EFFECTS OF PROPENE ON THE REMEDIATION OF NO_X FROM DIESEL EXHAUSTS*

Rajesh Dorai and Mark J. Kushner
University of Illinois
Department of Electrical and Computer Engineering
Urbana, IL 61801

Email : Mark J. Kushner - mjk@uiuc.edu
Rajesh Dorai - dorai@uiuc.edu

October 28 1999

* Work supported by Ford Motor Company

AGENDA

- Introduction
- Description of the model
- Reaction kinetics in the propene system
- Simulation results of the propene system
- Interesting implications of rate-coefficient data
- Use of multiple pulse inputs and impact on overall reaction chemistry
- Conclusions

INTRODUCTION

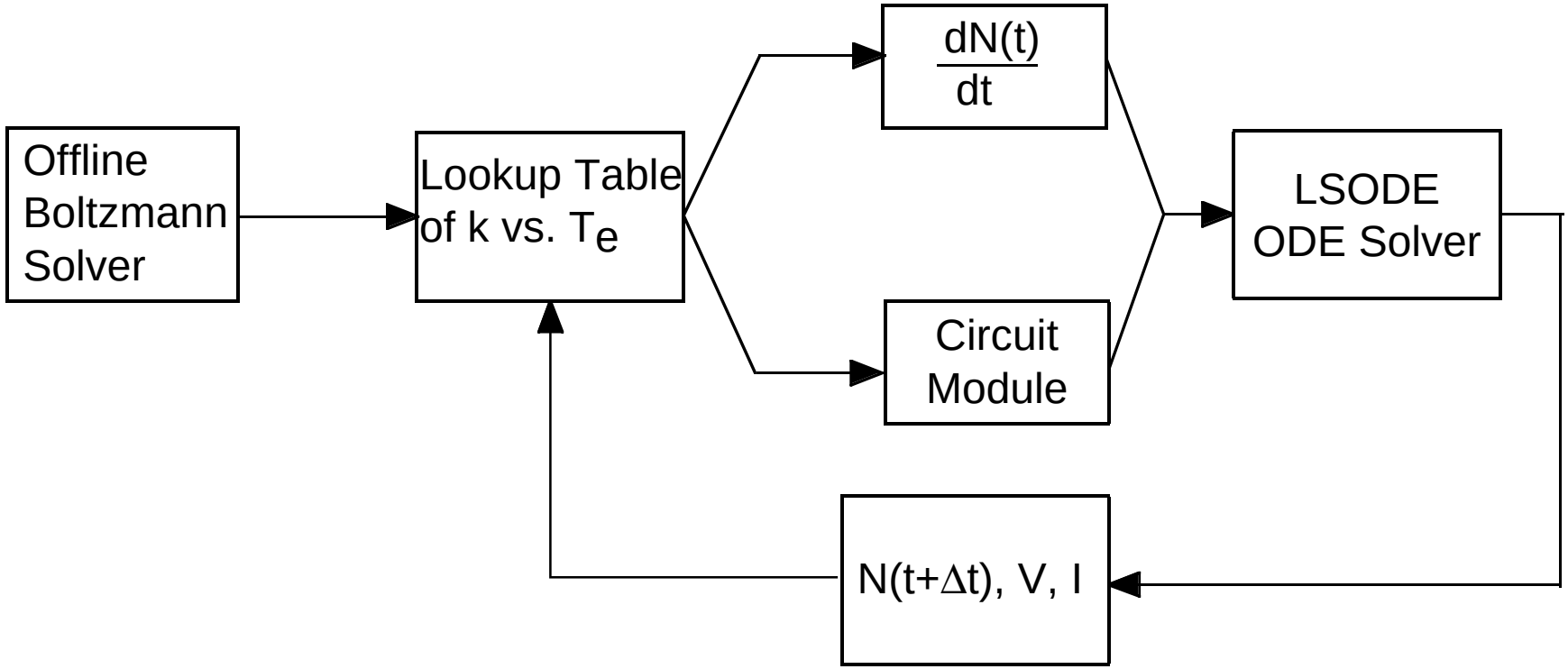
- Nitrogen Oxides, NO_X (NO and NO_2)
  - Hazard to human health
  - Precursors to urban ozone
  - Derivatives of NO_X are greenhouse gases.
  - Acid rain

- Dielectric Barrier Dishcharge Reactors
  - Best suited for the generation of gas-phase radicals with plasmas
  - Effective for the operation of the reactor at atmospheric pressure

UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

DESCRIPTION OF THE MODEL

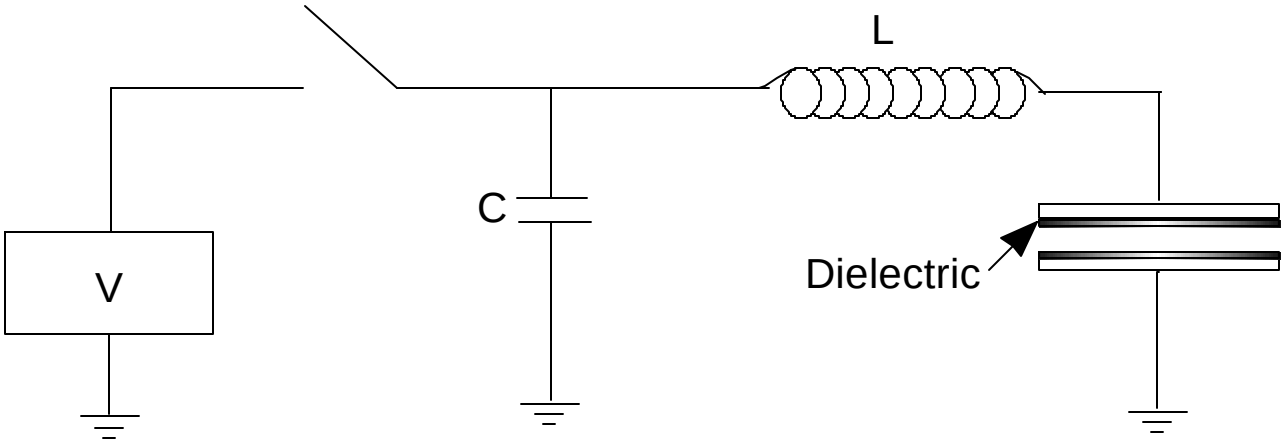
- The basis of the model is to integrate the non-linear ordinary differential equations describing the reaction chemistry over the residence time with the simultaneous solution of the equations for the circuit parameters.
- The rate coefficients for the electron impact reactions are obtained from a lookup table produced by an offline Boltzmann solver.



THE EXPERIMENTAL SETUP MODELLED

- A dielectric barrier discharge reactor has been modelled with the following characteristics.

  - Dielectric discharge height = 2.5 mm
  - Reactor pressure = 1 atm
  - Single pulse input



REACTOR OPERATING CONDITIONS

- Basic composition of the gas at reactor entrance :

  CO_2 = 7% O_2 = 8% H_2O = 6%

  CO = 400 ppm NO = 260 ppm H_2 = 133 ppm

  C_3H_6 = 0 -1100 ppm

  N_2 = Balance

- Temperature = 453 K
- Pressure = 1 atm
- Applied voltage = 14 - 25 kV

UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

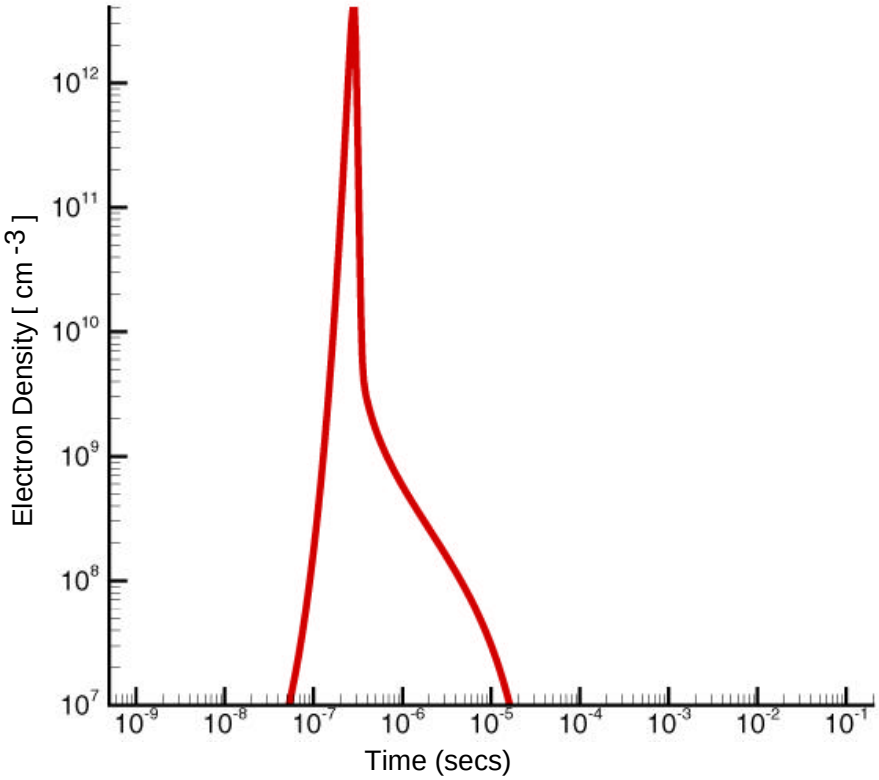
BASIC ELECTRON IMPACT REACTIONS TRIGGERING THE PLASMA PROCESSING

- The basic electron impact reactions are :
  - $e + O_2 \longrightarrow O + O + e$
  - $e + N_2 \longrightarrow N + N + e$
  - $e + H_2O \longrightarrow OH + H + e$
- OH radicals are also generated by the reactions of $O(^1D)$ with water
  - $O(^1D) + H_2O \rightarrow OH + OH$

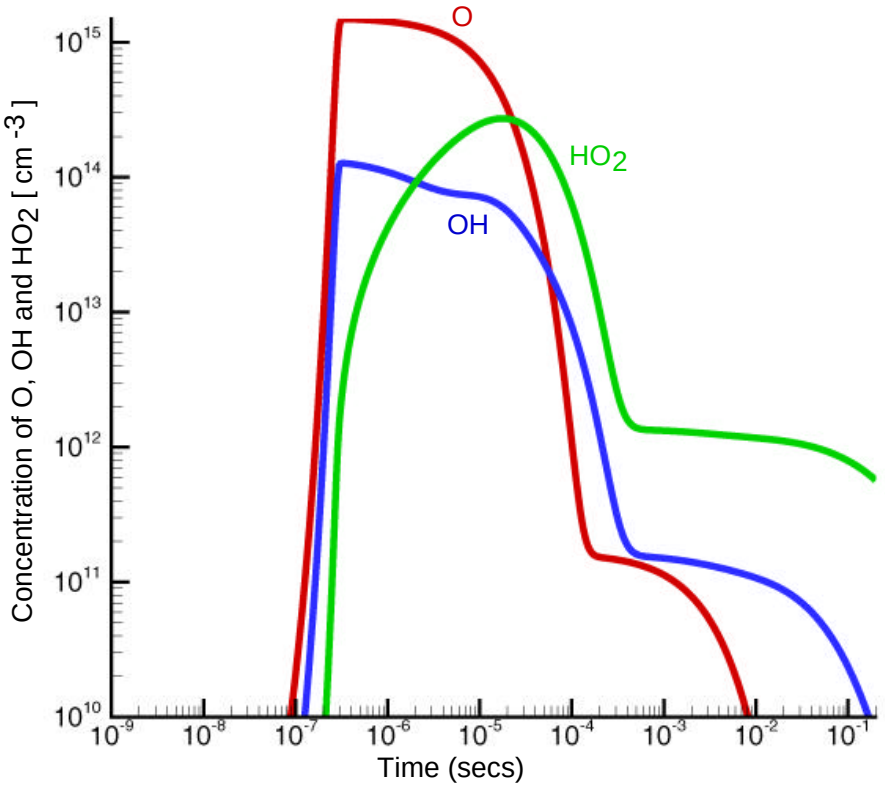
UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

TEMPORAL EVOLUTION OF SPECIES

- **Electron, O atom and OH radical densities peak around 100s of nano seconds**



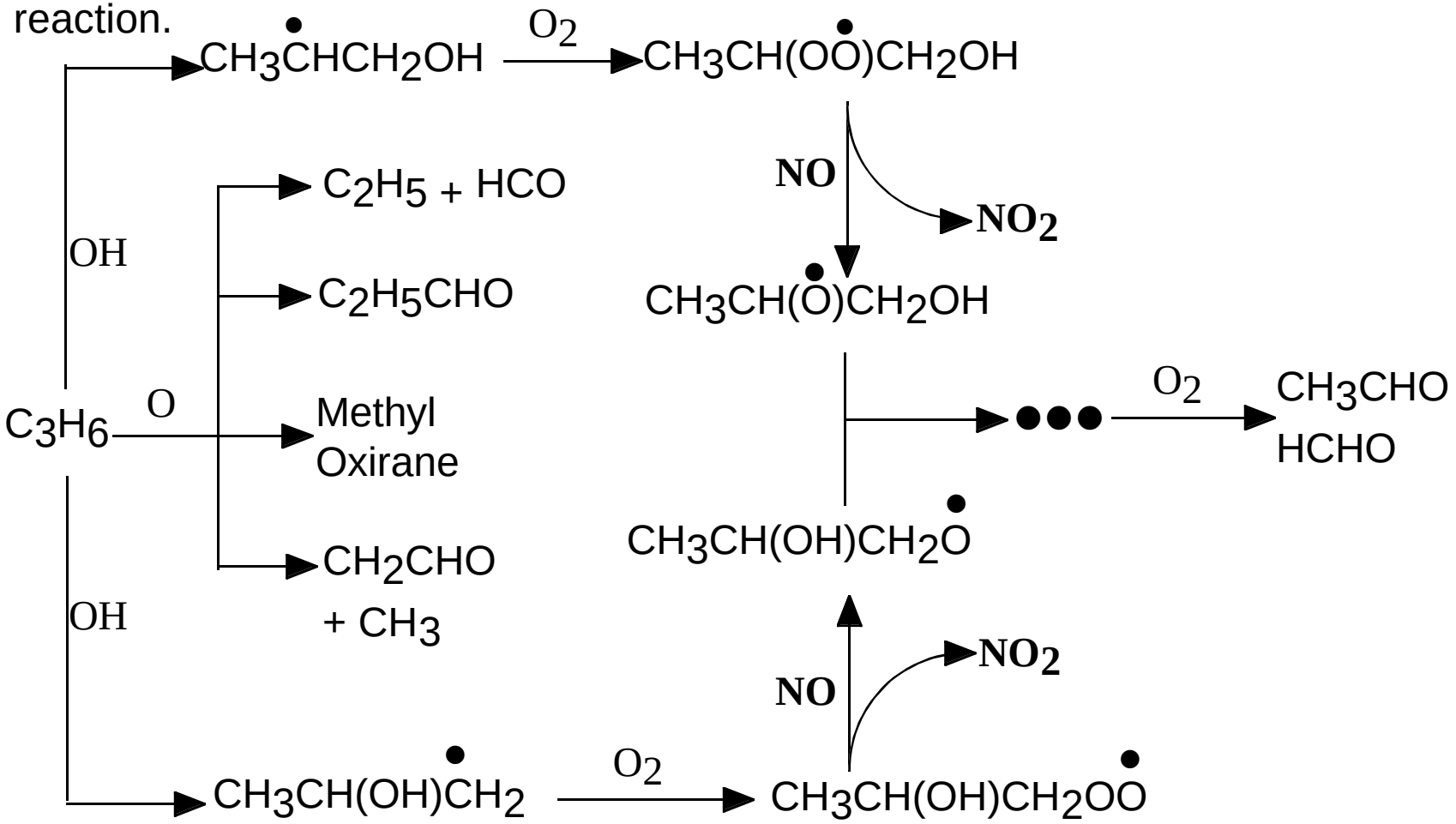
Electron density profile



Time evolution of OH, O, HO_2

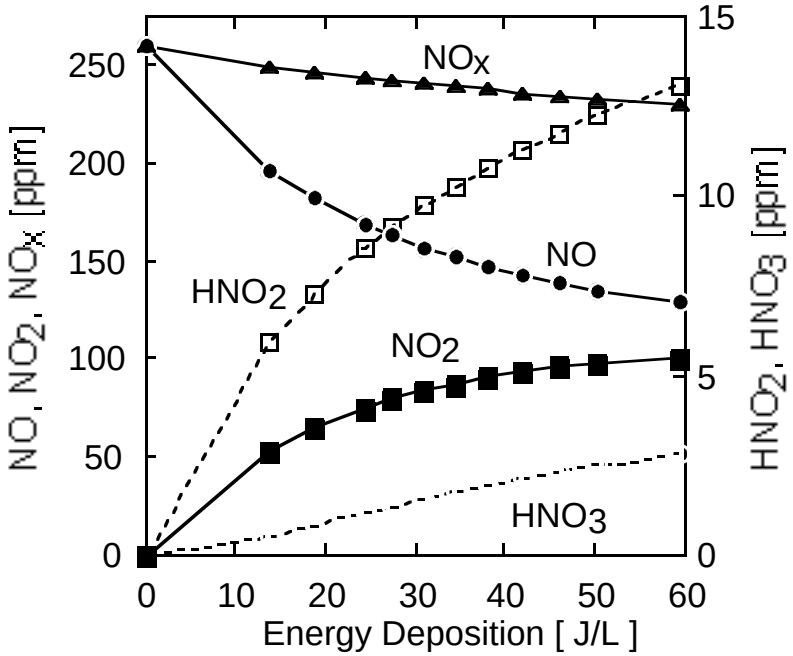
PROPENE AS A CONSTITUENT IN THE INLET GAS

- The presence of propene affects the reaction mechanism significantly.
- One of the major sources for the NO consumption is the peroxy radical produced by the reaction of O_2 with the products of the OH-propene reaction.

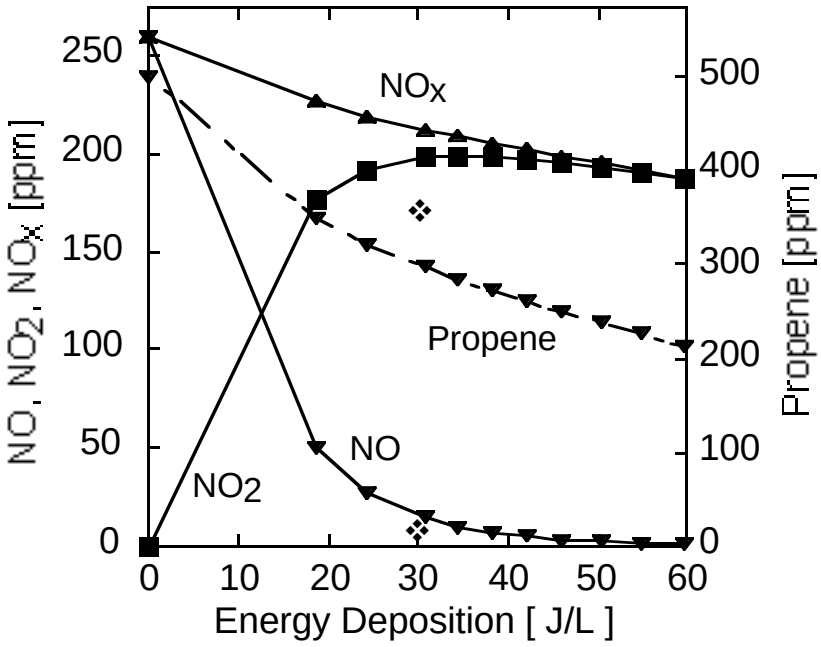


EFFECTS OF INPUT ENERGY ON PROPENE-NO_X SYSTEM

- In the absence of propene, increasing input energy results in an increased rate of NO reduction, but a much lesser rate of NO_X removal.
- The same trend continues with propene included in the system, except that the NO_X removal increases quite a bit.



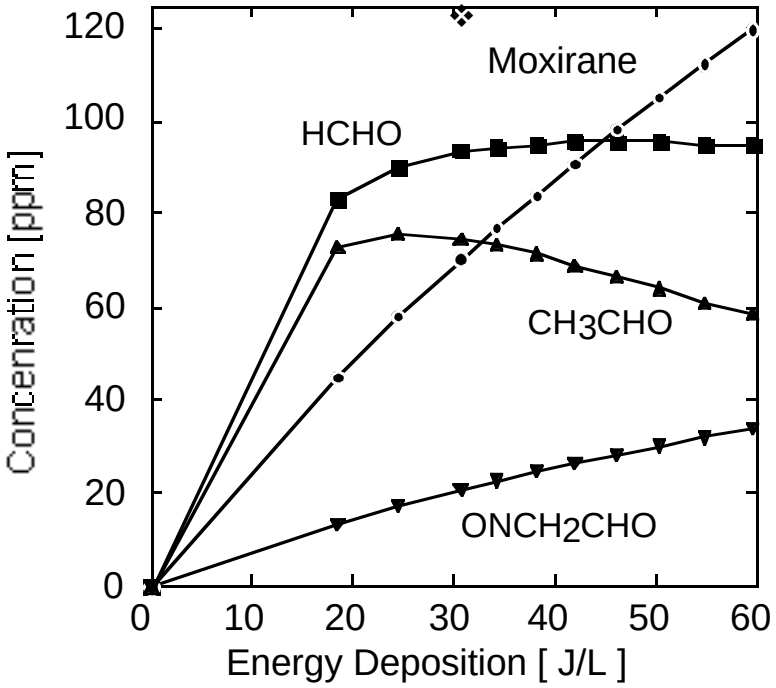
NO_X processing in the absence of propene



NO_X processing in the presence of propene

❖ Experiments by Hoard et al. Similar conditions except for addition of propane.

END PRODUCTS : EFFECTS OF INPUT ENERGY



- Higher energy inputs result in increased production of radicals which help in accelerating the reactions in the reaction network
- Increasing energy in general, results in increased production of end products, though at a higher cost of energy efficiency.
- $C_3H_6 + O \rightarrow$ Methyl Oxirane

  $C_3H_6 + O \rightarrow CH_2CHO + CH_3$

  $\downarrow$ NO

  $ONCH_2CHO$

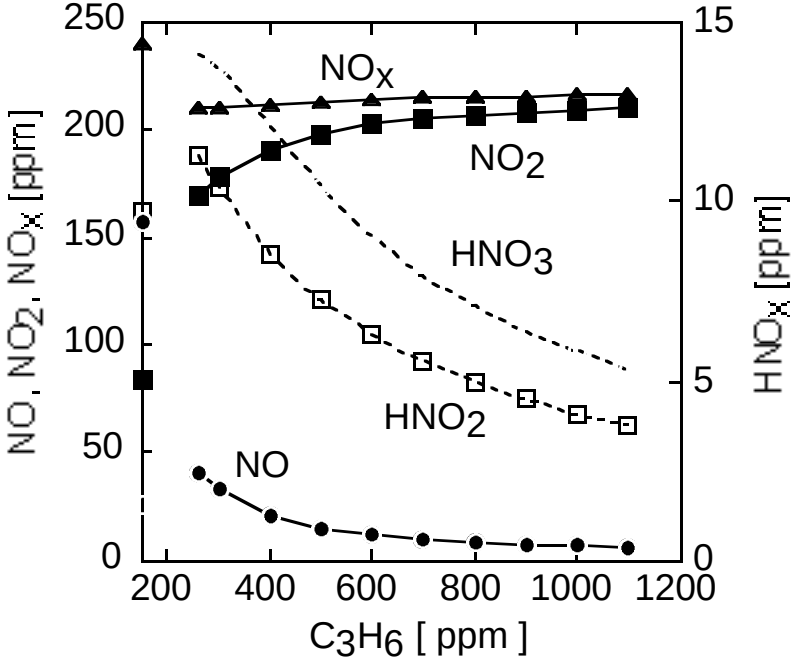
❖ Experiments by Hoard et al. Similar conditions except for addition of propane.

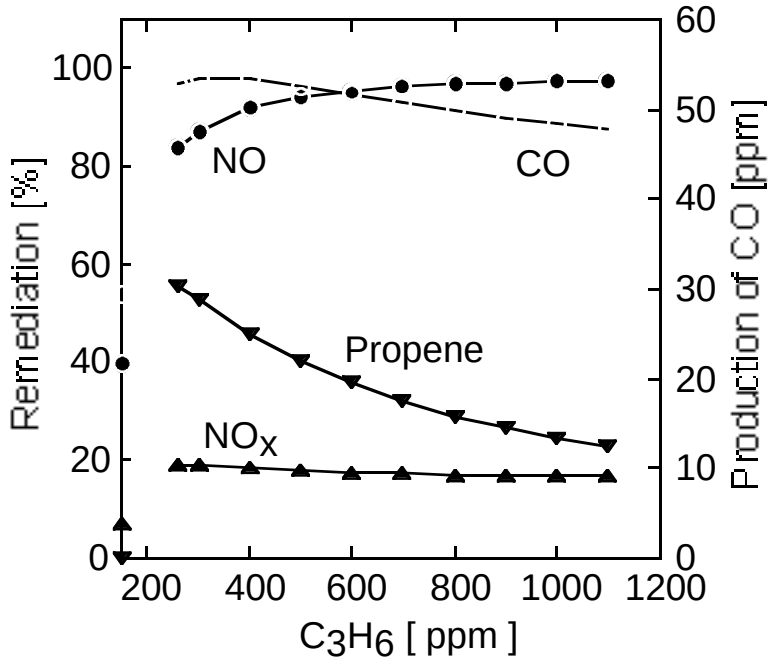
UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

EFFECT OF PROPENE CONCENTRATION

- Increasing amounts of the hydrocarbon in the inlet gas results in an increased conversion of NO to NO_2 and hence, the NO_X removal doesn't get affected.

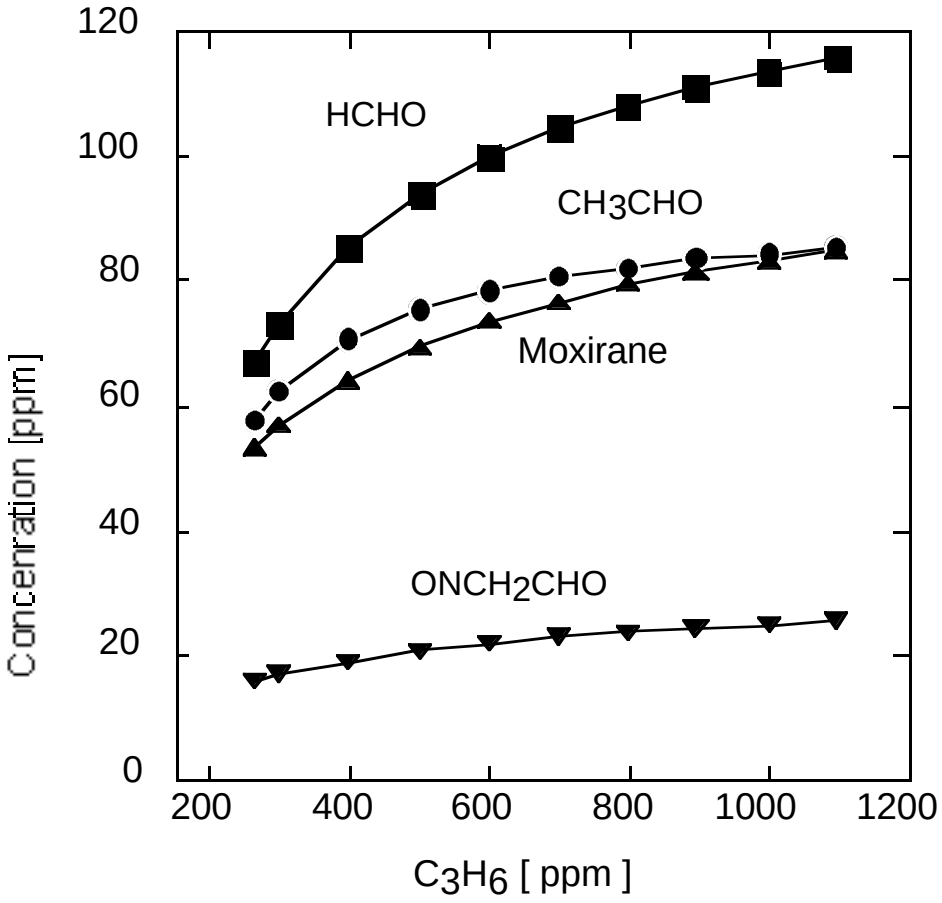
- More amount of inlet hydrocarbon effectively reduces the concentration of the radicals available to other species in the reactor. This is evident from the decrease in the concentration of HNO_X with propene.





- There is also a decrease in the propene conversion because the radicals such as OH, O are present in limiting quantities.

EFFECT OF INLET PROPENE ON END PRODUCTS

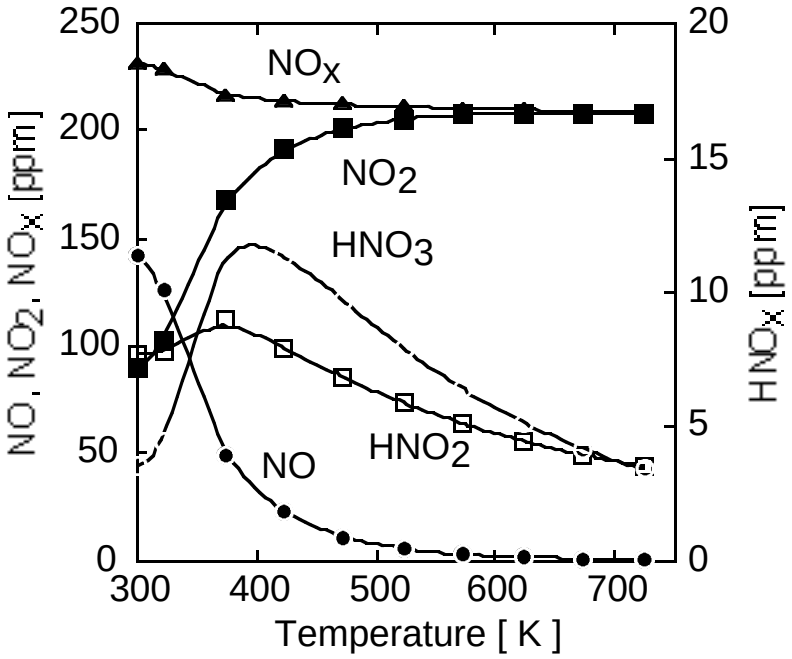


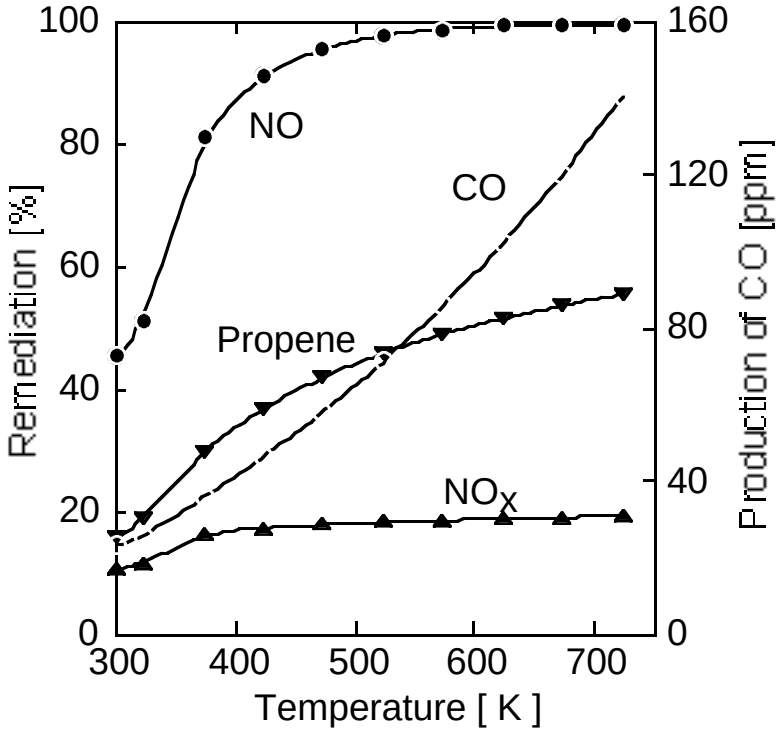
- As is expected, more hydrocarbon results in increased production of carbon-end-products.
- High quantities of formaldehyde and acetaldehyde are also produced.

UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

EFFECT OF GAS TEMPERATURE ON NO_X CONVERSION

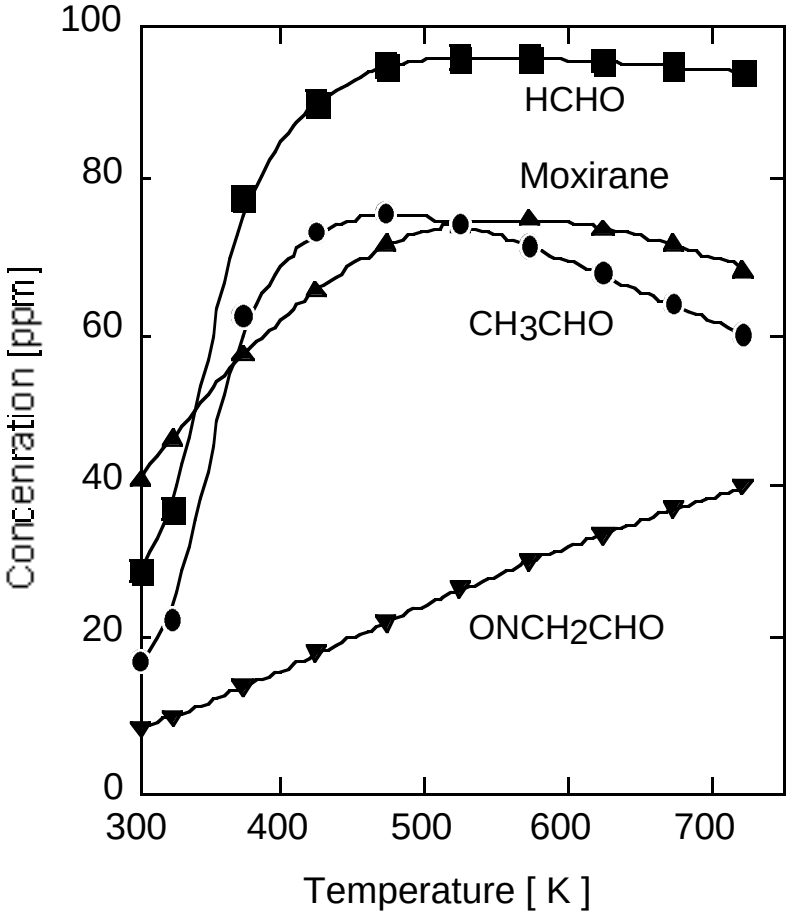
- Increasing the gas temperature seems to affect the NO_X concentration minimally.
- There is however an increase in the exit concentration of CO and other propene-initiated reaction products with reactor gas temperature.





UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

EFFECT OF TEMPERATURE ON END PRODUCTS



- The initial increases in temperatures result in increase in end product concentrations.
- The maxima seen in the graph are mainly due to the highly non-linear nature of the inherent reaction rate coefficients.

  $k = A\,(T/300)^{n} \exp(-E_a / T)$
- The change in temperature also affects the E/N in the plasma thereby causing a change in the rate coefficient values for electron impact reactions.

UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

THE $ONCH_2CHO$ CONTROVERSY (?) !!!

- Rate coefficients for the reaction of O with C_3H_6

Reaction	Rate Coefficient (cm^3/molecule/s) at 298 K	Source
$O + C_3H_6 \rightarrow$ Products	4.79e-12	J.P.C.R.D., 1991, **20** 221-224
$O + C_3H_6 \rightarrow$ Methyl Oxirane	4.81e-12	Gaedtke *et.al.*, Symp. (Int.) Combust., [Proc.]_1973,**14**,295
$O + C_3H_6 \rightarrow CH_2CHO + CH_3$	0.3 x (4.79e-12)	Knyazev *et.al.*, Int. J. Chem. Kinet., 1992 **24**,545-561.
$CH_2CHO + O_2 \rightarrow$ Products	2.6e-13	J.P.R.C.D., 1991, **21** 411-429.
$CH_2CHO + O_2 \rightarrow HCHO + CO + OH$	3.0e-14	-- Do --

- Since reactions of CH_2CHO with O_2 are so significant, the products need to be determined

UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

CH_3ONO - WHY WAS THIS NOT PREDICTED EARLIER(?)

- There are disparities in the reaction rate coefficients reported in the literature.
- The reaction of concern is : $CH_3ONO \rightarrow HCHO + HNO$

	Source	Rate Coefficient (cm^3/molecule/s)	Order	Reaction Rate (molecule/cm^3/s)
	Ohmori *et.al*	7.70e-12	2	= 7.70e-12 x [CH_3ONO] x [M]
1 →	Bull. Chem. Soc. Jpn., 1993, **66,** 51-56.			
	Batt *et. al.*	2.067e-08	1	= 2.07e-8 x [CH_3ONO]
2 →	Int. J. Chem. Kinet., 1975,**7**,441.			

MULTIPLE PULSES : EFFECT ON THE REACTION CHEMISTRY

- It has been observed experimentally that methyl nitrate (CH_3ONO_2) is produced in the plasma processing of the inlet gas with the composition that we have used. But, with the single pulse input, less than 1 ppm of it is produced at the maximum energy input.

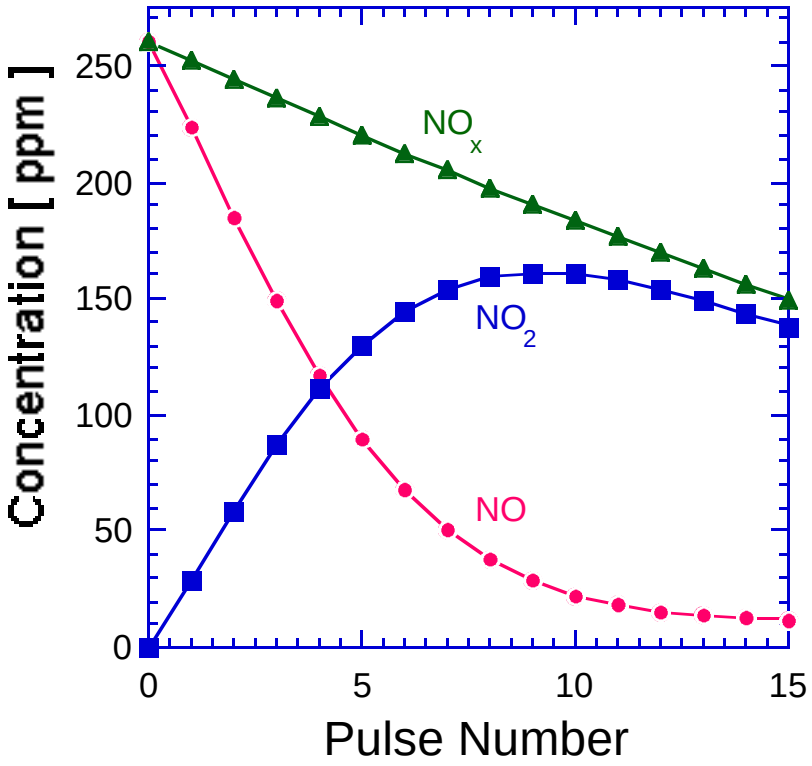
Why is this difference ?

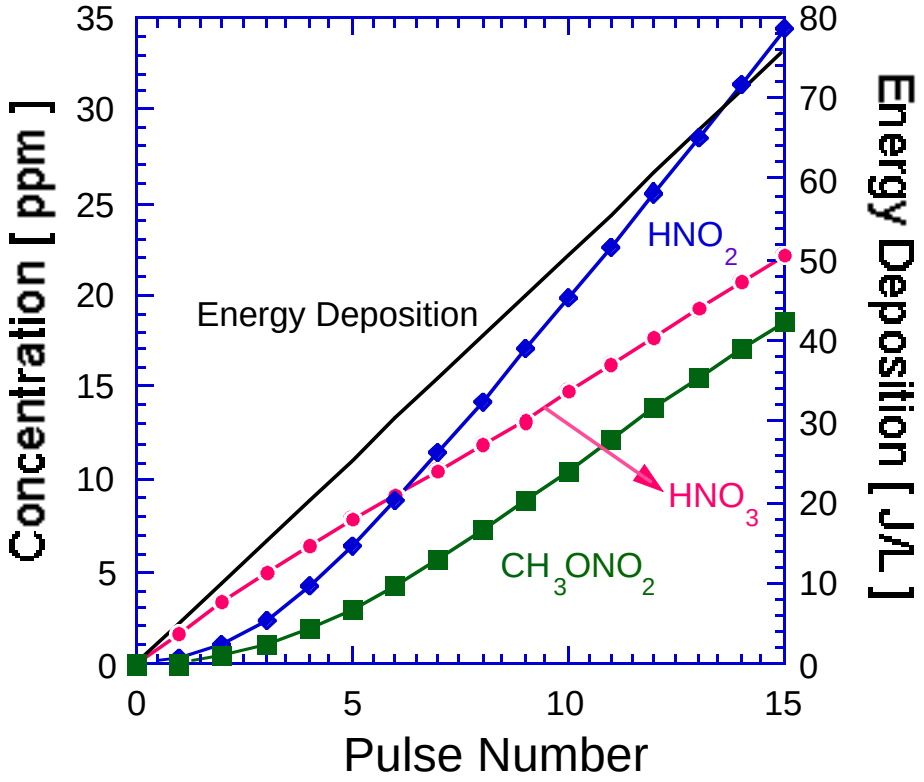
- The reason for this is the difference in way the plasma is being pulsed. It is important to note that the life-zones of the two species, CH_3O and NO_2 rarely overlap and even if they do, it is for a very short time period. Thus in a single pulse input, one does not see the formation of methyl nitrate.

- However, in the case of multiple pulse inputs, enough NO_2 gets formed for reaction with CH_3O to produce methyl nitrate.

MULTIPLE PULSES : PRELIMINARY RESULTS

- As more energy is deposited in the system, one sees more NO_x conversion.
- With the use of multiple pulsing, compounds such as methyl nitrate (CH_3ONO_2) are produced in significant amounts.





UNIVERSITY OF ILLINOIS
OPTICAL AND DISCHARGE PHYSICS

CONCLUSIONS

- Important end-products of the HC-NO_X include aldehydes, ketones, oxiranes, CO and NO_2.
- Increasing the energy input to the reactor improves the NO_X conversion, but at a high cost because the energy efficiency decreases with increasing energy deposition.
- Hydrocarbons play a significant role in the plasma processsing of NO_X and hence should not be neglected in any analysis of NO_X treatment processes.
- The inclusion of multiple pulses affects the overall reaction chemistry and care must be taken to include all possible reactions that could possibly occur under such circumstances.