

**A Parametric Study of the
Effect of Temperature and Hydrocarbon Species
on the Product Distribution
from a Non-Thermal Plasma Reactor**

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Objective: Use a non-thermal plasma to create a reactive gas mixture for lean NO_x catalysis or particulate removal

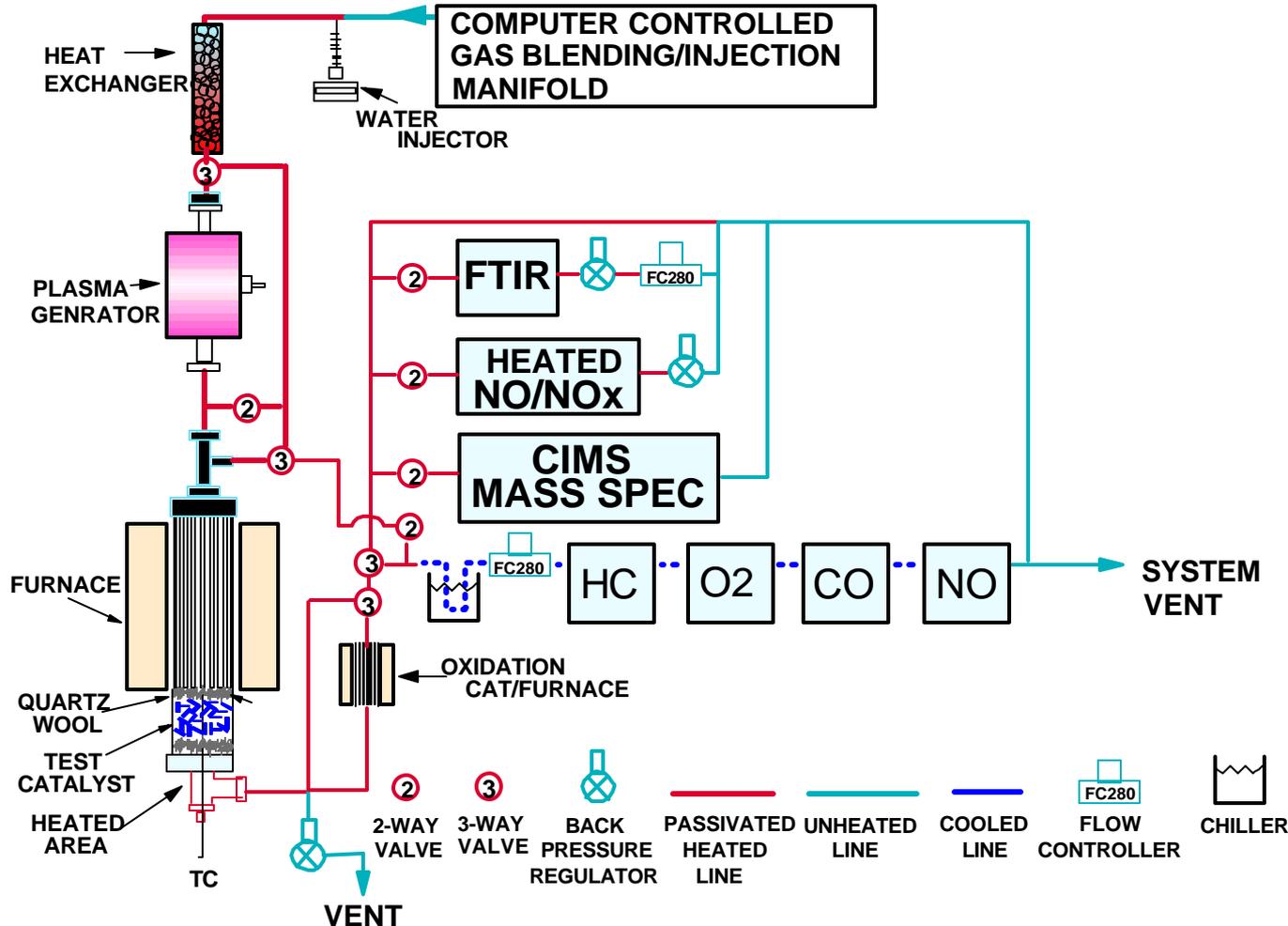
For optimal efficiency, the plasma must:

- **Efficiently convert NO to NO₂**
 - Selective conversion, no acids of nitrogen or N₂O
- **Create reactive hydrocarbons for downstream chemistry**
- Perform these functions at various temperatures, space velocities, and feed compositions
- Have behavior that agrees with model of plasma chemistry that covers complexity of actual exhaust conditions

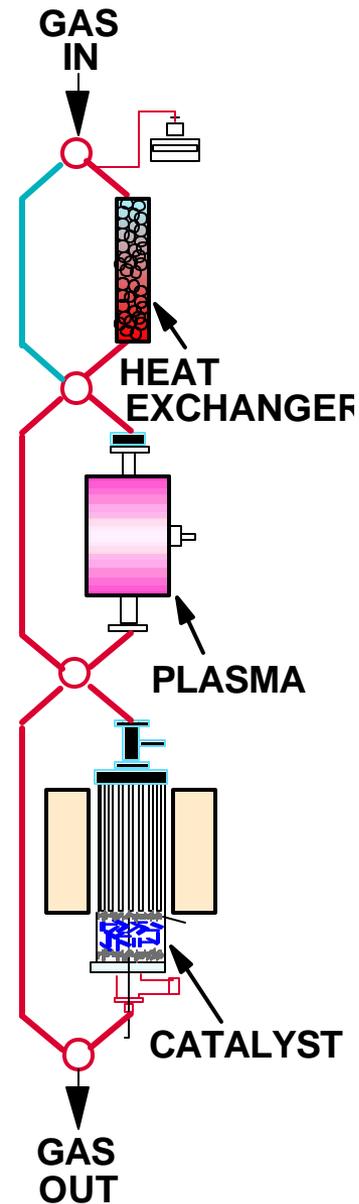
Question:

Which range of hydrocarbon species and temperatures can satisfy these requirements?

PLASMA/CATALYST CHARACTERIZATION SYSTEM



- Dominant measurement tool is Fourier Transform Infrared Spectrometer (FTIR)
- Chemical Ionization Mass Spectrometer (CIMS) complements FTIR and allows for transient studies



Experimental Conditions:

- Single cell reactor
- Heat exchanger to heat incoming gas stream
- Rough mimic of light-duty diesel exhaust compositions

10% O₂ 4.5% H₂O 5% CO₂ 200 ppm NO

T = 125° C to 475° C (varied at 50° C intervals)

500 ppm HC (varied from C₂ to C₅)

alkenes: C₂H₄, C₃H₆, iso-C₄H₈, 1-C₄H₈, cis 2-C₄H₈

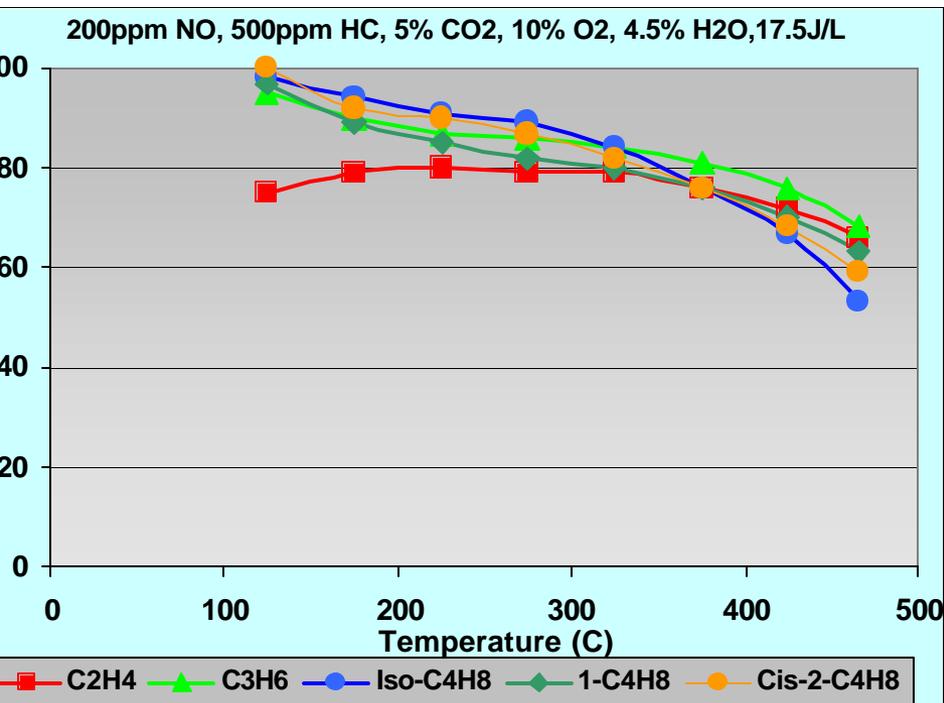
alkanes: C₂H₆, C₃H₈, n-C₄H₁₀, iso-C₅H₁₂

Flow = 10 L/min through plasma; SV = 0.75 M h⁻¹

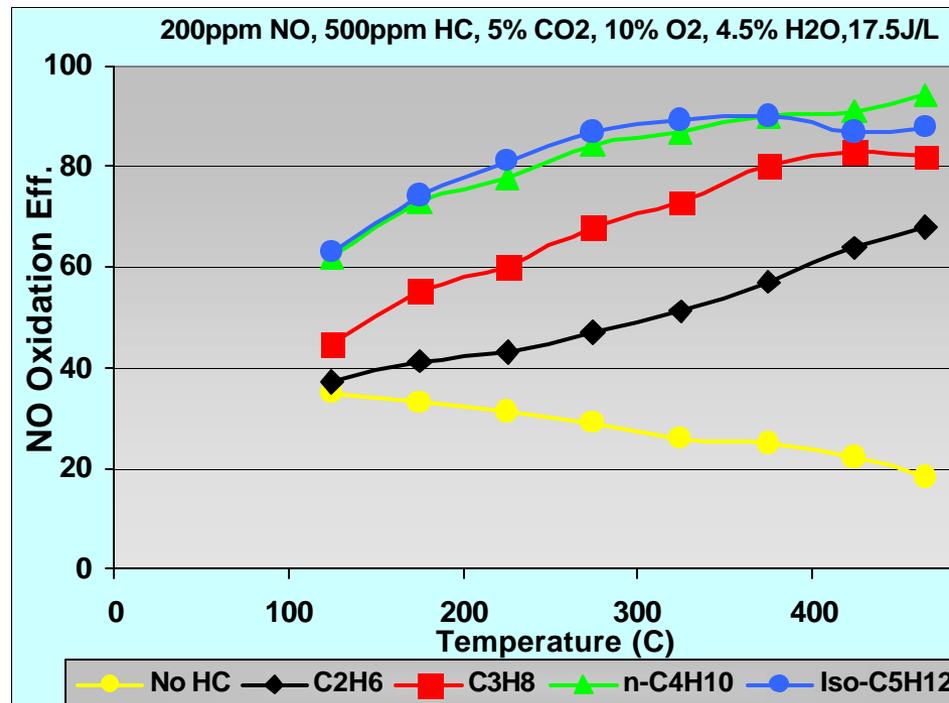
Power = 17.5 J/L

- Focus on effects of temperature and HC species on NO₂ and acetaldehyde production
- Other products also measured
- Flow, power, and HC concentration also varied

Unsaturated HCs (500 ppm) vs. Temperature



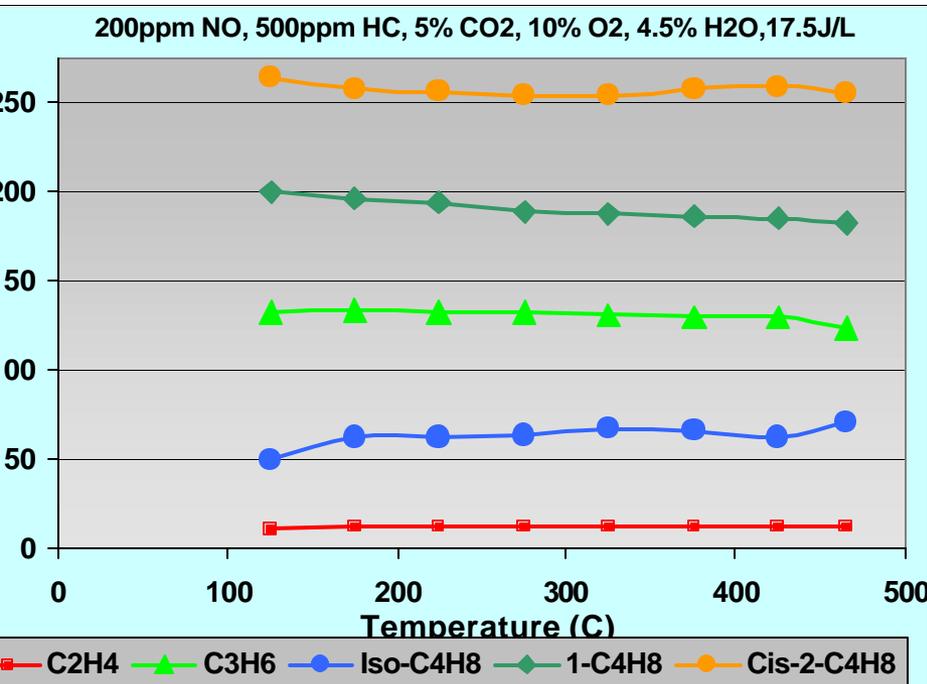
Saturated HCs (500 ppm) vs. Temperature



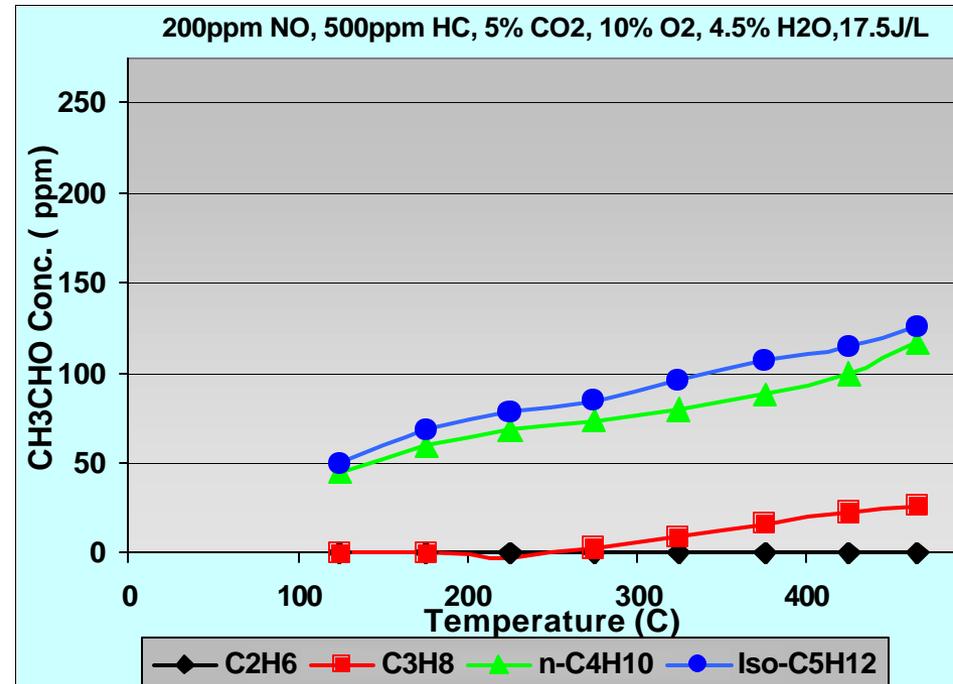
NO to NO₂ conversion efficiency depends on temperature & HC species

- HCs required at all temperatures to maximize NO-to-NO₂ conversion efficiency
- Longer chain HCs are more effective
- Alkenes HCs more active for NO conversion at lower temperatures (optimal at 125°C)
- Alkanes more active for NO conversion at higher temperatures (optimal at 465°C)

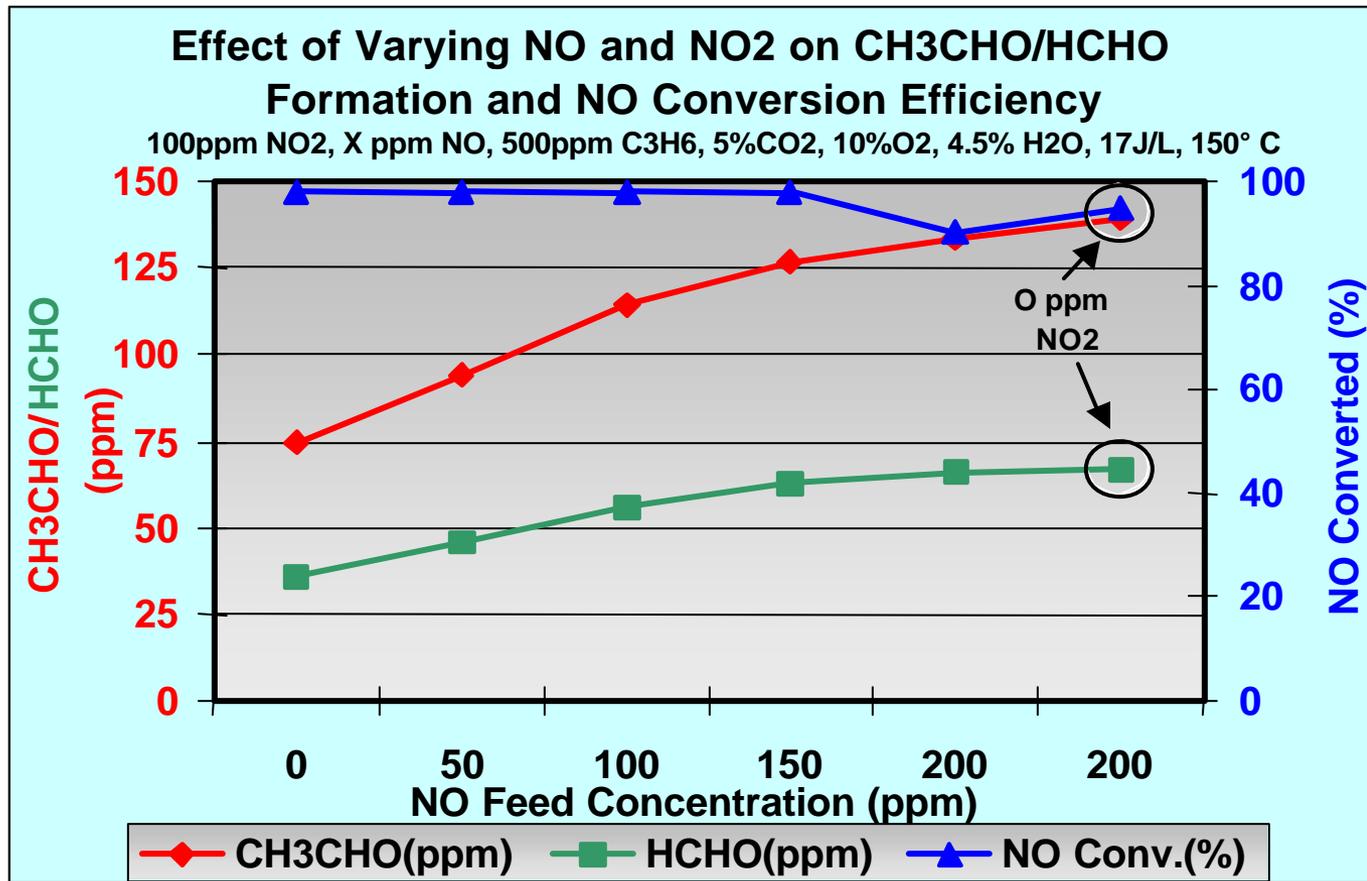
Unsaturated HC (500 ppm) vs. Temperature



Saturated HC (500 ppm) vs. Temperature



- Acetaldehyde (CH₃CHO) formation rates depend on the HC species**
 - Longer chain HCs are more effective in making acetaldehyde
 - Unsaturated HCs show no temperature dependence
 - Saturated HCs work better at higher temperatures
 - Best formation rates occur using straight chain unsaturated HCs with isolated double bonds

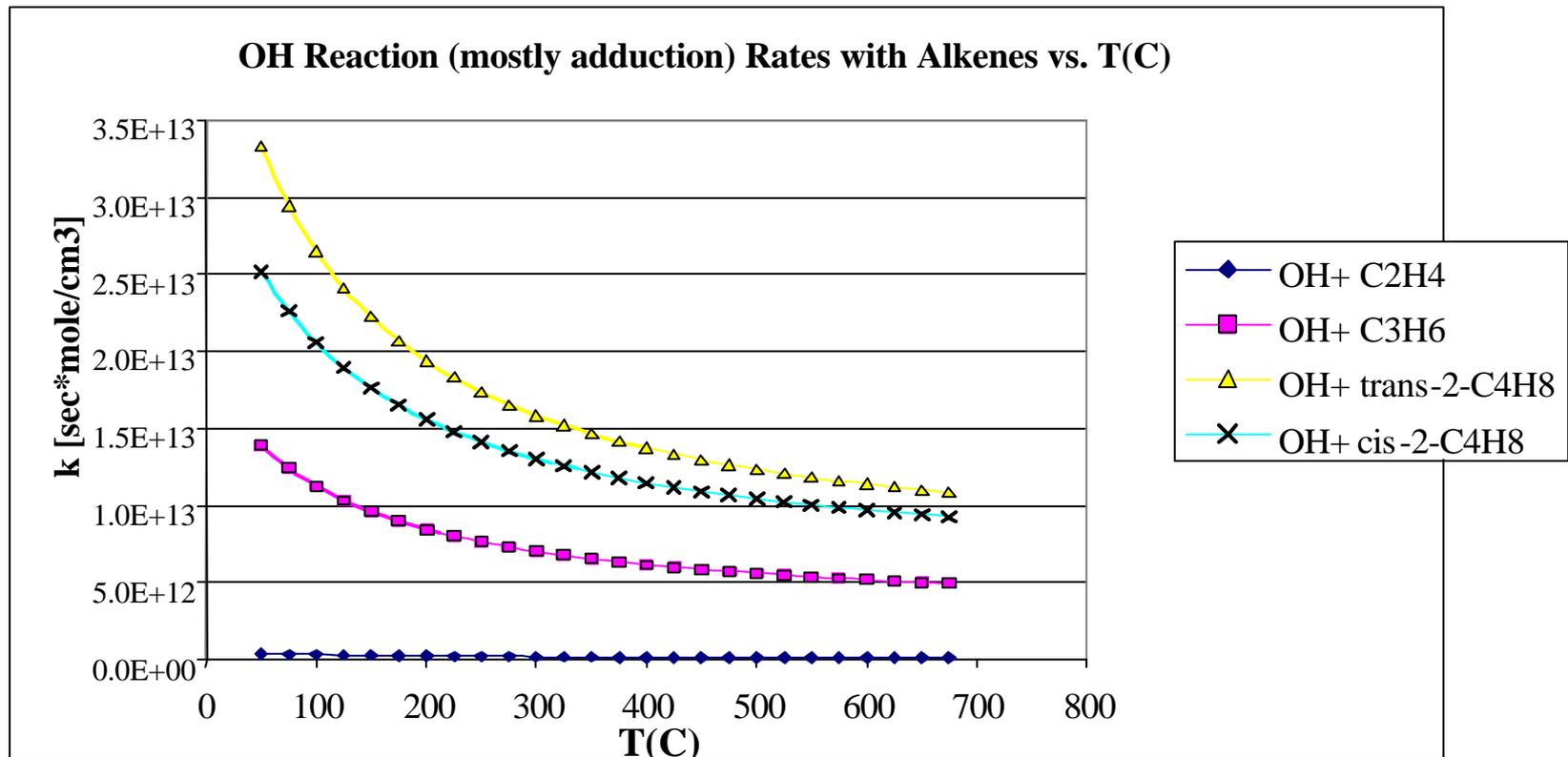


Aldehyde (CH₃CHO, HCHO) formation rates depends on NO concentration

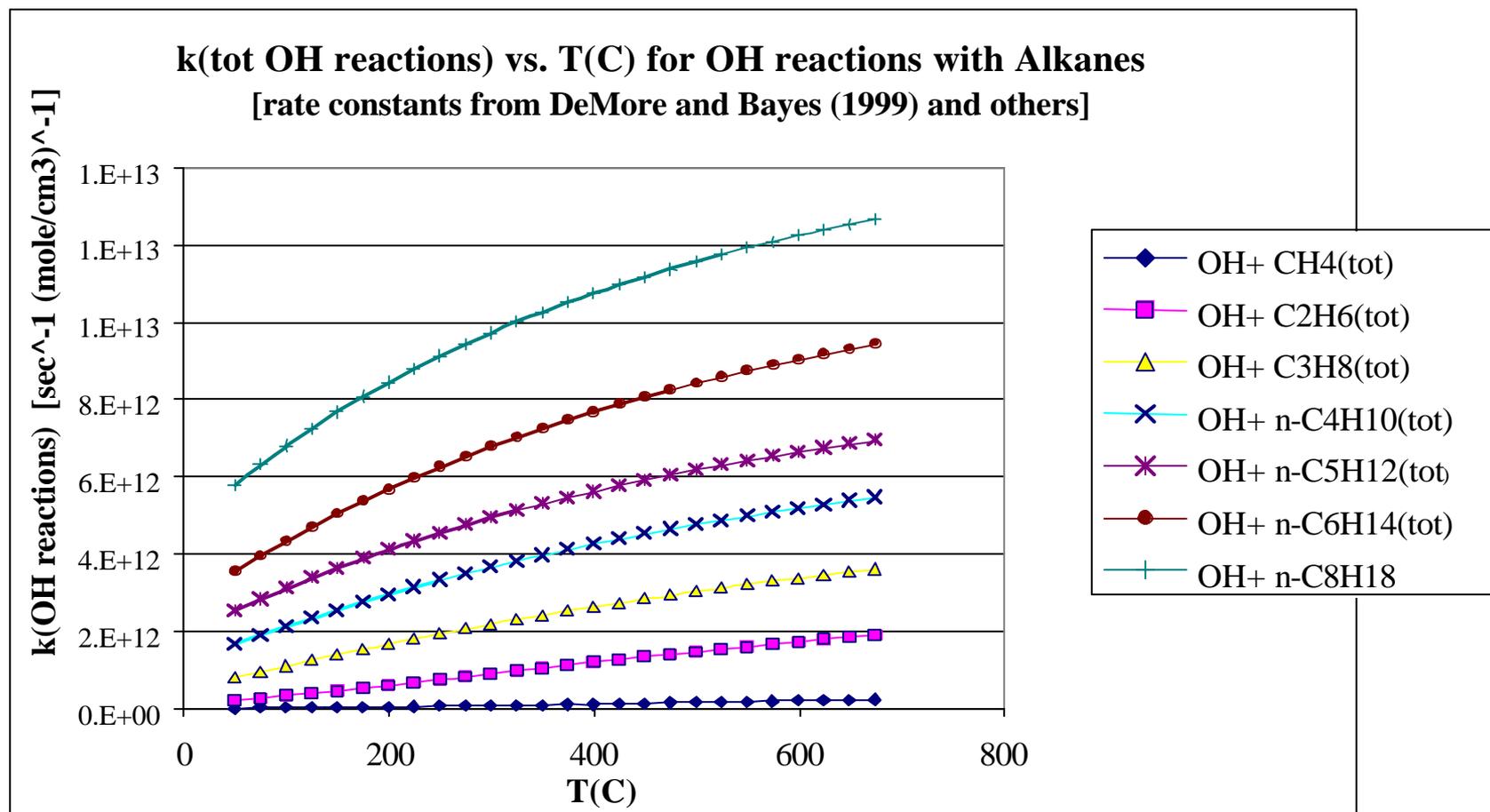
- Aldehyde formation increases with NO concentration
- NO₂ is not involved with aldehyde formation
- Formaldehyde seen from all HC species

- ◆ Modeling of NO-to-NO₂ and product formation rates
 - Production of radicals done using ELENDF and a low frequency barrier discharge model
 - Subsequent gas phase chemistry done using CHEMKIN code
- Alkene sequence, early steps in a reaction cycle:
 - 1) OH addition at one end of previous double bond
 - 2) O₂ addition as -O-O* at other end
 - 3) NO reaction of form $\text{ROO}^* + \text{NO} \Rightarrow \text{RO}^* + \text{NO}_2$
- Alkane sequence, early steps in a reaction cycle:
 - 1) H abstraction of form $\text{RH} + \text{OH} \Rightarrow \text{R}^* + \text{H}_2\text{O}$
 - 2) O₂ addition to form ROO^* radical
 - 3) NO reaction of form $\text{ROO}^* + \text{NO} \Rightarrow \text{RO}^* + \text{NO}_2$

- ◆ Modeling observations on rates:
 - Rates increase with carbon number for both alkenes and alkanes
 - OH addition on alkenes decreases with temperature
 - H abstraction by OH increases with temperature for alkanes
 - OH addition on alkenes is faster than H abstraction by OH on alkanes, but difference drops as T increases.
- ◆ Product observations from modeling:
 - Overall NO-to-NO₂ rates increase with carbon number for both alkenes and alkanes
 - At least C₃'s seem required to get much CH₃CHO
 - HCHO production from light HCs is almost ubiquitous
- ◆ These results agree at least qualitatively with experiment



- Alkene rates of OH addition - that control NO₂ formation - decrease with temperature
- Model suggests ethene is less effective, butenes more effective than propene



- **Alkane rates of H abstraction by OH - that control NO₂ formation - increase with temperature**
- Another temperature effect: Increasing T => Increasing back reactions with NO₂ => NO; rate depends on HC concentration

- **NO-to-NO₂ conversion efficiency depends on temperature and HC species – both experimentally and in reaction modeling**
 - > HCs required at all temperatures to maximize NO-to-NO₂ conversion
 - > Longer chain HCs are more effective
 - > Alkenes HCs more active for NO conversion at lower temperatures
 - > Alkanes more active for NO conversion at higher temperatures
- ⇒ **A combination of saturated and unsaturated HCs broadens the temperature window for good NO-to-NO₂ conversion**
- **Formation of active hydrocarbons, such as acetaldehyde, also depends on HC species - in experiment and modeling**
 - > Longer chain HCs ($\geq C_3$) make more acetaldehyde
 - > Acetaldehyde production by alkenes has little temperature dependence
 - > Acetaldehyde from alkanes increases with increasing temperature
 - > Acetaldehyde production increases with increasing NO concentration
- ⇒ **Acetaldehyde concentration increases with temperature for a combination of alkenes and alkanes, with larger alkanes present**
- **Further comparisons of experiment and detailed modeling may lead to a successful model for a wide range of exhaust compositions**