Topic 7
Peroxyl radical chemistry and autoignition
Low temperature combustion

- Combustion in the 500 - 1000 K range shows regions of slow reaction and regions of explosion or ignition.
- Cause of 'knock' in gasoline engine and of the desired autoignition in diesel engines.
- There is a region of "negative temperature coefficient", where the reaction changes from branching to termination as T increases, in the boundary between low temperature and high temperature combustion.
- Peroxy radical chemistry is central to combustion in the low temperature regime.
Autoignition chemistry

\[ RH \rightarrow OH \rightarrow R \rightarrow R' \]

\[ O_2 \rightarrow QO \rightarrow QOOH \rightarrow OH + R'OOH \]

Smaller radical (\( R_1 \)) + Alkene (\( A_1 \))

Termination

\[ HO_2 + Alkene (A_2) \]

Propagation

\[ OH + R'OOH \rightarrow R'O + OH \]

Branching
Computed ignition delay times for stoichiometric n-alkanes in air at 13.5 bar.

- Shock tube ignition delay times for n-heptane and n-decane, all at 13.5 bar pressure and stoichiometric fuel/air. Experiments are n-heptane (diamond) and n-decane (Triangle) n-Heptane (square) Computed results n-decane (circle)
Static reactors: Early studies of alkane oxidation kinetics and mechanism by Baldwin, Walker and co-workers

- The techniques rely on end product analysis using gas chromatography. Three techniques were used:
  - Addition of small amounts of alkane, RH, to a slowly reacting $\text{H}_2 + \text{O}_2$ mixture at ~ 750 K allowed measurements of, e.g. OH, H, HO$_2$ + RH. $\text{H}_2 + \text{O}_2$ provides a well-controlled environment containing the radicals. (JCS Faraday Trans 1., 1975, 71, 736)
  - Oxidation of aldehydes (550 – 800 K). Aldehydes act as a source of alkyl radicals, e.g. 2-C$_3$H$_7$ from 2-C$_3$H$_7$CHO (JCS Faraday Trans 2., 1987, 83, 1509)
  - Decomposition of tetramethylbutane (TMB) in the presence of $\text{O}_2$. System acts as a source of HO$_2$. (JCS Faraday Trans 1., 1986, 82, 89)
Whole system studies
Provide targets for mechanism evaluation
Flow reactor study of dimethyl ether oxidation at low T

• 550–850 K, 12–18 atm, at equivalence ratios of 0.7 - 4.2
• FTIR, non-dispersive IR (NDIR) (for CO and CO₂), and electrochemical (for O₂)
Sensitivity analysis

See also Fischer et al. Int J Chem Kinet (32, 713, 2000) for a study at higher T (2.5 atm, 1118 K) using the same technique.


Figure 28 Sensitivity coefficients for dimethyl ether oxidation. 3030 ppm DME, $\phi = 1.19$, $P = 12.5$ atm, $\tau = 2.1$ s.
Jet stirred reactor, coupled with synchrotron vacuum ultraviolet photoionization molecular-beam mass spectrometry

- Provided direct observation of speciated hydroperoxides for the first time
Experimental and modelling observations, oxidation of n-butane

- **Experiment:** m/z 48 (green circles), 56 (white squares, the signal is divided by 7.5), 62 (purple circles), 72 (black squares), 90 (blue circles, the signal is divided by 4) and 104 (red circles)

- **Calculated:** (ppm) CH3OOH (48) (green line, mole fraction divided by 5), C2H5OOH (62) (purple line), C4H9OOH (90) (blue line), the C4 ketohydroperoxides (104) (red line), butenes (56) (dash line, mole fraction divided by 5), and C4H8O products (72) (black line)
Evidence for a third $O_2$ addition in 2-methylhexane combustion


Keto-dihydroperoxide
Dihydroperoxy cyclic ether

Diketo-hydroperoxide
Ketohydroperoxide cycli ether
Mechanism extensions following observations

- Blue arrows show extensions to mechanism of Mohamed et al, J Phys Chem, 120 (2010) 3169
Rapid compression machines and ignition delay times: methyl cyclohexane (Proc Comb Inst, 31, 267 (2007))

- Measured ignition delay times (symbols) for MCH/O\textsubscript{2}/diluent stoichiometric mixtures for 10 atm pressure at the end of compression (◇, 100% N\textsubscript{2}; □, 50% N\textsubscript{2}/50% Ar; and △, 100% Ar). The predicted ignition delays (curves) are for the three estimates of RO\textsubscript{2} isomerization rates for MCH.
Individual reactions or groups of reactions
$\text{CH}_3 + \text{O}_2$


Shows experimental data with fits using Troe method

Experimental methods: pulsed photolysis and discharge flow
\[ \text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2^* \]

\[ \text{C}_2\text{H}_5\text{O}_2^* + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M} \]

\[ \text{C}_2\text{H}_5\text{O}_2^* \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2 \]

\[ \text{C}_2\text{H}_5\text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2 \]

- The overall rate constant is pressure dependent at low T and becomes pressure independent at high T.
- The ethene yield decreases with pressure at low T. It increases with T, and dominates at high T.
Two hydrogen-transfer transition states
  - $^2A''$ electronic state
  - $^2A$ electronic state derived from a $2A'$ planar structure

At the best level of theory used, DZP (double zeta plus polarization) CCSD(T) $^2A''$ transition state lies 4.5 kcal mol$^{-1}$ above the reactants

From Zador Progress in Energy and Combustion Science 37 (2011) 371
Importance of level of theory in determining the $C_2H_5 + O_2$ PES (Klippenstein, Proc Comb Inst 36 (2017) 77-111)

- Plot of the $C_2H_5 + O_2$ interaction energy along the $R$ (C-O) distinguished coordinate minimum energy path. The black, red, and blue lines correspond to CASPT2, MRCI + Q, and MRCI calculations, respectively. The solid lines denote direct calculations of the interaction energy, while dashed lines denote calculations of the doublet-quartet splitting combined with CCSD(T) calculations of the quartet interaction energy.
- Rate constant: theory, high pressure limit; experiment: 1 atm except Fernandes, 100 atm
Determination of product yields in $\text{C}_2\text{H}_5 + \text{O}_2$ pulsed photolysis at higher pressures

- Taatjes et al. (J. Phys. Chem. A 104 (2000) 11549 - 11560) observed the formation of OH and HO$_2$, determining the fractional yields. Used 100% yield of HO$_2$ from CH$_2$OH + O$_2$ to calibrate the system.
- HO$_2$ yield↑ as T↑ and p↓
- Two timescales at higher T
- OH yield is small.

\[
\begin{align*}
\text{C}_2\text{H}_5 + \text{O}_2 & \rightarrow \text{C}_2\text{H}_5\text{O}_2^* \\
\text{C}_2\text{H}_5\text{O}_2^* + \text{M} & \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2 \\
\text{C}_2\text{H}_5\text{O}_2^* & \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2 \\
\text{C}_2\text{H}_5\text{O}_2 + \text{M} & \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2
\end{align*}
\]
• Three regimes, low, transition, high T.
• In transition region, thermal rate constant jumps from one eigenvalue to the other - the two eigenvalues are mixed in this region.
• At high T, ethyl peroxy is stabilised and HO₂ is formed from its dissociation. k is, in practical terms, independent of p.
• At low T, reaction involves the pressure dependent formation of RO₂ and direct formation of HO₂.
$C_2H_5, C_3H_7 + O_2$
\[ R + O_2 \rightleftharpoons RO_2 \quad (R = \text{allyl}) \]

Morgan et al. JCS Faraday Trans 2 78, 1323-1330 (1982)

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Estimated enthalpies and entropies of reaction in kJ mol\(^{-1}\):

<table>
<thead>
<tr>
<th>R</th>
<th>(-\Delta H_{298}^\circ)</th>
<th>(-\Delta S_{298}^\circ)</th>
<th>(T_c/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>127</td>
<td>126</td>
<td>862</td>
</tr>
<tr>
<td>C(_2)H(_5)</td>
<td>121</td>
<td>135</td>
<td>778</td>
</tr>
<tr>
<td>i-C(_3)H(_7)</td>
<td>129</td>
<td>144</td>
<td>776</td>
</tr>
<tr>
<td>t-C(_4)H(_9)</td>
<td>131</td>
<td>166</td>
<td>709</td>
</tr>
<tr>
<td>C(_3)H(_5)</td>
<td>75</td>
<td>122</td>
<td>547</td>
</tr>
<tr>
<td>(76.2 \pm 2.1)</td>
<td>(122 \pm 5)</td>
<td>(550 \pm 5)(^b)</td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_5)CH(_2)</td>
<td>70</td>
<td>122</td>
<td>503</td>
</tr>
</tbody>
</table>

- Ceiling temperatures/K (0.1 atm O\(_2\))
- (b) experimental values
Radical dissociation: 1-butyl
Knyazev and Slagle, J. Phys. Chem. 1996, 100, 5318-5328

- Pulsed photolysis, photoionization mass spectrometry
- Data fitted with master equation analysis, coupled with TS model based on electronic structure calculations
- Gave limiting high and low pressure rate constants and fall off data based on Troe modification of Lindemann Hinshelwood model
A detailed example: $\text{CH}_3\text{OCH}_2 + \text{O}_2$


- Left hand plot shows examples of experimental decays using pulsed photolysis / laser induced fluorescence. Main figure shows examples of bimolecular plots (first order decay constant from individual experiments vs $[\text{CH}_3\text{OCH}_3]$). Experiments over the range 195 - 850 K
- Right hand plot shows these data and literature data, with fit giving $k = (1.54\pm0.48)\times(7/298\text{ K})1.89\pm0.16\exp(-184\pm112)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (195 - 1423 K) Errors are 95% confidence limits)
- Note the results from isotope substitution: blue - OH + d-DME, red OD + d-DME - used in fits to theory

$$k(T) = \alpha \frac{kT}{h} \frac{Q^+_S}{Q_A Q_{BC}} \exp \left( \frac{-\Delta \varepsilon_0}{kT} \right)$$
Fits to theory

- Left hand plot shows turning points on PES: Geometric parameters were optimized at the CCSD/AVDZ level and the energies were calculated at the FCC/CBS//CCSD/AVDZ level with zero-point energy corrections.
- Right hand plot shows best fit. Dashed line with no adjustments to theory. Full line - best fit barrier energy adjusted to +0.6 kJ mol\(^{-1}\), hindrance parameters scaled by factor of 2.5. Tunnelling using WKB method, reaction path calculated at CCSD(T)/aug-cc-pVDZ level of theory.
- Used two transition state model, using a master equation analysis
3 transition states - not all independent

- Initial OH/DME complex with $C_{2v}$ or $C_4$ symmetry
- TS2 Out-of-plane transition state with upward pointing OH
- TS1 - In-plane transition state with $C_5$ symmetry
- TS3 Out-of-plane transition state with downward pointing OH
**CH₃OCH₂ + O₂**


Pulsed laser photolysis, laser induced fluorescence detection of OH

Measured the yield of OH and the rate constants via the formation of OH

Fits to data varying association rate constant (A,n), energy transfer parameters and some TS parameters
$\text{CH}_3\text{OCH}_2 + \text{O}_2$: major mechanism

$\text{CH}_3\text{OCH}_2 + \text{O}_2$ → IM1, RO$_2$

IM1, RO$_2$ → TS1 → IM2, QOOH

QOOH → TS2 → OH$^+$

OH$^+$ → IM3, R'O

IM3, R'O → TS5 → CH$_2$O...CH$_2$OOH

CH$_2$O...CH$_2$OOH → TS6 → 2CH$_2$O + OH

CBS-QB//mpw1k/avtz + $\Delta$ZPE
Master equation analysis. Species profiles, 550 K, 1 bar
Master equation: rate constant analysis

\[
I_1 = RO_2 \\
I_2 = QOOH
\]
Phenomenological rate coefficients from a Bartis Widom analysis
Analytic expressions for the two smallest eigenvalues

- Lifetime of IM2 (=QOOH) is always much less than those for R and RO2
- Let $x = R$, $y = RO2$, $z = QOOH$. Apply QSSA $z$

\[
z = \frac{k_5x + k_3y}{k_4 + k_6 + k_9}
\]

\[
\frac{dc}{dt} = \begin{pmatrix}
-(k_1 + k_5 \left(1 - \frac{k_8}{k}\right) + k_7) & k_1 + \frac{k_5k_4}{k} \\
k_2 + \frac{k_5k_6}{k} & -(k_2 + k_3 \left(1 - \frac{k_4}{k}\right) + k_8)
\end{pmatrix} c = \begin{pmatrix}
-A & B \\
C & -D
\end{pmatrix} c
\]

\[
\lambda_\pm = \frac{-(A + D) \pm \sqrt{(A + D)^2 - 4(AD - BC)}}{2}
\]

If $(A + D)^2 \gg 4(AD - BC)$, binomial expansion gives

\[
\lambda_- = -(A + D)
\]

\[
\lambda_+ = \frac{-(AD - BC)}{A + D}
\]

- CSEs from master equation solution. Two smallest eigenvalues are $\lambda_1, \lambda_2$
- $\lambda_1 = \lambda_+ ; \lambda_2 = \lambda_-$
Time dependence of the OH profiles at 300 K and at 550 K

- At low T, the OH signal is biexponential.
- The decay corresponds to loss of OH, e.g. by diffusion from the reaction zone and reaction.
- The increase corresponds to $\lambda_2$.

- At higher T, the signal becomes triexponential.
- The fast rise is $\lambda_2$ and the slower rise is $\lambda_1$; the decay is again loss of OH.
Global Uncertainty Propagation and Sensitivity Analysis in the CH3OCH2 + O2 System: Combining Experiment and Theory To Constrain Key Rate Coefficients in DME Combustion

Shannon et al J Phys Chem DOI: 10.1021/acs.jpca.5b00620

Sensitivity indices for the parameters involved in the master equation modeling with theory-constrained parameter ranges (top) and experimentally constrained parameter ranges (bottom). The labels on the top axis give the pressure at which the calculations were run in kPa and identify the type of observable: Y indicates the OH yield, L indicates the rate coefficient for CH2OCH3 loss, λ1, indicates the time constant corresponding to the longer time formation of OH and R indicates a particular elementary rate coefficient. Where the sensitivities sum to be significantly less than 1, this can be attributed to contributions from the second-order sensitivities that are not included. Where there is a colon between two parameters, this indicates a second-order sensitivity for this pair of inputs.
Harnessing the Combined Power of Theoretical and Experimental Data through Multiscale Informatics

Is there any experimental evidence for the second OH addition and for branching from these pulsed photolysis experiments?

- Anderson and Carter: Molecular Physics 2008, 106, 367-396
Difficulty of observing second O2 addition with this experimental system

Simulated O$_2$QOOH formation using a model based upon MESMER rate coefficients from Eskola et al (black) at 1 bar (solid line) and 10 bar (dashed line) of air ($T = 550$ K). These are compared with results using rate coefficients from the Fischer, Dryer, Curran model (red) (Int J Chem Kinet (32, 741, 2000) see slides 7-9).

OH simulation at 550 K and 500 Torr with [O2] = 1 × 10$^{17}$ molecule cm$^{-3}$: QOOH + O$_2$ rate coefficient of:
- 0 (black short dashed line),
- 1.16 × 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (red long dashed line),
- 2.32 × 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (blue solid line)

Effect on OH is small and at long times
Cyclohexyl + O₂
Time dependence of OH formation

a) 586 K, 7.9 bar

b) 586 K, 7.9 bar

c) 625 K, 6.5 bar

d) 625 K, 6.5 bar

e) 732 K, 7.0 bar

f) 828 K, 6.9 bar
Importance of well-skipping (formally direct) route to OH

Fig. 5  Calculated OH concentration at 7.9 bar and 586 K using different models. The solid black line is the Knepp et al.\textsuperscript{13} model; the dashed black line is the Knepp et al. model, but without formally direct pathways. The dashed blue line is the Silke et al.\textsuperscript{41} mechanism, and the solid blue line is Silke et al. model, adding all rate coefficients from the ME calculation.
Evidence for chain branching at lower T

Effect of the chain branching on model calculations at (a)–(b) 586 K and (c) 828 K.
Direct observation of QOOH - difficult for dimethyl ether oxidation

\[
CH_3OCH_2 + O_2 \xrightarrow{TS1} IM1, RO_2 \xrightarrow{TS2} QOOH \xrightarrow{TS3(c,t)} OH + c-OCOC \xrightarrow{TS4} IM2 \xrightarrow{TS5} 2CH_2O + OH
\]

[QOOH] is small and lifetime is short because of fast isomerisation back to RO_2
Direct observation of QOOH
Savee et al, Science, 2015, 346 (6222), p643

R = 2-butyl (red, derived from n-butane), 3-oxopent-2-yl (blue, derived from 3-pentanone) and 3,5-cycloheptadienyl (gray, Ra) and 2,4-cycloheptadienyl (black, Rb) (both derived from c-hpd and calculated in the present work).
Energy resolved mass spectra

- Above 8.5 eV, the spectrum depends on its observation time interval, suggesting the presence of at least two isomers consistent with QOOH$_{\alpha\beta}$ (AIE = 7.21 eV) and R$_\alpha$OO (8.70 eV) and/or R$_\beta$OO (8.78 eV). Calculated AIEs are marked by arrows.
QOOH kinetics

Rise:
QOOH_{\alpha\beta} + O_2 \rightarrow \text{Products}

Decay:
R_\beta + O_2 \rightarrow QOOH_{\alpha\beta}

Remember A \rightarrow B \rightarrow C

Present case: k_1 < k_2
Peroxy radicals in atmospheric chemistry
Oxidation of volatile organic compounds (VOCs)
General oxidation scheme for VOCs

\[ O_3 + h\nu \rightarrow O^{1D} + O_2 \]
\[ O^{1D} + H_2O \rightarrow 2OH \]
\[ OH + RH (+O_2) \rightarrow RO_2 + H_2O \]
\[ RO_2 + NO \rightarrow NO_2 + RO \]
\[ RO \rightarrow HO_2 (+R'CHO) \]
\[ HO_2 + NO \rightarrow OH + NO_2 \]
\[ NO_2 + h\nu \rightarrow NO + O; O + O_2 \rightarrow O_3 \]

Secondary chemistry from R’CHO photolysis
Termination: \( OH + NO_2 \rightarrow HNO_3, HO_2/RO_2 + HO_2/RO_2 \rightarrow \)
Products. The termination route depends on the NO\textsubscript{x}: VOC ratio

OVERALL
\[ NO_x + VOC + sunlight \rightarrow \text{ozone} \]
The same reactions can also lead to formation of secondary organic aerosol (SOA)
Free radical propagated oxidation cycle

Chain reaction:
- Radical initiation, e.g. OH production from $O_3$
- Propagation
- Termination: $OH + NO_2$

$HO_2/RO_2 + HO_2/RO_2$

Dependence on:
- $NO_x$
- VOC
- Light

VOC

Chain reaction:
- Radical initiation, e.g. OH production from $O_3$
- Propagation
- Termination: $OH + NO_2$

$HO_2/RO_2 + HO_2/RO_2$

Dependence on:
- $NO_x$
- VOC
- Light

Ozone formation from conversion of NO to NO$_2$
Observations incompatible with conventional mechanism

- A number of recent field measurements in the Amazon, Pearl River Delta and Borneo found much higher concentrations of OH than conventional mechanisms predict.

- Measurements were made in regions with moderate to low concentrations of NOx high concentrations of the biogenic compound isoprene, $\text{C}_5\text{H}_8$.

- This led to a focus on the chemistry of the peroxy radicals formed by reaction with $O_2$ and the radicals formed by OH addition to isoprene.
OH adduct is an allylic radical, which is resonance stabilised. The per oxy radical formed from it is less stable than alkyl peroxy radicals (see earlier slide).

As a result, the allylic QOOH is formed quite quickly.

QOOH eliminates HO₂ to form O=CHC(CH₃)=CHCH₂OOH, which is photolysed to form OH and an oxy radical.
Composition of aerosol around the world - large contribution from organic compounds
Reactions form three categories: fragmentation, functionalization, or oligomerization, based on whether the carbon number decreases, stays the same, or increases. The figure shows the first two pathways. The branching ratio ($\beta$) between these pathways is critical. Functionalization will reduce volatility considerably, whereas fragmentation can generate more-volatile species, which are less likely to partition to the OA.
• Experimental evidence that highly oxidized compounds derived from biogenic emissions play an important role, in conjunction with sulphuric acid, in the formation of new particles in the boundary layer, requiring a mechanism in which the increased functionality occurs rapidly.
Autoxidation of aromatic compounds in the atmosphere
Crounse et al, J Phys Chem Lett 2013, 4, 3513

- A single cycle in the oxidation of 3-pentanone leads to a 4-fold increase in the O:C ratio