Furan oxidation mechanisms: How simple is too simple? How complex is too complex?

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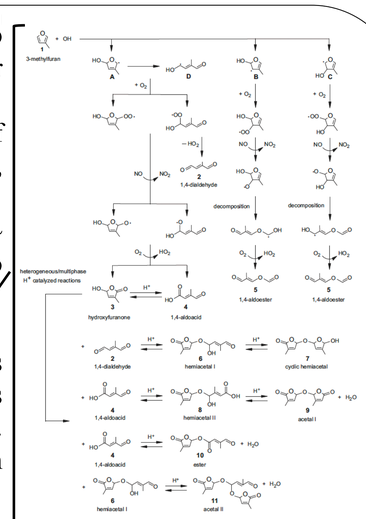
BACKGROUND: FURANS

- Furans are emitted directly (via biomass burning) or from the degradation of VOCs.
- (They are also produced during the roasting of coffee beans, so if you have a coffee in your hand, sniff it! You just experienced furan exposure!)
- They rapidly oxidize in the atmosphere (lifetime ~ hours) to produce furan derivatives and contribute to SOA formation.
- This chemistry can quickly become complex [1]
- While some laboratory and measurement studies exist, much of furan oxidation chemistry is uncertain, unknown, and/or unconstrained (e.g. branching ratios, reaction rates, SOA formation potential, etc.).
- Thus most mechanisms are simplified/lumped.



Strollo and Ziemann [2013]

ASP CHEMICAL MECHANSM

- ASP (Aerosol Simulation Program) is a gas-phase, aerosol-phase, and heterogeneous chemical mechanism developed to simulate young biomass burning plumes [2, 3] including O_3 and SOA formation.
- ASP is developing gas and particle wall-loss corrections to study and understand chamber study observations
- ASP has a reduced-form representation of furan chemistry (see table below), which we are in the process of expanding and constraining with this project.

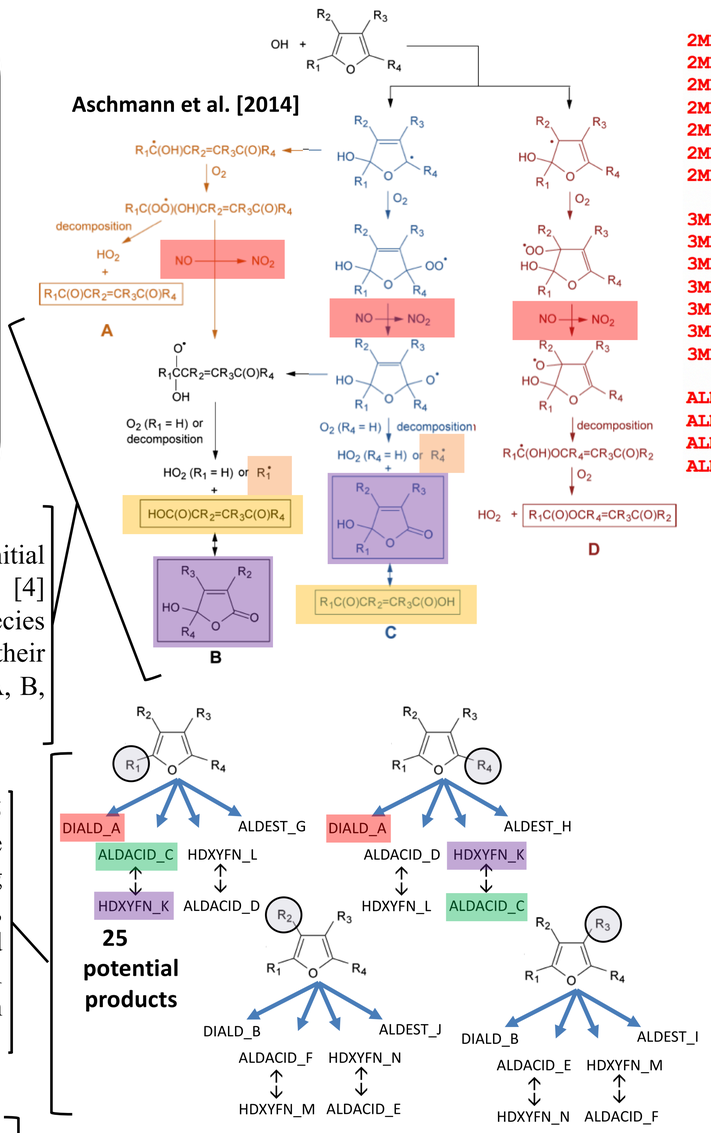
Table 2. Lumped Chemical Mechanism for Furans Used in This Work

Reaction	A	n	E_a/K	Reference[a]
FURAN + OH → HO_2 + RP20	6.2e-11	0	0	1
RP20 + OH → 0.53 $RO_2$59 + 0.47 $RO_2$60 + RO_2T	5.6e-11	0	0	2
RP20 → UR25	–	–	–	3
$RO_2$59 + NO → NO_2 + HO_2 + UR24	2.08e-12	0	180.0	4
$RO_2$59 + HO_2 → OH + HO_2 + UR24	3.14e-13	0	800.2	4
$RO_2$59 + RO_2_T → HO_2 + UR24 + RO_2T	1.0e-15	0	0	4
$RO_2$60 + NO → NO_2 + HO_2 + 2.0 MGLY	2.08e-12	0	180.0	4
$RO_2$60 + HO_2 → OH + HO_2 + 2.0 MGLY	3.14e-13	0	800.2	4
$RO_2$60 + RO_2T → HO_2 + 2.0 MGLY + RO_2T	1.0e-15	0	0	4

[a]References are as follows: 1, *Bierbach et al.* [1995]; 2, *Bierbach et al.* [1994]; 3, assumed equal to ALD2 in CACM [*Griffin et al.*, 2002, 2005]; 4, stoichiometry adapted from University of Leeds Master Chemical Mechanism (http://mcm.leeds.ac.uk/) with reaction rates adapted from CACM and *Jenkin et al.* [1997].

We base our initial mechanism off of [4] creating individual species differentiated by their structure and branch [A, B, C, or D].

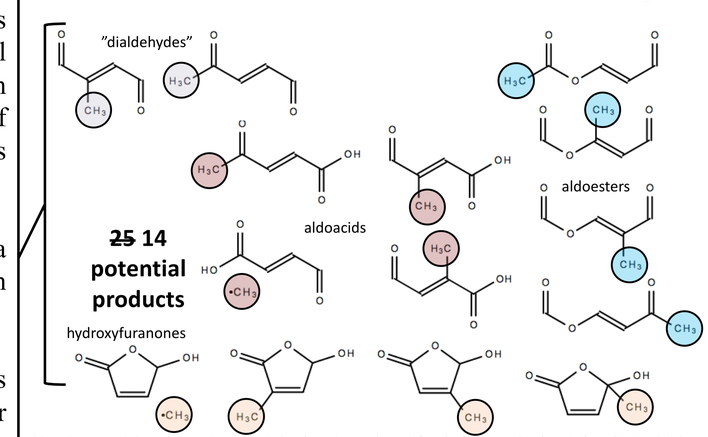
This produces 25 distinct possible products including dialdehydes, aldoacids, hydroxyfuranones, and aldoesters with methyl groups bonded in different locations.



Some of these products have identical chemical structures, which reduces the number of individual molecules from 25 to 14.

These are coded into a chemical mechanism (upper right).

The branching ratios and reaction rates for these reactions are largely unknown.

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2MF + OH + O2          → DIALD_A          + HO2
2MF + OH + 2*O2 + NO   → ALDACID_C + NO2  + CH3
2MF + OH + 2*O2 + NO   → ALDACID_D + NO2  + HO2
2MF + OH + 2*O2 + NO   → HDXYFN_K  + NO2  + CH3
2MF + OH + 2*O2 + NO   → HDXYFN_L  + NO2  + HO2
2MF + OH + 2*O2 + NO   → ALDEST_G  + NO2  + HO2
2MF + OH + 2*O2 + NO   → ALDEST_H  + NO2  + HO2

3MF + OH + O2          → DIALD_B          + HO2
3MF + OH + 2*O2 + NO   → ALDACID_E + NO2  + HO2
3MF + OH + 2*O2 + NO   → ALDACID_F + NO2  + HO2
3MF + OH + 2*O2 + NO   → HDXYFN_M  + NO2  + HO2
3MF + OH + 2*O2 + NO   → HDXYFN_N  + NO2  + HO2
3MF + OH + 2*O2 + NO   → ALDEST_J  + NO2  + HO2
3MF + OH + 2*O2 + NO   → ALDEST_I  + NO2  + HO2

ALDACID_F <--> HDXYFN_M
ALDACID_E <--> HDXYFN_N
ALDACID_C <--> HDXYFN_K
ALDACID_D <--> HDXYFN_L
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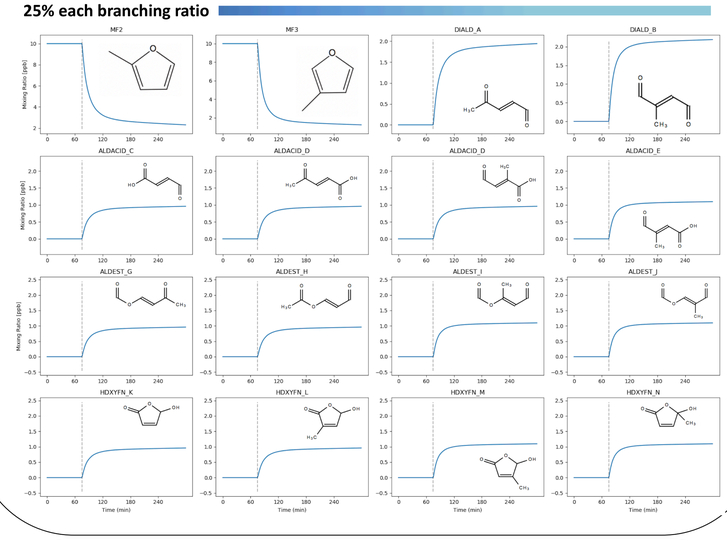
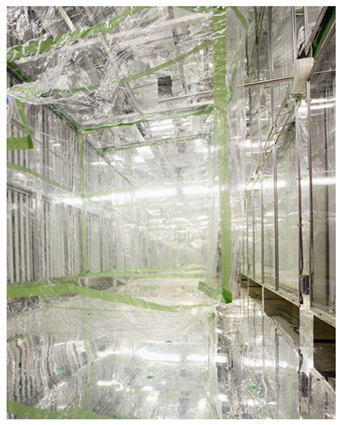
The 2- and 3-methylfuran mechanism outlined in this poster is coded here. Initial ASP simulations of these reactions are plotted below using previously identified reaction rates and assuming 25% branching ratios for each of the A, B, C, and D branch [1, 4].

These aldoacids & hydroxyfuranones continue to react and oligomerize forming (hemi)acetals, esters, & others. This is where furan chemistry can get quite complex.

PRELIMINARY ASP RESULTS:



GEORGIA TECH CHAMBER



Gas-phase measurements

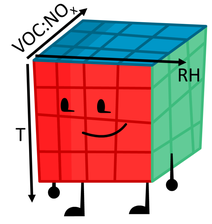
- Gas Chromatograph Flame Ionization Detector (GC-FID): VOC measurements
- High Resolution Time of Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS): oxidized gas-phase compounds, radicals
- UV absorption O_3 analyzer
- Chemilumnescence NO/NO_2/NO_x analyzer
- CAPS NO_2 monitor

Particle-phase measurements

- **High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS)**: Aerosol composition (organics, sulfate, nitrate, ammonium, chloride), mass loading, aerosol size distribution
- **Filter Inlet for Gases and AEROsols High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (FIGAERO-HR-ToF-CIMS)**: molecular level particle-phase composition
- Scanning Mobility Particle Sizer (SMPS): aerosol size distribution, volume distribution
- Condensation Particle Counter (CPC): aerosol number concentration
- Offline filter characterization

CONCLUSIONS / NEXT STEPS

- Furan oxidation is important for SOA formation and AQ, but there is a lack of constraints on the overall mechanism.
- The Georgia Tech Chamber is making observations for initial oxidation products (varying VOC:NO_x, T, RH) in order to identify primary branches and appropriate branching ratios
- We are adding additional detail to the ASP chemical mechanism, including:
  - NO_3 oxidation
  - NO → NO_2 chemistry (org. nitrates)
  - Furfural chemistry
  - Oligomerization parameterizations
- Chamber constraints and mechanism detail will be synthesized and mechanisms at different complexities will be produced.



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