Study of Thermal Decomposition of CH_3CHO Using a Miniature Tubular Flow Reactor

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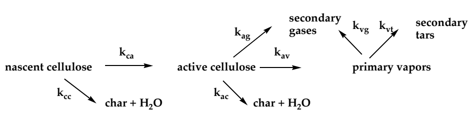
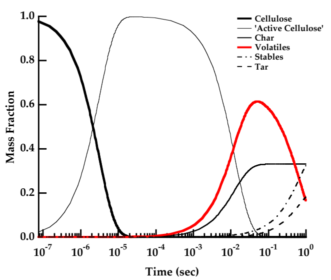
Thermal Cracking of Biomass

- Biomass is plant material: agricultural crops, trees, and grasses. Structural polymers — cellulose, hemicellulose, and lignin
- Thermochemical processing converts solid biomass ⇒ clean liquid fuels and chemicals. All from local sources in a way that reduces dependence on carbon stored over geological times.
- All thermal methods use heat to break the chemical bonds of large structural biopolymers ⇒ smaller semi-volatile or volatile units & "char".

Diebold's Cellulose Decomposition Scheme





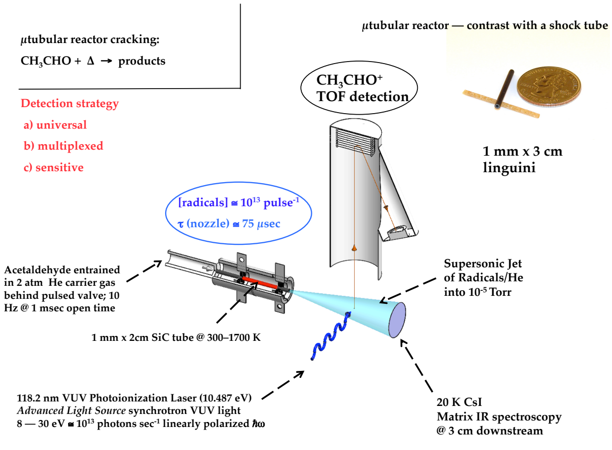
Phenomenological kinetics/rapid heating to 500° J W Daily

Experimental Apparatus

µtubular reactor cracking:

$CH_3CHO + \Delta \rightarrow$ products

Detection strategy
a) universal
b) multiplexed
c) sensitive



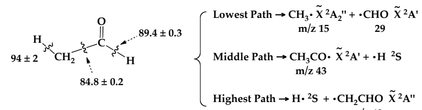
Thermochemical Decomposition

Radical decomposition: $CH_3CHO + \Delta \rightarrow CH_3 + [HCO] \rightarrow CH_3 + H + CO$
Elimination: $CH_3CHO + \Delta \rightarrow H_2 + CH_2{=}C{=}O$
Isomerization/elimination: $CH_3CHO + \Delta \rightarrow [CH_2{=}CH\text{-}OH] \rightarrow HC{\equiv}CH + H_2O$

Simplest organic aldehyde is acetaldehyde:

$CH_3CHO + \Delta \rightarrow$ products (monitor by PIMS and IR)

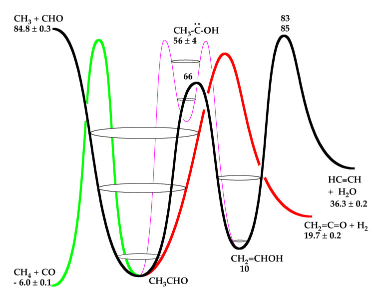
What are the bond energies of CH_3CHO ?



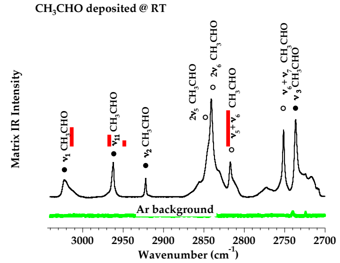
$\Delta_{rxn}H_{298}(CH_3\text{-}CHO \rightarrow CH_3 + CHO) = 84.8 \pm 0.2$ kcal mol^{-1}

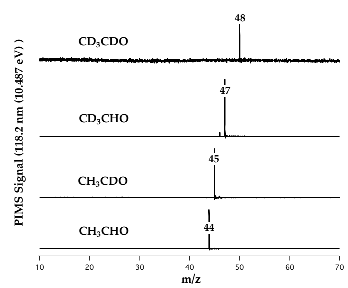
$\Delta_{rxn}H_{298}(CH_3C(O)\text{-}H \rightarrow CH_3CO + H) = 89.4 \pm 0.3$ kcal mol^{-1}

$\Delta_{rxn}H_{298}(H\text{-}CH_2CHO \rightarrow H + CH_2CHO) = 94 \pm 2$ kcal mol^{-1}

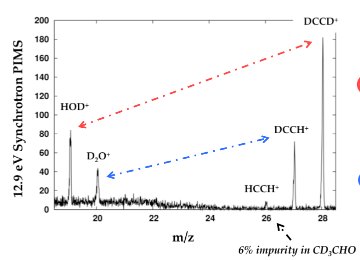


Detecting Acetaldehyde

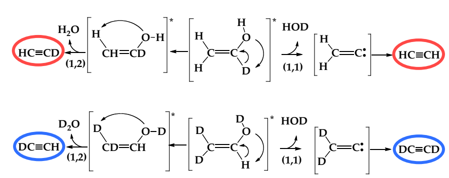




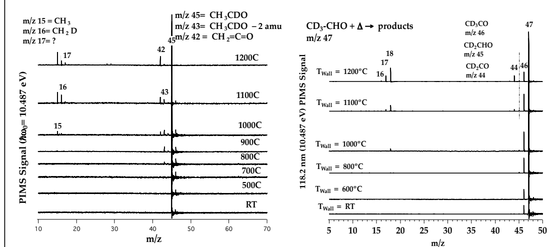
$CD_3CHO + 1100°C \rightarrow$ products

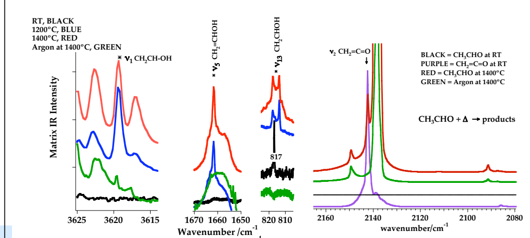


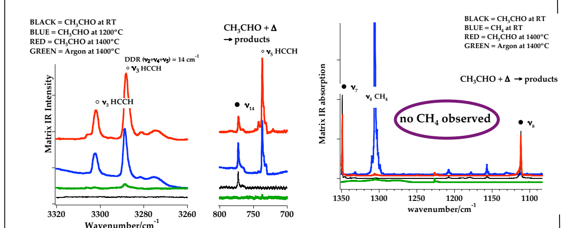
$CH_2{=}CH\text{-}OH \Rightarrow H_2O + HCCH$?



Pyrolysis of Acetaldehyde







Thermal Cracking of Acetaldehyde yields

- acealdehyde d_0

$CH_3CHO + \Delta \rightarrow CH_3$ (PIMS) ⊕ CO (IR, PIMS) ⊕ H, H_2 (PIMS) ⊕ $CH_2{=}C{=}O$ (IR, PIMS) ⊕ $CH_2{=}CHOH$ (IR, PIMS) ⊕ HC≡CH (IR, PIMS)

- acealdehyde d_1

$CH_3CDO + \Delta \rightarrow CH_3$, CH_2D, CD_2H, CD_3 (PIMS) ⊕ CO (IR, PIMS) ⊕ CH_2CO (IR, PIMS) ⊕ $CH_2{=}CDOH$ (IR, PIMS) ⊕ HC≡CH, HOD (IR, PIMS) ⊕ DC≡CH (IR, PIMS)

- acealdehyde d_3

$CD_3CHO + \Delta \rightarrow CD_3$, CD_2H, CH_2D, CH_3 (PIMS) ⊕ CO (IR, PIMS) ⊕ CD_2CO (IR, PIMS) ⊕ $CD_2{=}CHOD$ (IR, PIMS) ⊕ DC≡CH, D_2O (IR, PIMS) ⊕ DC≡CD, HOD (IR, PIMS)

- acealdehyde d_4

$CD_3CDO + \Delta \rightarrow CD_3$ (PIMS) ⊕ CO (IR, PIMS) ⊕ CD_2CO (IR, PIMS) ⊕ $CD_2{=}CDOD$ (IR, PIMS) ⊕ DC≡CD, D_2O (IR, PIMS)