Role of Laboratory Measurements

Kinetic and photochemical parameters, needed in chemical models for predicting capability of Air Quality and Climate, can be determined under isolated and controlled conditions in the laboratory.

Example  **Acetone**, $\text{CH}_3\text{C(O)}\text{CH}_3$
- ubiquitous key species
- large abundance (~1ppb)
- source of PAN ($\text{CH}_3\text{C(O)}\text{O}_2\text{NO}_2$) and HOx

Focus: Evaluate it as a source of HOx
Atm Loss processes: OH Reaction and Photolysis
Evaluation of Acetone as source of HOx in the UT

Net HO\textsubscript{x} Production

- Photolysis
  \[
  \text{CH}_3\text{C(O)CH}_3 \xrightarrow{\text{h}_\nu/\text{O}_2/\text{NO}} 3\text{HO}_2
  \]

- OH Reaction
  \[
  \text{CH}_3\text{C(O)CH}_3 \xrightarrow{\text{OH}/\text{O}_2/\text{NO}} \text{HO}_2
  \]

Use laboratory measurements to Evaluate the Relative Significance of OH Reaction and Photolysis

Upper Troposphere is dry
Atmospheric Loss: OH Reactivity

OH + CH₃C(O)CH₃ → Products

- OH rate coefficient
- Products

**Arrhenius Plot**


\[ k \left(10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}\right) \]

\[ \tau_{OH} \sim 2 \text{ months} \]

Pulsed Laser Photolysis- Laser Induced Fluorescence Apparatus

Wollenhaupt and Crowley, 2000

\[ \text{CH}_3\text{C(O)CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{C(O)CH}_2 + \text{H}_2\text{O} \quad 50 \% \]

\[ \rightarrow \text{CH}_3\text{C(O)OH} + \text{CH}_3 \quad 50 \% \]
OH Reaction Products - Atmospheric Impact

Direct detection of products:
\[
\text{CH}_3\text{C}(O)\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{C}(O)\text{CH}_2 + \text{H}_2\text{O} \quad 96 \pm 11 \%
\]
\[
\rightarrow \text{CH}_3\text{C}(O)\text{OH} + \text{CH}_3 \quad <1\%
\]

Branching Ratio: Independent of Temperature (237 - 353 K)

- Reaction occurs via H-abstraction pathway under all atmospheric conditions.

- CH$_3$C(O)OH is not produced
  - Degradation products stay in the atmosphere and lead to HOx

Flow Tube-Mass Spectrometer

Atmospheric Loss: UV Photochemistry

\[ J \text{ value} = \int \sigma(\lambda, T) \times \Phi(\lambda, [M], T) \times F(\lambda, z, \chi) \]

UV abs cross section  Quantum yield  Solar flux

\[ \Phi = \frac{\text{# of destroyed molecules}}{\text{# of photons absorbed}} \]

Quantum yield, \( \Phi(\lambda, [M], T) \)

\[ \text{CH}_3\text{C(O)}\text{CH}_3 \xrightarrow{\text{hv}} \left[\text{CH}_3\text{C(O)}\text{CH}_3\right]^* \rightarrow \text{CH}_3\text{CO} + \text{CH}_3 \]

Dissociation, \( k_d \)

\[ \text{CH}_3\text{C(O)}\text{CH}_3 \xrightarrow{M} \text{CH}_3\text{C(O)}\text{CH}_3 \]

Quenching, \( k_q \)

QY needs to be measured as function of \((\lambda, [M], T)\)

Important \( \lambda \) range: 290-330 nm
\( \Phi \) is small and \( \sigma \) is small-- difficult to measure

Sensitive technique has been developed in our laboratory.

- Uncertainties in QY exist.
  - Impacts \( J \)
  - Impacts HOx production rate
- Primary products were not measured.

Detect the primary photolysis product, \( \text{CH}_3\text{CO} \)

\[
\text{CH}_3\text{C(O)CH}_3 \xrightarrow{hv} \text{CH}_3\text{CO} + \text{CH}_3
\]

- Developed spectroscopic method.
Direct Sensitive Detection of Acetyl Radical, CH$_3$CO

- CH$_3$CO Visible spectrum measured for the **first time**

New way to detect acetyl radical
- Enables direct measurement of a primary photolysis product

**CH$_3$CO Quantum Yields in the Actinic region**

Results from ongoing Experiments

### Stern-Volmer Plots

\[
\frac{1}{\Phi} = \frac{1}{\Phi_0} + P \left( \frac{k_q}{k_d} \right)
\]

Pressure and Temp dependence of QY at each $\lambda$ are required for atmospheric photolysis rate calculations
Summary and Conclusions

- Determined the OH rate Coefficients accurately under atmospheric conditions
- Quantified the Products of OH reaction
- Characterized and quantified the Visible spectrum of CH₃CO for the first time.
- We are currently measuring the Photolysis quantum yields under atmospheric conditions.

Once the Quantum Yields are determined under atmospheric conditions, we can evaluate the HOx production efficiency of acetone.

Laboratory studies of reactivity and mechanisms of elementary processes provide key building blocks for understanding atmospheric chemistry.