Relative Rate Studies of Chlorine Atoms with Crotonaldehyde and Methyl Vinyl Ketone

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Abstract

The relative rates of reactions of chlorine atoms (Cl) with two organic compounds, crotonaldehyde (CA) and methyl vinyl ketone (MVK), have been studied. Each organic compound along with Cl$_2$ was introduced into a 30 L Teflon bag with N$_2$ or air as diluent. The mixture was then photolyzed repetitively for brief periods and, after each photolysis cycle, a sample was analyzed using the analytical technique of gas chromatography-flame ionization detection (GC-FID). The rate constant for the reaction of MVK with Cl was determined to be $(2.3 \pm 0.5) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Preliminary data for the reaction of CA with Cl were obtained. These relative rates and their atmospheric implications are presented.
Motivation

- CCA and CMVK are considered unique chlorine-containing compounds that can serve as “markers” of chlorine atom chemistry.

- Wang and Finlayson-Pitts (2001) identified CCA and CMVK as the chlorine-containing products from the chlorine atom reaction with the anthropogenic specie 1,3-butadiene.
Atmospheric Layers

- Variations are due to alterations in the chemical and physical nature of the atmosphere with altitude.
- Troposphere contains about 75% of the total mass of the atmosphere.
- Stratosphere is also called the ozone layer.
Cl Chemistry in Coastal Areas

1,3-Butadiene

Products

ClO

O₃

Cl

ClNO

ClNO₂

Cl₂

NO₂

N₂O₅

O₃

OH

ClONO₂

HCl

HNO₃

NaCl

Sea Salt Particles

1,3-Butadiene (HAP)

Created by W. Wang, Department of Chemistry, University of California, Irvine
Reactions of Cl⁻

- Generation of Cl radical from salt
  - NaCl + 2NO₂ → NaNO₃ + ClNO
    - Photolysis: ClNO + hν → NO + Cl⁻
  - NaCl + N₂O₅ → NaNO₃ + ClNO₂
    - Photolysis: ClNO₂ + hν → NO₂ + Cl⁻

- Reactions with organics
  - Abstraction
    - RH + Cl⁻ → HCl + R⁻
  - Addition
    - R₂C=CR₂ → R₂C⁻-CR₂Cl
Studied Compounds

Methyl Vinyl Ketone

Crotonaldehyde

Nonane
Experimental Apparatus

50 L Teflon collapsible reaction chamber

black lamps
300-400 nm

septum for liquid injections

to vacuum pump

pressure gauge

Carle gas valve

GC with capillary column

FID

vacuum manifold

0.497 L collection bulb

Created by A. Ezell, Department of Chemistry, University of California, Irvine
Flame Ionization Detector (FID)

- Most used detector for gas chromatography.
- Responds to compounds that produce ions and electrons when burned in a H₂-air flame.
- Insensitive toward non-combustible gases.

From HP 5890 SERIES II Gas Chromatograph Reference Manual
Relative Rate Technique

- Reference compound
  - Nonane
- Organics of interest
  - MVK
  - CA
- Ratio of rate constants
  \[
  \ln \left( \frac{[\text{organic}]_0}{[\text{organic}]_t} \right) = \left( \frac{k_{\text{organic}}}{k_{\text{ref}}} \right) \ln \left( \frac{[\text{reference}]_0}{[\text{reference}]_t} \right)
  \]
Relative Rates Methodology

- **Sampling**
  - Prepare mixtures of reference, organic and chlorine.

- **Data Collection**
  - GC-FID measures the loss of organic compounds after photolysis.

- **Data Analysis**
  - \[ \ln \left( \frac{[organic]_0}{[organic]_t} \right) = \left( \frac{k_{organic}}{k_{ref}} \right) \ln \left( \frac{[reference]_0}{[reference]_t} \right) \]
Relative Rates of Methyl Vinyl Ketone *versus* Nonane

![Graph showing the relative rates of Methyl Vinyl Ketone versus Nonane. The graph plots ln(MVK) against ln(nonane) with three linear regression lines. The equations and R^2 values for each line are provided: y = 0.4938x + 0.0081, R^2 = 0.9897; y = 0.4835x + 0.0047, R^2 = 0.9977; y = 0.4704x - 0.0031, R^2 = 0.9970.](image-url)
Relative Rates of Crotonaldehyde *versus* Nonane

![Graph showing the relative rates of crotonaldehyde versus nonane with fitted lines and their equations.](image)
## Results of Relative Rates

<table>
<thead>
<tr>
<th>Organic Compound</th>
<th>$k_{\text{ref}}$ ($10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)</th>
<th>Relative Rate</th>
<th>$k_{\text{organic}}/k_{\text{ref}}$</th>
<th>$k_{\text{organic}}$ ($10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MVK</td>
<td>4.8</td>
<td>0.49 ± 0.11</td>
<td>2.3 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>4.8</td>
<td>1.3 ± 0.5</td>
<td>6.0 ± 2.4</td>
<td></td>
</tr>
</tbody>
</table>
Experimental Results

**MVK vs Nonane**
- $\ln(MVK) = 0.4938x + 0.0081$
- $\ln(MVK) = 0.4704x - 0.0031$

**CA vs Nonane**
- $\ln(CA) = 1.4764x + 0.0056$
- $\ln(CA) = 1.1566x + 0.031$
- $\ln(CA) = 1.278x - 0.0645$
Conclusions

- The rate constant for the reaction of MVK with Cl was determined to be \((2.3 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

- The rate constant for the reaction of CA with Cl was determined to be \((6.0 \pm 2.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

- The rate constant for CA seems to be high and hence not reasonable, thus more experiments need to be done regarding this reaction.
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