Molecular properties of the "anti-aromatic" species cyclopentadienone, C$_5$H$_4$=O

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4 π electrons — "anti-aromatic"

Our Essential Collaborators

• Thomas K. Ormond — Dept. Chemistry (Univ. Colorado)
• John W. Daily — Mechanical Engineering (Univ. Colorado)
• John F. Stanton — Institute of Theoretical Chemistry (Univ. Texas)
• Musahid Ahmed — LBNL, Advanced Light Source, Beamline 9.0.2
• Patrick Hemberger — PSI, Swiss Light Source
• Timothy S. Zwier — Department of Chemistry, Purdue Univ.
Transportation fuels developed at engineering/chemistry interface—"Real fuels" are complicated.

Engineering models are correspondingly complex—Mechanisms include 100s of intermediates and 1000s of reactions. Under-determined.

We use a hot micro-reactor to study the thermal cracking of complex fuels.

Goal ⇒ identify all decomposition products (atoms, radicals, metastables) formed in first 100 μsec.
Properties of "anti-aromatic" molecule, cyclopentadienone, C$_5$H$_4$=O

1. The $r_e$ structure of C$_5$H$_4$=O by Chirped Pulsed-FT microwave spectroscopy

2. Polarized, matrix IR spectrum of C$_5$H$_4$=O

3. Photoelectron Spectroscopy finds $IE$(C$_5$H$_4$=O)
   PEPICO experiments @ Swiss Light Source

4. Rx dynamics of thermal cracking of cyclopentadienone:
   C$_5$H$_4$=O (+ M) $\rightarrow$ CO + HC≡C-CH=CH$_2$
   C$_5$H$_4$=O (+ M) $\rightarrow$ CO + HC≡CH + HC≡CH
   experiments @ Beamline 9.0.2 — Advanced Light Source (Berkeley)
Fuel (+ M) $\rightarrow$ products

≤ 0.1 % fuel entrained in 1 atm
Ar carrier gas behind pulsed valve (open time 1 msec @ 10 Hz)

Supersonic Jet of Radicals/Ar into $10^{-6}$ Torr

½ mm x 2 ½ cm SiC tube @ 300–1700 K

20 K CsI window
Matrix IR spectroscopy @ 3 cm

The Nature of the Micro-Reactor
Our experiments

- thermally decompose complex organics in ≈ 300 Torr helium
- micro reactor a small furnace; T ≈ 1000 – 1700 K; τ ≈ 50 — 200 μsec
- molecules leaving micro reactor into vacuum; all chemistry “quenched”
- identify all cracking products (radicals, metastables) via VUV photoionization, matrix IR, REMPI, μwaves

0.01 % sample entrained in 0.5 atm He carrier gas with mass flow controller

**CW reactor**

Pyrolysis in a μreactor Detection strategy:

a) universal
b) multiplexed
c) sensitive
Prof. John Daily (Mechanical Engineering) “not a Chen nozzle but a tubular reactor”

Micro-reactor → complement to shock tube

1 mm x 3 cm linguini

1 mm x 3 cm SiC tube @ 300 K — 1700 K resistively heated by ≈ 10 Amps

**CFD modeling** — numerical solutions Navier-Stokes equations

many lignin monomers yield $\text{C}_5\text{H}_4=\text{O}$

cyclopentadienone
m/z 80
Cyclopentadienone formed in high temperature oxidation of aromatics


High Temperature Benzene Oxidation \( (T \geq 1100 \text{ K}) \)

cyclopentadienyl radical, \( C_5H_5 \ X^{2E_1} \ m/z 65 \)
High Temperature (T \geq 1100 \text{ K}) Cyclopentadienyl Oxidation

Cyclopentadienone Preparation

- o-phenylene sulfite
  - m/z 156

- o-quinone
  - m/z 108

- cyclopentadienone
  - m/z 80

Reaction: 2 HC≡CH → m/z 26

118.2 nm (10.487 eV) PIMS

1300 K

900 K

400 K
Unimolecular Chemistry
Cross-over experiment

\[ HC=\text{CH} \]

\[ HC\equiv\text{C}-\text{CH}=\text{CH}_2 \]

\[ \text{C}_6\text{H}_4\text{O}_2\text{SO} \]
\[ \text{C}_6\text{D}_4\text{O}_2\text{SO} + 1500 \text{ K} \]

50:50 mixture

SO

\[ \text{C}_5\text{H}_4=\text{O} \]
Purdue: CP FTMW spectrometer
Prof. T. S. Zwier (Purdue)

\[
\begin{align*}
&\text{µtubular reactor/1200 K} \\
&\text{SO, CO} \\
&\text{HC=CH} \\
&\text{HC=CH} \\
&\text{HC=CH} \\
&\text{HC=CH} \\
&\text{HC=CH} \\
\end{align*}
\]
8 isotopically substituted cyclopentadienone species observed by CP-FTMW spectroscopy (Purdue)

\[ ^{12}\text{C}_5\text{H}_4\text{=O}, \ ^{12}\text{C}_5\text{D}_4\text{=O} \]

\[ C_1\ ^{13}\text{C}_5\text{H}_4\text{=O}, \ C_2\ ^{13}\text{C}_5\text{H}_4\text{=O}, \ C_3\ ^{13}\text{C}_5\text{H}_4\text{=O} \]

\[ C_1\ ^{13}\text{C}_5\text{D}_4\text{=O}, \ C_2\ ^{13}\text{C}_5\text{D}_4\text{=O}, \ C_3\ ^{13}\text{C}_5\text{D}_4\text{=O} \]

Microwave spectra were interpreted by CCSD(T) \textit{ab initio} electronic structure calculations (Univ. Texas)

\[
r_e \text{ Structure of Cyclopentadienone, } C_5H_4=O \tilde{X}^1A_1
\]

molecule is exactly planar: inertial defect, \( \Delta_e = 0 \)
C$_5$H$_4$=O Polarized Infrared Spectrum

Matrix (Ne) isolation of C$_5$H$_4$=O and C$_5$D$_4$=O achieved @ 4 K

$\Gamma_{\text{vib}} = 9a_1 \oplus 3a_2 \oplus 4b_1 \oplus 8b_2$

20/24 fundamentals assigned for C$_5$H$_4$=O

17/24 fundamentals assigned for C$_5$D$_4$=O

X$^1$A$_1$ C$_5$H$_4$=O

- $a_1$ modes: $\nu_1 = 3107$, $\nu_2 = (3100, 3099)$, $\nu_3 = 1735$, $\nu_5 = 1333$, $\nu_7 = 952$, $\nu_8 = 843$ and $\nu_9 = 651$.
- inferred $a_2$ modes are: $\nu_{10} = 933$, and $\nu_{11} = 722$.
- $b_1$ modes are: $\nu_{13} = 932$, $\nu_{14} = 822$, and $\nu_{15} = 629$.
- $b_2$ fundamentals are: $\nu_{17} = 3143$, $\nu_{18} = (3078, 3076)$ $\nu_{19} = (1601$ or $1595)$, $\nu_{20} = 1283$, $\nu_{21} = 1138$, $\nu_{22} = 1066$, $\nu_{23} = 738$, and $\nu_{24} = 458$.

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\[ \nu_3(C_5H_4=O) \quad 1735 \text{ cm}^{-1} \]

Experimental spectra (black)

CCSD(T)/harmonic adjusted VPT2 (red)

\[ \text{IE}(C_5H_4=O) = 9.49 \pm 0.02 \text{ eV (} ^2 \text{A}_2 \text{)} \]
\[ \tilde{\text{X}} ^2 \text{B}_2 10.01 \text{ eV, } n_0 \]

\[ \tilde{\text{X}} ^1 \text{A}_1 (C_5H_4=O) = |... (7a_1)^2 (1b_1)^2 (2b_1)^2 (5b_2)^2 (1a_2)^2 (3b_1)^0 \rangle \]
Ionization Energy of cyclopentadienone

$\Lambda^+ \, ^2B_2$ 

\[ IE(m/z \, 80) = 9.408 \pm 0.018 \text{ eV} \]

\[ \nu_4^+ \, 1460 \pm 50 \text{ cm}^{-1} \]

\[ \nu_6^+ \, 1020 \pm 50 \text{ cm}^{-1} \]

\[ \nu_9^+ \, 660 \pm 50 \text{ cm}^{-1} \]
Chemistry ⇒ How does C₅H₄=O thermally crack apart?

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HC\(\equiv\)C\(\equiv\)C\(\equiv\)O
HC\(\equiv\)C\(\equiv\)C\(\equiv\)O
\overset{SO}{\arrow}{\overset{CO}{\arrow}}
(+ M)
\rightarrow
HC\(\equiv\)C\(\equiv\)C\(\equiv\)CH
HC\(\equiv\)C\(\equiv\)C\(\equiv\)CH
k₁
\rightarrow
HCC-CH=CH₂ + CO
m/z 52
k₂
\rightarrow
2 HCCH + CO
m/z 26
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\(\sigma\) (HCCH)
\(\Phi\) (E)
\(\sigma\) (HCCH-CH=CH₂)

\(o\)-phenylene sulfite
m/z 156
cyclopentadienone
m/z 80

To measure channels? ⇒ Beer’s Law

\[ M + \hbar\omega \rightarrow M^+ + e \]

\[ I = I_0 e^{-n\sigma(\nu)z} \]

Ion current \(= j^+ = (I_o - I) = I_o(1 - e^{-n\sigma(\nu)z}) \equiv n\sigma(\nu)z I_o \)

or

\[ S_{26}^+ = n_{HCCH} \sigma_{HCCH}(E) \ C \ \Phi(E) \]

\[ S_{52}^+ = n_{HCC-CH=CH_2} \Phi(E') \ \sigma_{HCC-CH=CH_2}(E') \ C \ \Phi(E') \]

Possible to measure \(n(\text{HC} \equiv \text{CH})\), \(n(\text{HC} \equiv \text{CH-CH=CH₂})\) with tunable VUV radiation (synchrotron)
Ormond et al.

“Pyrolysis of Cyclopentadienone: Mechanistic Insights From a Direct Measurement of Product Branching Ratios”

Molecular properties of C₅H₄=O now well known:

- Chirped Pulsed-FT microwave $\Rightarrow r_e$ structure

- Polarized Infrared Spectra (Ne matrix)
  $\Gamma_{vib} = 9a_1 \oplus 3a_2 \oplus 4b_1 \oplus 8b_2$
  20/24 fundamentals assigned for C₅H₄=O

- $IE(C_5H_4=O) = 9.408 \pm 0.018 \text{ eV}$

- $EA(C_5H_4=O) = 1.06 \pm 0.01 \text{ eV}$


- $C_5H_4=O \rightarrow CO + 2 \text{HC≡CH}$ or $\text{HC≡C}-\text{CH=CH}_2$ measured