formaldehyde directly

- Formic acid formation from methylene sulfate is extremely hindered
MultiWell simulates molecular collisions in gas phase (RRKM)

- Formaldehyde + SO$_3$: 63%
- Formic acid + SO$_2$: 37%
(\(\text{at } 298 \text{ K, 1 atm}\))

- Most opened intermediate undergoes b-scission without closing to the methylene sulfate

- Methylene sulfate greatly prefers cycloreverting to formaldehyde, but…

- All molecules go to product; no methylene sulfate is collisionally stabilized, so…

- Methylene sulfate does not explain Hatakeyama’s results 😞
Methylated reaction paths

- Examine role of carbonyl substituent.

- Entire reaction scheme duplicated with syn- and anti-methyl groups

- Reaction Energies similar to parent system (see below)

- These numbers are strictly enthalpy; negative enthalpic barriers are allowed provided the total free-energy barrier is positive

\[ \Delta E: -9.0_{5}, \quad \Delta E: -12.9_{8} \]

\[ \Delta E: -18.1_{6} \quad \text{Barrier: } 1.8_{9} \quad \Delta E: -18.8_{1} \quad \text{Barrier: } -0.1_{7} \]
Methylated RRKM results

- Anti-acetaldehyde oxide generates syn-methylated adduct; vice versa

- Syn adduct generates: formaldehyde > ester > acid 59% 42% 0.6%

- Anti adduct generates: formaldehyde > acid > ester 74% 26% 0.03%

- Substitution has a significant effect: several methylene sulfate pathways are completely closed by methylation of reactant
Conclusions and Continuing research

- Reaction of carbonyl oxide with atmospheric SO2 generates mostly aldehyde products (and SO3), with acids or esters as a secondary product as a function of substitution (returning SO2).

- Reaction rates are difficult to calculate due to barrierless adduct formation. Completion of NO2 and H2O reaction rate calculations compared to literature values will enable an estimate.

In progress: optimize molecular geometries using high levels of theory and large basis sets so as to determine very accurate energies and find more accurate MultiWell results.

6-31G(d) -> 6-31+G(d,p) -> 6-311++G(3df,2pd) -> B3LYP -> QCISD
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References


