The Oxidation of Fuel Radicals

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AIM OF WORK

Develop a quantitative understanding of the processes responsible for the degradation of real fuels during combustion

By building a database of fundamental and transferable information base of rate expressions and thermodynamic and physical properties of reactants and intermediates

Providing information necessary for the simulation of combustion processes and hence serve as a complement to physical testing
APPROACH

Combine existing literature (experiments and theory) with experiments in single pulse shock tube

Highlights importance of fundamental approach

permits interpolation and extrapolation

use of data in mixtures

calibration of theory

Focus on the decomposition and isomerization reactions of fuel and fuel radicals characteristic of real fuel mixtures

pyrolysis (C,H)

oxidation (C, H, O)
PREMISE OF WORK

There are simple correlations between structure of fuel molecules and their rate constants for decomposition and isomerization.

These correlations can be uncovered from an examination of the literature, suitable experiments, and theoretical treatments.
Kinetics Modules in Databases

Widely used Problems with rich mixtures

GRIMECH - methane (light hydrocarbon) combustion

Pyrolysis of fuels

Oxidation of larger fuels

Soot formation

Target of most models
Focus of current NIST work

Recent NIST experimental and data evaluation program

Many models, begin with unsaturates
SPECIAL ROLE OF UNIMOLECULAR REACTIONS

Only unimolecular and bimolecular reactions in simulation database

Bimolecular reactions shuffle atoms
\[ \text{OH} + \text{RH} = \text{H}_2\text{O} + \text{R}^* \]

Rate constants are the same for similar groupings

Unimolecular reactions reduces size of molecule
Reduces fuel to small unsaturates and radical found in existing databases

Unimolecular rate expressions are fundamental properties of any polyatomic molecule and hence should be calculable

How accurate are the calculations?
GENERIC TYPES OF UNIMOLECULAR REACTIONS

Reaction from Boltzmann Distribution

*limiting high pressure rate constant, no pressure dependence*

*High pressure rate expression: All experimental accessible properties of transition state*

Reaction from truncated Boltzmann Distribution: reaction from higher energy levels faster than equilibration by collisions

*Pressure dependence of rate constants “fall-off”*

Reaction from arbitrary initial distribution function: Chemical activation

*Branching ratios for reactions and stabilization: pressure dependence*
DETERMINATION OF MECHANISMS AND RATE CONSTANTS

Need for clearly defined experimental systems

understand the role of interfering processes

Ideal conditions most easily realizable in shock tubes

well defined boundary conditions

very little possibility of surface reactions

short reaction times

Detection of practically all stable products

(particularly suitable for large molecules)
SINGLE PULSE SHOCK TUBE AND ASSOCIATED WAVE PROCESSES
When combined with activation energies lead to present day accepted bond energies
PAST WORK: RATE CONSTANTS FOR DODECANE DECOMPOSITION

Per C\textsubscript{n}-C\textsubscript{n} bond for n=2 to 10

Per C-C\textsubscript{11} bond
RADICALS STUDIED

C H3CH2CH2CH2CH2*
CH3CH2CH2CH2CH2CH2*
CH3CH2CH2CH2CH2CH2CH2*
CH3CH2CH2CH2CH2CH2CH2CH2CH2*
CH2=CHCH2CH2CH2*
CH2=CHCHCH2CH2CH2*
CYCLOHEXYL
CYCLOPENTYL
CH3CH(CH3)CH2CH2CH2*
CH3CH(CH3)CH2CH2CH2CH2*
MECHANISM AND BRANCHING RATIOS FOR THE DECOMPOSITION OF OCTYL RADICALS

4 isomers undergoing 6 beta bond scissions and 6 reversible isomerizations
OXIDATION OF FUEL RADICALS: PAST WORK

No direct studies leading to high pressure unimolecular rate expressions
Products from flame and cool flames sampling

*Oxygenated organics*

*Unsaturated organics*

*Cyclic ethers*

*Thermal rate constants used in models; no consideration of chemical activation processes*

OH and HO$_2$ from smaller fuel molecules and modeling

*Sandia (Taatjes)*

*Ab-initio calculations*

*Green et al*

*Merle et al*

*Bozzellie et al*

*Sandia (Klippenstein)*
Rate Constants from Chemical Activation Processes

Radical + O_2, \rightleftharpoons \text{RadicalOO}^* \rightarrow \text{Variety of products} \\
\quad \downarrow \quad \text{M} \\
\quad \text{RadicalOO}

\[ k = k_{ca} \times \text{branching \_ ratio} \]

\[ \text{branching \_ ratio} = \frac{(\text{decomposition})_i \text{ or } (\text{stabilization})_i}{\sum \text{all channels}} \]
STRATEGY FOR STUDYING RADICAL OXIDATION

Generate radicals as in pyrolysis experiments

* Dilute concentrations of radicals
* Vast excess of chemical inhibitor

Add sufficient amount of oxygen molecules to change reaction direction from pyrolysis to oxidation

* Determine cracking patterns as function of oxygen concentration

Reproduce oxidative cracking pattern through solution of the master equation for chemical activation process
SOURCES OF n-BUTYL RADICALS

n-butyl-I = n-butyl + I
but potential interfering process n-butyl-I = a-butene + HI
general source of radicals for pyrolysis experiments

custom synthesis

N-pentyl-O-NO = n-pentoxy + NO
n-pentoxy = n-butyl + H2CO
potential interfering process: isomerization and decomposition processes of pentoxy

home synthesis
Oxidative Decomposition of n-Butyl Radical

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OO} \cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \cdot \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OOH} \rightarrow \text{HO} + \text{C}_2\text{H}_4 + \text{CH}_2\text{OOH} \]

Pyrolytic Decomposition of n-Butyl Radical (through n-Butyl iodide)

\[ \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HI} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{I} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot \]

\[ \text{CH}_3\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4 + \cdot \]
PRODUCT YIELDS FROM THE DECOMPOSITION OF 100 PPM IODOBUTANE IN 1% MESITYLENE

- Ethylene
- Propene
- 1-Butene
- Butanal
- THF

Legend:
- 150 torr O % O2
- 150 torr 1.54% O2
- 150 torr 4.07% O2
- 150 torr 9.21% O2
- 300 torr 10.35% O2
- 600 torr 10.15% O2
MASS BALANCE

- **No oxygen 150 torr initial pressure**
- **9.15% oxygen 150 torr initial pressure**
- **10.15% oxygen 600 torr initial pressure**
- **10.35% oxygen 300 torr initial pressure**

All mixtures containing 100 ppm n-butyl-1 and 1% mesitylene.
PRODUCT DISTRIBUTION FROM THE DECOMPOSITION OF N-PENTYL NITRITE 100 ppm IN 1% MESITYLENE
ETHYLENE/THF RATIOS AS A FUNCTION OF TEMPERATURE AND OXYGEN CONCENTRATION
Ethylene/THF Yields as a Function of $1/O_2$: Extrapolation to Infinite Oxygen Concentration

Log $[C_2H_4/(2xTHF)] = 7.35 - 6000/T = 1.1$ at 930 K
PROPENE/THF RATIOS AS A FUNCTION OF TEMPERATURE AND OXYGEN CONCENTRATION

\[ \log \left[ \frac{C_3H_6}{THF} \right] = 2.92 - \frac{2120}{T} = .64 \ (930K) \]
THEORETICAL BASIS FOR PRESENT WORK

Need for fundamental molecular properties of molecules, intermediates and transition states

None of the required information is available from experiments

Reliance on ab initio calculations

Bozzi

Hadad

Green

Uncertainties

< 1.5 kcals/mol for molecules using isodesmic reactions

no tests for transition states
MASTER EQUATION SOLVER: PROGRAM TO DETERMINE MOLECULAR DISTRIBUTION FUNCTION
RELEVANT RATE CONSTANTS RESPONSIBLE FOR PRODUCT YIELDS

1-Butene
propene
ethylene
CALCULATED BRANCHING RATIOS FOR THE CHEMICALLY ACTIVATED DECOMPOSITION OF PROPYLPEROXY RADICALS: 900 K, 3 BAR

n-butyl + O2
Ethylene + CH2CH2OOH
Propene + CH2OOH
1-Butene + OOH
THF + OH
1-Butanal + OH
C4H9OO
1-C4H9OO
2-C4H9OO
3-C4H9OO
BRANCHING RATIOS WITH SOME RATE EXPRESSIONS ADJUSTED TO FIT OBSERVATIONS 900 k 3 BAR

Log [branching ratio] vs Log [time, s]

- nC4H9 + O2
- Ethylene + CH₂CH₂OOH
- Propene + CH₂OOH
- 1-Butene + HO₂
- OH + THF
- 1-Butanal + OH

Adjustments made to fit observations at 900 k 3 bar.
SUMMARY

Single pulse shock tube has been used to study the oxidation of n-butyl radical

Pyrolysis decomposition extends to regions of high oxygen concentration and lower temperatures

In contrast to the pyrolytic situation many new channels are opened

The necessity of treating the reactions as chemical activation processes

The problems involved in converting results to fundamental unimolecular high pressure rate expressions are described