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The Products of the Thermal Decomposition of CH$_3$CHO

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Abstract
We have used a heated 2 cm x 1 mm SiC microtubular (µtubular) reactor to decompose acetaldehyde: \( \text{CH}_3\text{CHO} + \Delta \rightarrow \) products. Thermal decomposition is followed at pressures of 75 — 150 Torr and at temperatures up to 1700 K, conditions that correspond to residence times of roughly 50 — 100 µsec in the µtubular reactor. The acetaldehyde decomposition products are identified by two independent techniques: VUV photoionization mass spectroscopy (PIMS) and infrared (IR) absorption spectroscopy after isolation in a cryogenic matrix. Besides CH\(_3\)CHO, we have studied three isotopologues, CH\(_3\)CDO, CD\(_3\)CHO, and CD\(_3\)CDO. We have identified the thermal decomposition products CH\(_3\) (PIMS), CO (IR, PIMS), H (PIMS), H\(_2\) (PIMS), CH\(_2\)CO (IR, PIMS), CH\(_2\)=CHOH (IR, PIMS), H\(_2\)O (IR, PIMS), and HC≡CH (IR, PIMS). Plausible evidence has been found to support the idea that there are at least three different thermal decomposition pathways for CH\(_3\)CHO:

Radical decomposition: \( \text{CH}_3\text{CHO} + \Delta \rightarrow \text{CH}_3 + [\text{HCO}] \rightarrow \text{CH}_3 + \text{H} + \text{CO} \)

Elimination: \( \text{CH}_3\text{CHO} + \Delta \rightarrow \text{H}_2 + \text{CH}_2=\text{C}=\text{O} \)

Isomerization/elimination: \( \text{CH}_3\text{CHO} + \Delta \rightarrow [\text{CH}_2=\text{CH-OH}] \rightarrow \text{HC}=\text{CH} + \text{H}_2\text{O} \)

Both PIMS and IR spectroscopy show compelling evidence for the participation of vinylidene, CH\(_2=\text{C} \), as an intermediate in the decomposition of vinyl alcohol: \( \text{CH}_2=\text{CH-OH} + \Delta \rightarrow [\text{CH}_2=\text{C} \] + H\(_2\)O \rightarrow HC≡CH + H\(_2\)O
The thermal decomposition of acetaldehyde has been extensively studied in shock tubes, flow reactors, and flames over the last 75 years. The weakest bond in acetaldehyde is the CH$_3$-CHO linkage. It is commonly accepted that the major thermal decomposition channel is formation of radicals via cleavage of the C-C bond:

$$\text{CH}_3\text{CHO} + \Delta \rightarrow \text{CH}_3 + \text{HCO}$$  \hspace{1cm} (1)

The formyl radical (HCO) is only weakly bound and will not survive for long at temperatures over 1300 K. The dynamics of the thermal cracking of CH$_3$CHO are generally modeled as a sequence of radical reactions. Recently, it has been reported that acetaldehyde could thermally decompose by a roaming process. Roaming mechanisms are characterized by formation of a dynamically-bound complex of radicals that subsequently disproportionate. The products are not radicals but closed shell species; in this case, methane and carbon monoxide: CH$_3$CHO + $\Delta \rightarrow [\text{CH}_3$, HCO] $\rightarrow \text{CH}_3\cdot\text{H} + \text{CO}$.

We have studied the thermal cracking of CH$_3$CHO in a heated microtubular reactor, a 1 mm i.d. x 2 cm long SiC tube that can be heated to temperatures up to 1700 K. A dilute sample of acetaldehyde is mixed with an inert carrier gas and passed through the heated SiC tube. Gases exiting the microtubular reactor emerge in an under-expanded jet at roughly 10$^{-5}$ Torr. The translational, vibrational, and rotational temperatures drop rapidly within a few diameters and all chemistry ceases. The products are identified by their photoionization (PIMS) mass spectra as well as their matrix infrared absorption spectra. The PIMS experiment uses a reflectron time-of-flight mass spectrometer to analyze the ions resulting from photoionization by 118.2 nm (10.487 eV) photons. In separate experiments, we send a gas mixture of CH$_3$CHO in Ar
carrier gas through the µtubular reactor and the resultant molecular beam impinges on a CsI window cooled to 20 K. The matrix frozen onto the CsI window is subsequently analyzed by IR absorption spectroscopy. Additional experiments were carried out at the chemical dynamics beamline (9.0.2) at the LBNL Advanced Light Source (ALS), where PIMS spectra can be obtained as a function of photon energy, which also allows for the recording of photoionization efficiency (PIE) profiles.

The dynamics of pyrolysis and transport through the SiC µtubular reactor is poorly characterized. Preliminary computational fluid dynamics simulations estimate that the gas pressure in the µtubular reactor is about 10% of the stagnation pressure. Within the reactor, there is a range of temperatures within the gas as it is heated by the walls. As a result, not all molecules see the same temperature time history. In reactor language there is a residence time distribution. However, as the gas approaches the tube exit, it is fairly uniformly heated such that the centerline temperature is within 100 – 200 K of the wall temperature. From simulations of the gas velocity, we estimate the residence time within the heated SiC tube to be roughly 50 — 100 µsec.

When acetaldehyde and its isotopologues are thermally decomposed in the µtubular reactor, the products monitored by 118.2 nm (10.487 eV) PIMS are shown in Fig. 1. The bottom trace in Fig. 1 shows the products resulting from heating CH₃CHO to 1500 K. We observe the CH₃CHO⁺ cation at m/z 44 as well as a feature at m/z 43. The latter is tentatively attributed to the acetyl cation, CH₃CO⁺, via dissociative ionization of vibrationally excited acetaldehyde, a process for which the room temperature threshold has been established to be approximately 10.8 eV. We also observe the ketene cation, CH₂CO⁺, at m/z 42, and CH₃⁺ at m/z 15. The second trace in Fig. 1 is that of CH₃CDO. The species at m/z 45 is the parent peak of CH₃CDO⁺ and a dissociative
ionization product, analogous to the m/z 43 peak found for CH₃CHO, is observed. The cation of ketene is found at m/z 42. As expected, we observe the CH₃⁺ ion at m/z 15. Surprisingly we also detect the CDH₂⁺ and CD₂H⁺ ions at m/z 16 and 17. The third trace in Fig. 1 is that of CD₃CHO heated to 1500 K. The bands at m/z 47 and 46 are the parent and the product of the aforementioned dissociative ionization process. The feature at m/z 44 is that of CD₂=C=O⁺. The perdeuterated methyl cation is observed at m/z 18 and we also observe signals from CD₂H⁺(17), CDH₂⁺(16), and CH₃⁺ (15). Examination of the PIE curves demonstrates that the signals in Fig. 1 at m/z 15, 16, 17, and 18 all result from ionization of methyl radicals. The final spectrum in Fig. 1 is that of CD₃CDO heated to 1500 K. Peaks for the parent cation, m/z 48, and that for dissociative ionization, m/z 46, are detected. The weak band at m/z 47 is assigned as CHD₂CDO⁺ and arises from a known contamination (roughly 2%) of the CD₃CDO sample. The band at m/z 44 is that of CD₂=C=O⁺ while that at m/z 18 is CD₃⁺.

A portion of the matrix IR absorption spectra resulting from the thermal cracking of acetaldehyde is shown in Fig. 2. The bottom trace (green) is a control scan of the Ar carrier gas after passing through the µtubular reactor heated to 1700 K. The black scan is that of CH₃CHO/Ar exposed to the same conditions. The peak at 3619 cm⁻¹ is assigned to the O-H stretch of vinyl alcohol, ν₁(CH₂CHO-H), while the bands at 3302 cm⁻¹ and 3288 cm⁻¹ belong to acetylene, ν₃(HCCH), and are the absorptions associated with the well-known Darling-Dennison mixing of ν₃ and ν₂ + ν₄ + ν₅. The red trace in Fig. 2 is that for CH₃CDO at the same conditions. The peak at 3621 cm⁻¹ is that of ν₁(CH₂CDO-H) and the features of HCCH at 3302 cm⁻¹ and 3288 cm⁻¹ are present. In addition to these features, the red trace in Fig. 2 clearly shows the C-H and C-D bands belonging to acetylene-d₁, HCCD, at 3323 cm⁻¹ (ν₁) and 2587 cm⁻¹ (ν₃), which has
significant mechanistic implications, as discussed below.

Matrix IR spectroscopy\textsuperscript{26} from the products of heated CH\textsubscript{3}CHO or CH\textsubscript{3}CDO also shows bands\textsuperscript{33} belonging to CO and CH\textsubscript{2}=C=O. When CD\textsubscript{3}CHO or CD\textsubscript{3}CDO are thermally cracked at 1700 K, the characteristic O-D stretches of the corresponding vinyl alcohols, v\textsubscript{1}(CD\textsubscript{2}CHO-D) at 2674 cm\textsuperscript{-1} and v\textsubscript{1}(CD\textsubscript{2}CDO-D) = 2675 cm\textsuperscript{-1}, are detected. When either CD\textsubscript{3}CHO or CD\textsubscript{3}CDO is pyrolyzed, IR signals from CD\textsubscript{2}=C=O, D\textsubscript{2}O, and HOD are observed. Equations (2) — (5) summarize the results of the matrix IR spectra:

\begin{align*}
\text{CH}_3\text{CHO} + 1400^\circ & \rightarrow \text{CO} \oplus \text{CH}_2\text{CO} \oplus \text{CH}_2=\text{CHOH} \oplus \text{H}_2\text{O} \oplus \text{HC}=\text{CH} \quad (2) \\
\text{CH}_3\text{CDO} + 1400^\circ & \rightarrow \text{CO} \oplus \text{CH}_2\text{CO} \oplus \text{CH}_2=\text{CDOH} \oplus [\text{H}_2\text{O} \oplus \text{HC}=\text{CD}] \text{ and } [\text{HOD} \oplus \text{HC}=\text{CH}] \\
\text{CD}_3\text{CHO} + 1400^\circ & \rightarrow \text{CO} \oplus \text{CD}_2\text{CO} \oplus \text{CD}_2=\text{CHOD} \oplus [\text{D}_2\text{O} \oplus \text{DC}=\text{CH}] \text{ and } [\text{HOD} \oplus \text{DC}=\text{CD}] \\
\text{CD}_3\text{CDO} + 1400^\circ & \rightarrow \text{CO} \oplus \text{CD}_2\text{CO} \oplus \text{CD}_2=\text{CDOD} \oplus \text{D}_2\text{O} \oplus \text{DC}=\text{CD} \quad (5)
\end{align*}

Fig. 3 shows the PIMS resulting from cracking CD\textsubscript{3}CHO at 1200\textsuperscript{o} when the ALS synchrotron is used to photoionize the pyrolysis products. In Fig. 3, h\omega\textsubscript{VUV} is set to 12.9 eV, which is sufficient to ionize acetylene, methane, and water.\textsuperscript{27} The features at m/z 19 and 20 are identified\textsuperscript{34} by the associated PIE curves as HOD\textsuperscript{+} and D\textsubscript{2}O\textsuperscript{+} as are the peaks at m/z 26, 27, and 28 to HCCH\textsuperscript{+}, DCCH\textsuperscript{+}, and DCCD\textsuperscript{+}. The tiny HCCH\textsuperscript{+} signal is an artifact arising from the aforementioned impurity in the CD\textsubscript{3}CHO sample.\textsuperscript{28}

One might be concerned that some of the acetaldehyde chemistry could be resulting from wall reactions. The PIMS spectra in Fig. 1 demonstrate that methyl radicals are exchanging H atoms. Thermal decomposition of CH\textsubscript{3}CDO in Fig. 1 will generate both CH\textsubscript{3} and D atoms. If there are rapid homogeneous, radical/radical
reactions in the µtubular reactor, chemically activated methane will be produced. The product methane will be activated by the CH$_3$-D bond energy$^{13}$ and CH$_3$D* would not be expected to survive in the hot SiC tube: CH$_3$ + D $\rightarrow$ CH$_3$D* $\rightarrow$ CH$_2$D + H. This interpretation is one explanation for the H atom exchanges of both CH$_3$CDO and CD$_3$CHO in Fig. 1. If methyl radicals are abstracting H atoms from the walls of the SiC tube, we would expect to find that the CD$_3$ radicals from CD$_3$CDO decomposition would be scrambled by $^1$H-dominated wall chemistry: CD$_3$ $\rightarrow$ [CHD$_2$, CDH$_2$, CH$_3$]. However the CD$_3$ radicals produced by cracking CD$_3$CDO do not undergo H/D exchange; only signals at m/z 18 are observed, implying that hydrogen exchange chemistry on the reactor walls is negligible.

Besides H atom abstractions from the wall, one might also be concerned about proton-catalyzed reactions at the wall. The IR spectra clearly detect the presence of vinyl alcohol when CH$_3$CHO is cracked. The classical mechanism$^{35}$ for keto-enol tautomerization is by proton catalysis. Consequently H$^+$ catalysis by the SiC walls would predict that CD$_3$CHO would isomerize to CD$_2$=CH-OH. This is not observed; the matrix IR following 1500 K decomposition of CD$_3$CHO clearly detects the O-D stretch of the product vinyl alcohol, $\nu_1$(CD$_2$CHO-D); the corresponding spectral feature from CD$_2$CHO-H is not observed. The ALS PIMS results confirm this conclusion.

It is natural to wonder how the present results might relate to the proposed roaming pathway$^{12}$ for acetaldehyde decomposition. Any methane formed by roaming would be chemically activated by roughly 4 eV and is unlikely to survive in the hot µtubular reactor. Hence, the fact that we do not observe prominent spectral signatures of methane in this work – indeed, no trace of methane is seen in the IR studies$^{36}$ – is not particularly illuminating; it does not suggest that methane is not formed via roaming
under the reaction conditions. What does seem clear is that the additional pathways for acetaldehyde decomposition observed here should be included in models of this important reaction.

Table 1 is a summary of our experimental findings. It is certain that the decomposition of CH₃CHO in the μtubular reactor is a significantly more complicated process than that implied by the simple picture provided by (1). Our results are consistent with three different decomposition channels.

\[
\text{CH}_3\text{CHO} + \Delta \rightarrow \text{CH}_3 + [\text{HCO}] \rightarrow \text{CH}_3 + \text{H} + \text{CO} \quad \text{radical decomposition (6)}
\]

\[
\text{CH}_3\text{CHO} + \Delta \rightarrow \text{H}_2 + \text{CH}_2=\text{C}=\text{O} \quad \text{elimination (7)}
\]

\[
\text{CH}_3\text{CHO} + \Delta \rightarrow [\text{CH}_2=\text{CH}-\text{OH}] \rightarrow \text{HC}≡\text{CH} + \text{H}_2\text{O} \quad \text{isomerization/elimination (8)}
\]

The detection of HOD and D₂O from the cracking of CD₃CHO in Fig. 3 demonstrates that vinyl alcohol can decompose by a (1,2) elimination, eq. (9), as well as by a (1,1) elimination, eq. (10). The latter pathway generates the well-known but fleeting reactive intermediate, vinylidene, which rapidly rearranges to acetylene with a negligible energy barrier:

\[
\text{CD}_2≡\text{CH}=\text{OD} \rightarrow \text{DC}≡\text{CH} + \text{D}_2\text{O} \quad (9)
\]

\[
\text{CD}_2≡\text{CH}=\text{OD} \rightarrow [\text{CD}_2=\text{C}]=+ \text{HOD} \rightarrow \text{DC}≡\text{CD} + \text{HOD} \quad (10)
\]

In Fig. 3 the peak intensities of HOD⁺ and DCDD⁺ are about twice that of D₂O⁺ and DCCH⁺. This ratio suggests that (1,1) elimination via the CD₂=C: carbene is favored over direct-(1,2) elimination, although more careful quantitative work is needed to draw any definitive conclusion. The present work, however, provides evidence that the
vinylidene channel is at least competitive with the (1,2) elimination. In a related system, it is known that (1,1) elimination is 3 times more likely than (1,2) elimination in vinyl chloride photodissociation, \( \text{CH}_2\text{=CHCl} + h\omega \rightarrow \text{HC\equivCH} + \text{HCl} \), where HC\(\ell\) loss occurs on the ground electronic state.\(^{37}\)

Vinylidene is one of the most fundamental carbenes and its properties and the \([\text{CH}_2\text{=C:} \rightarrow \text{HC\equivCH}]\) isomerization dynamics have been the subject of many investigations.\(^{38-45}\) Several previous workers\(^{46-48}\) had suspected the importance of vinyl alcohol in acetaldehyde decomposition. There are few predictions of the role of HC\equivCH and, especially, CH\(\equiv\text{C}\) in the decomposition of acetaldehyde. Besides vinylidene, we also considered the possibility that the methylhydroxycarbene,\(^{49}\) \(\text{CH}_3\text{-C-OH}\), might be a participant in the thermal decomposition of \(\text{CH}_3\text{CHO}\); however we believe that this is unlikely.\(^{50}\)

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References


(13) Some Bond Dissociation Energies are: $D_{0}(\text{CH}_3\text{-CHO}) = 83.0 \pm 0.2$ kcal mol$^{-1}$; $D_{0}(\text{CH}_3\text{CO-H}) = 87.9 \pm 0.4$ kcal mol$^{-1}$; $D_{0}(\text{H-CH}_2\text{CHO}) = 95 \pm 1$ kcal mol$^{-1}$; $D_{0}(\text{H-CO}) = 14.4 \pm 0.1$ kcal mol$^{-1}$; $D_{0}(\text{CH}_3\text{H}) = 103.4 \pm 0.1$ kcal mol$^{-1}$; $\Delta_{\text{rxn}}H_{0}(\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}) = -6.0 \pm 0.1$ kcal mol$^{-1}$; $\Delta_{\text{rxn}}H_{0}(\text{CH}_3\text{CHO} \rightarrow \text{HCCH + H}_2\text{O}) = 34.5 \pm 0.5$ kcal mol$^{-1}$; $\Delta_{\text{rxn}}H_{0}(\text{CH}_3\text{CHO} \rightarrow \text{H}_2 + \text{CH}_2=\text{C}=\text{O}) = 19.7 \pm 0.2$ kcal mol$^{-1}$


(25) In studies at LBNL's Advanced Light Source, the threshold for observation of the m/z 43 peak at 1150 K was found to be as low as 10.1 eV. Consequently, given both experimental estimates of the room temperature threshold, and the bond energy [CH$_3$CO-H]$^+$ bond energy that we have calculated to be about 0.6 - 0.7 eV (which implies a 0 K threshold for CH$_3$CHO $\rightarrow$ CH$_3$CO$^+$ + H of about 10.8 - 10.9 eV), this suggests a substantial amount of vibrational excitation (of order 0.7 eV) in the 1150 K acetaldehyde. This seems to be very large, and is, in fact, inconsistent with preliminary studies of heated acetaldehyde vibrational states via chirped-pulse mm microwave spectroscopy [Kirill Kuyanov-Prozument and R. W. Field, unpublished results, 2011]. An alternative
explanation, which cannot be excluded at this point, is that the m/z = 43 signal comes from dissociative ionization of vinyl alcohol (CH$_2$=CH-OH), because $IE$(CH$_2$CHOH) $\leq$ 9.33 ± 0.05 eV. There might be a relatively low energy dissociative ionization channel leading to protonated ketene: CH$_2$CHOH$^+$ $\rightarrow$ CH$_2$=C=OH$^+$ + H.


(27) Important ionization energies: $IE$(CH$_3$CHO) = 10.2298 ± 0.0007 eV; $IE$(CH$_2$=CHOH) $\leq$ 9.33 ± 0.05 eV; $IE$(H$_2$O) = 12.61737 ± 0.00025 eV; $IE$(CH$_3$) = 9.8380 ± 0.0004 eV; $IE$(CH$_2$) = 12.618 ± 0.004 eV; $IE$(CH$_3$CH$_3$) = 11.56 ± 0.02 eV; $IE$(HCCH) = 11.4006 ± 0.0006 eV; $IE$(CH$_2$O) = 10.8850 ± 0.0002 eV; $IE$(CH$_2$CH$_3$) = 10.51268 ± 0.00003 eV; $IE$(CH$_2$CO) = 9.617 ± 0.003 eV

(28) The commercial samples of CD$_3$CHO and CD$_3$CDO are produced by equilibrating acetaldehyde with D$_2$O and base. The proton NMR spectrum of the CD$_3$CHO sample shows that 6% is CD$_2$HCHO arising from incomplete proton/deuteron exchange. This is evident in the 118.2 nm PIMS in Fig. 1. The black trace for CD$_3$CHO shows a small feature at m/z 45 which is assigned to CD$_3$HCO$^+$ produced by dissociative ionization of CD$_2$HCHO. Likewise, the final red trace for CD$_3$CDO displays a weak band at m/z 47 which is CHD$_3$CDO$^+$. The extent of impurity in the CD$_3$OD sample, 2 %, was determined by integrating the corresponding peaks in the room temperature mass spectrum.


(34) The feature at m/z = 20 also arises, in part from Ar$$^{++}$$, which is always observed at the ALS facility due to stray high-energy radiation.


(36) Shimanouchi, T. *Tables of Vibrational Frequencies. Consolidated Volume I*; NSRDS-NBS 39, 1972. Methane has four vibrational modes but only the degenerate CH stretch, $$\nu_3$$, and the degenerate deformation, $$f_2 \nu_4$$, are IR active. In the gas-phase $$\nu_3$$ CH$_4$ is observed at 3019.9 cm$^{-1}$ and $$\nu_4$$ CH$_4$ is found at 1306.2 cm$^{-1}$. These values shift in an Ar matrix to $$\nu_3 = 3032\text{ cm}^{-1}$$ and $$\nu_4 = 1305\text{ cm}^{-1}$$. The signal from $$\nu_4$$ is very intense and easy to detect in an cryogenic matrix.


(48) See P. R. Westmoreland's comments at the end of Gupte et al.'s 2007 paper.

Acetaldehyde could rearrange to the vinyl alcohol *via* the methylhydroxycarbene: $$\text{CH}_3\text{CHO} \rightarrow [\text{CH}_3\text{-C-OH}] \rightarrow \text{CH}_2=\text{CH-OH}. \text{But this pathway would predict that the vinyl alcohol resulting from CH}_3\text{CDO would be CH}_3\text{CDO} \rightarrow [\text{CH}_3\text{-C-OD}] \rightarrow \text{CH}_2=\text{CH-OD.}$$ Fig. 2 shows that the vinyl alcohol resulting from CH\textsubscript{3}CDO is CH\textsubscript{2}=CD-OH. Likewise, when CD\textsubscript{3}CHO rearranges, we observe CD\textsubscript{2}=CHOD and not CD\textsubscript{2}=CD-OH.
Table 1

A summary of thermal cracking products from acetaldehyde as identified by PIMS and IR spectroscopy.

1. $\text{CH}_3\text{CHO} + \Delta \rightarrow \text{CH}_3 (\text{PIMS}) \oplus \text{CO} (\text{IR, PIMS}) \oplus \text{CH}_2\text{CO} (\text{IR, PIMS}) \oplus \text{CH}_2=\text{CHOH} (\text{IR, PIMS}) \oplus \text{HC}=\text{CH} (\text{IR, PIMS})$

2. $\text{CH}_3\text{CDO} + \Delta \rightarrow \text{CH}_3, \text{CH}_2\text{D}, \text{CD}_2\text{H}, \text{CD}_3 (\text{PIMS}) \oplus \text{CO} (\text{IR, PIMS}) \oplus \text{CH}_2\text{CO} (\text{IR, PIMS}) \oplus \text{CH}_2=\text{CDOH} (\text{IR, PIMS}) \oplus \text{HC}=\text{CH}, \text{HOD} (\text{IR, PIMS}) \oplus \text{DC}=\text{CH} (\text{IR, PIMS})$

3. $\text{CD}_3\text{CHO} + \Delta \rightarrow \text{CD}_3, \text{CD}_2\text{H}, \text{CH}_2\text{D}, \text{CH}_3 (\text{PIMS}) \oplus \text{CO} (\text{IR, PIMS}) \oplus \text{CD}_2\text{CO} (\text{IR, PIMS}) \oplus \text{CD}_2=\text{CHOD} (\text{IR, PIMS}) \oplus \text{DC}=\text{CH}, \text{D}_2\text{O} (\text{IR, PIMS}) \oplus \text{DC}=\text{CD}, \text{HOD} (\text{IR, PIMS})$

4. $\text{CD}_3\text{CDO} + \Delta \rightarrow \text{CD}_3 (\text{PIMS}) + \text{CO} (\text{IR, PIMS}) \oplus \text{CD}_2\text{CO} (\text{IR, PIMS}) \oplus \text{CD}_2=\text{CDOD} (\text{IR, PIMS}) \oplus \text{DC}=\text{CD}, \text{D}_2\text{O} (\text{IR, PIMS})$
Figure Captions

Fig. 1  Photoionization mass spectra of the thermal cracking products of acetaldehyde are shown. The fixed-frequency PIMS uses the 9th harmonic of a YAG laser, 118.2 nm or 10.487 eV, for photoionization. Samples of acetaldehyde entrained in He buffer gas are subjected to pyrolysis by a 1 mm x 2 cm SiC tube heated to 1500 K. Typical samples have 0.3 % acetaldehyde mixed with 2 atm He and are delivered to the μtubular reaction via a General Valve pulsed at 10 Hz. The approximate pressure in the μtubular reactor is 150 Torr and the centerline temperature is within 100 – 200 K of the wall temperature. The transit time through the heated SiC tube is roughly 50 — 100 μsec. There are 4 different spectra in this figure. Bottom Trace (black): CH₃CHO; 2nd Trace (red): CH₃CDO, 3rd Trace (black): CD₃CHO, 4th Trace (red): CD₃CDO.

Fig. 2  Matrix infrared absorption spectra of the thermal cracking products of acetaldehyde are shown. Samples of acetaldehyde entrained in an Ar buffer gas are subjected to pyrolysis by a 1 mm x 2 cm SiC tube heated to 1700 K. Typical samples have 0.3 % acetaldehyde mixed with 1 atm Ar and are delivered to the μtubular reaction via a General Valve pulsed at 10 Hz. The approximate pressure in the μtubular reactor is 75 Torr and the centerline temperature is within 100 – 200 K of the wall temperature. The transit time through the heated SiC tube is roughly 50 — 100 μsec. There are 3 different spectra in this figure. Bottom Trace (green): Ar carrier gas heated to 1700 K, 2nd Trace (black): CH₃CHO/Ar, 3rd Trace (red): CH₃CDO/Ar.

Fig. 3  The PIMS resulting from cracking CD₃CHO at 1400 K when the synchrotron at the LBNL’s Advanced Light Source is used to photoionize the pyrolysis products. The tunable VUV light source is set to 12.9 eV in order to ionize methane,
acetylene and water. Samples of acetaldehyde-$d_3$ entrained in Ar buffer gas are subjected to pyrolysis by a 1 mm x 2 cm SiC tube heated to 1400 K. Typical samples have 1 % acetaldehyde mixed with 1 atm Ar and are delivered to the $\mu$tubular reaction via a General Valve pulsed at 10 Hz. The approximate pressure in the $\mu$tubular reactor is 75 Torr and the centerline temperature is within 100 – 200 K of the wall temperature. The transit time through the heated SiC tube is roughly 50 — 100 $\mu$sec.
CH$_3$ CDO/Ar 1700 K, RED
CH$_3$ CHO/Ar 1700 K, BLACK
Ar @ 1700 K = GREEN

Fig. 2
CD$_3$CHO + 1400 K $\rightarrow$ products

![Diagram](image-url)
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