PLASMA REMEDIATION OF NO_X IN THE PRESENCE OF HYDROCARBONS USING DIELECTRIC BARRIER DISCHARGES: MICROSTREAMER DISCHARGE DYNAMICS*

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October 2001

* **Work supported by Ford Motor Company and NSF (CTS99-74962)**

AGENDA

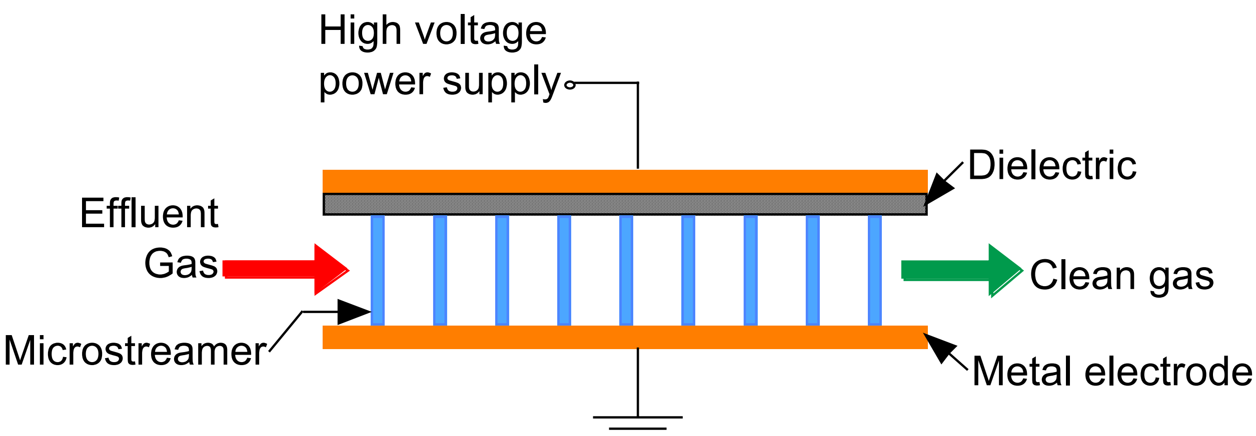
- Introduction
- Description of the model – DBDONED
- Reaction mechanisms - Unburned hydrocarbons (UHCs)
- Results
  - Effect of transport – Advection
  - Effect of UHCs on NO_x Remediation
  - Products of NO_x Remediation
- Concluding remarks

INTRODUCTION

- **Nitrogen oxides (NO, NO_2) - NO_X, are one of the six major pollutants identified by the EPA, others being CO, Pb, SO_X, volatile matter and particulates. All emissions have decreased except for NO_x (EPA, 1998).**

- **Plasma remediation using dielectric barrier discharges has been investigated for the removal of NO_x.**

- **Dielectric barrier discharges are well suited for generation of gas-phase radicals at atmospheric pressure.**



$$e + N_2 \rightarrow N + N + e$$

$$e + O_2 \rightarrow O + O + e$$

$$e + H_2O \rightarrow OH + H + e$$

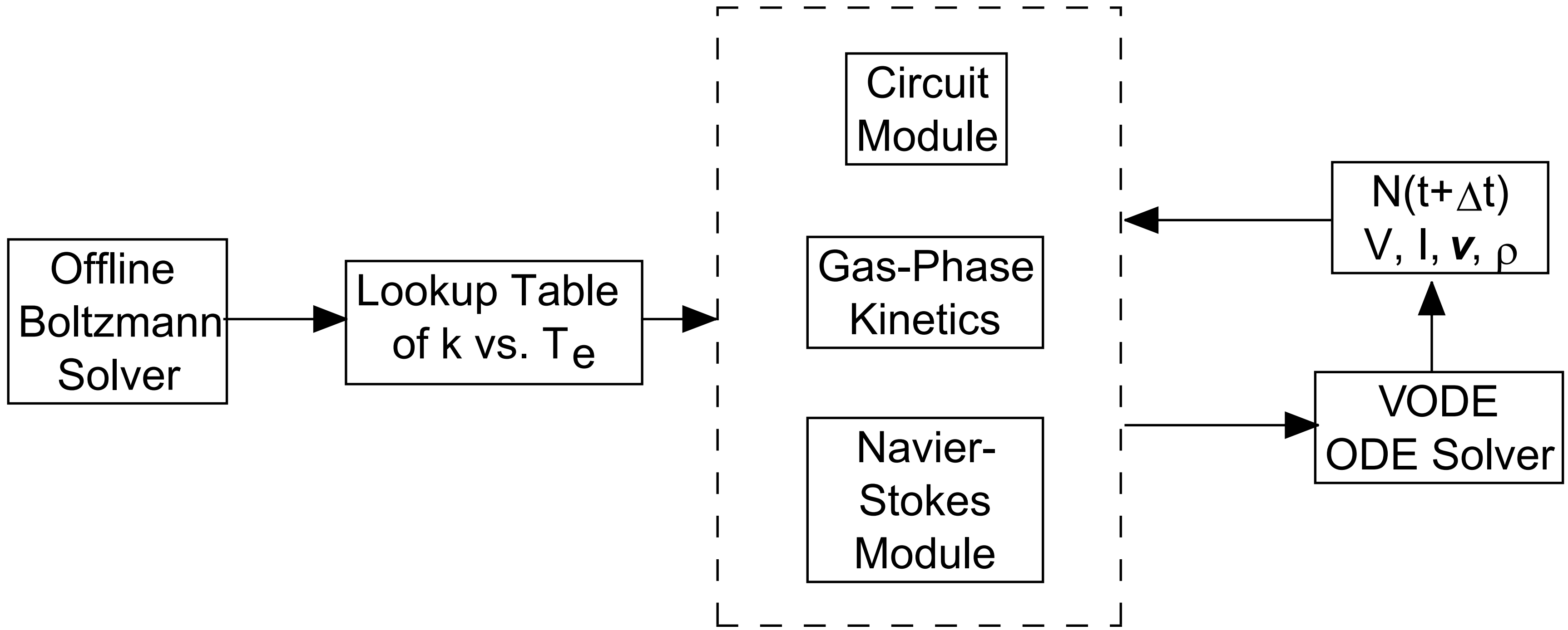
$$NO + N \rightarrow N_2 + O$$

$$NO + O \rightarrow NO_2$$

DESCRIPTION OF THE MODEL - DBDONED

- **DBDONED is a one dimensional (radial) plasma chemistry simulation coupled with hydrodynamics and circuit modules.**

- **To obtain e-impact reaction rate coefficients, the model uses a lookup table generated by an offline Boltzmann solver.**



DBDONED – EQUATIONS SOLVED

- **Species continuity:**

$$\frac{\partial N_i}{\partial t} = -\nabla \cdot \left(N_i \bar{v} - \rho D_i \nabla \left(\frac{N_i}{\rho} \right) \right) + 0 - d\ kinetics$$

- **Momentum:**

$$\frac{\partial(\rho \bar{v})}{\partial t} = -\nabla P - \nabla \cdot \left(\rho \bar{v} \bar{v} \right) - \nabla \cdot \bar{\bar{\tau}}$$

- **Gas energy:**

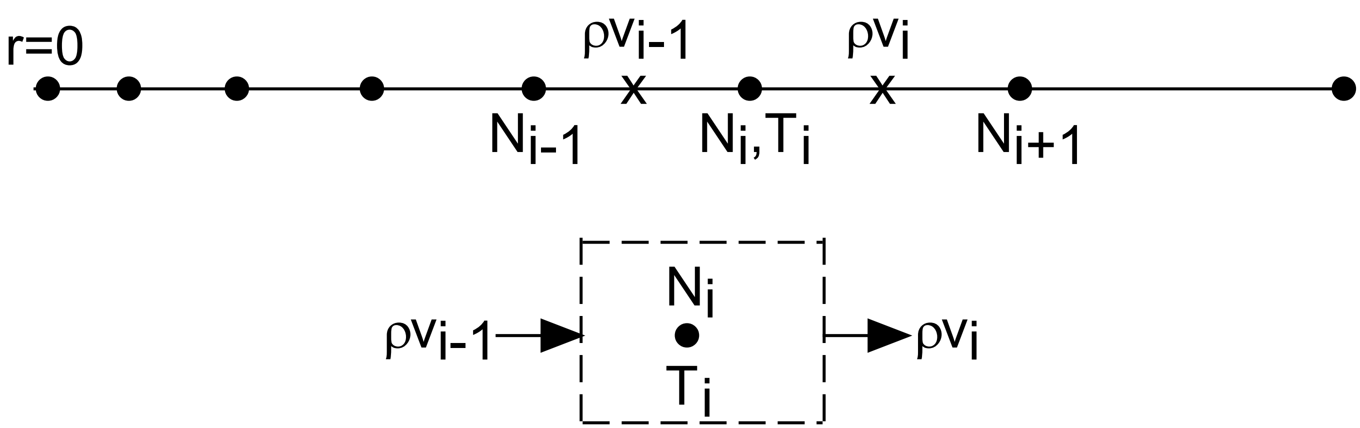
$$\frac{\partial(\rho C_v T)}{\partial t} = \nabla \cdot (k \nabla T) - \nabla \cdot \left(\rho \bar{v} C_v T \right) - P(\nabla \cdot \bar{v}) + \bar{j} \cdot \bar{E} - \sum_i \frac{dN_i}{dt} \Delta H_i + 2\mu \left(\nabla \cdot \bar{v} \right)^2$$

DBDONED – MESH DESCRIPTION

- **DBDs are operated at high pressure on the order of a few bar and so a number of microstreamers or breakdown channels are generated.**

- **In this investigation, the volume in and around the microstreamer is divided into concentric cylinderical shells with their radii increasing geometrically.**

- **Species densities and gas temperature are measured at the center of the cells and mass flux is calculated at the cell walls.**



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OPERATING CONDITIONS

- Typical diesel exhausts contain N_2, O_2 (excess air); H_2O (product), and trace amounts of NO and unburned hydrocarbons (UHCs).

- To simulate actual exhausts, we have used propene (C_3H_6) as representative of the UHCs.

- Previous studies have shown that saturated hydrocarbons (propane) do not contribute significantly to the overall NO_x remediation and hence, they were not included in this investigation.

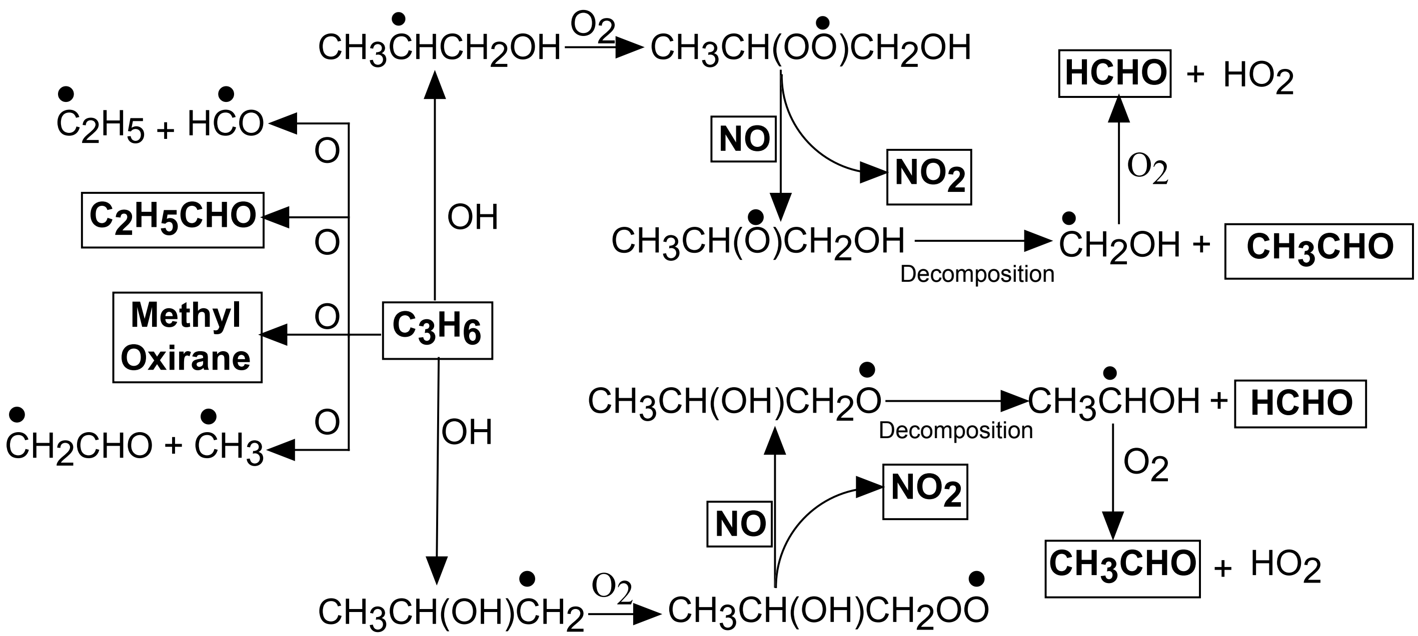
- Inlet gas composition

  $N_2/O_2/H_2O$=86/8/6   NO=260 ppm, C_3H_6=500 ppm.

- T=180 ^{o}C, P=1atm.

REACTION MECHANISM: NO-C_3H_6

- C_3H_6 reactions are initiated by O and OH.
- Peroxy radicals formed from OH-initiated reactions with propene, oxidize NO to NO_2.
- NO_x is also converted to other organic nitrates and nitrites, but most of the initial NO_x (NO) is primarily oxidized to NO_2.



PLASMA PARAMETERS - n_e, T_e

- **The current pulse lasts ~ 70 ns and the streamer volume averaged energy deposition ≈ 80 J/l.**

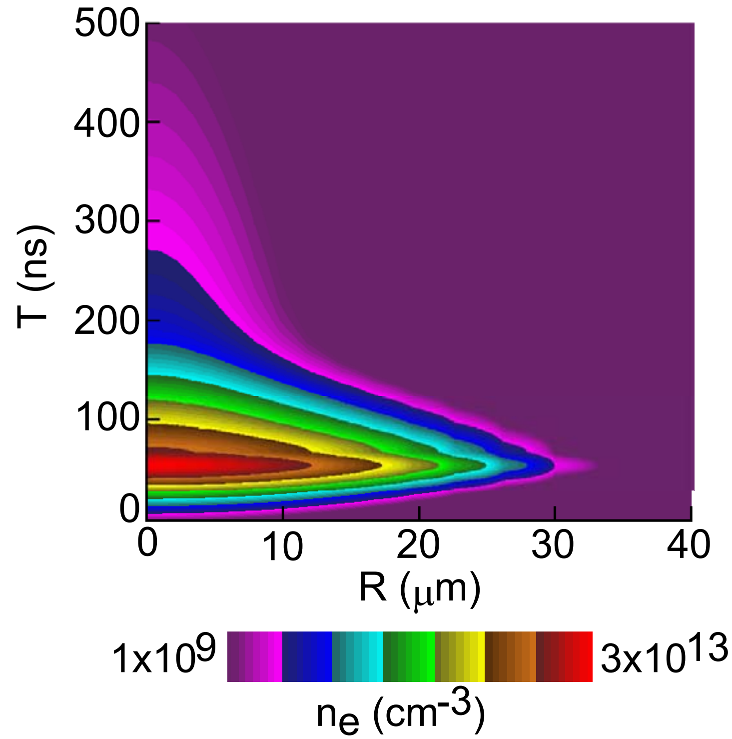
- **Peak values: $T_e \approx 3$ eV, $n_e \approx 10^{13}$ cm^{-3}.**

- **Electrons are produced by the ionization of the background gases, N_2, O_2, and H_2O.**

$$e + N_2 \rightarrow N_2^+ + e + e$$
$$e + O_2 \rightarrow O_2^+ + e + e$$
$$e + H_2O \rightarrow H_2O^+ + e + e$$

- **After the current pulse, electrons are lost primarily by dissociative attachment to O_2 and H_2O.**

$$e + O_2 \rightarrow O^- + O$$
$$e + O_2 + M \rightarrow O_2^- + M$$
$$e + H_2O \rightarrow H^- + OH$$

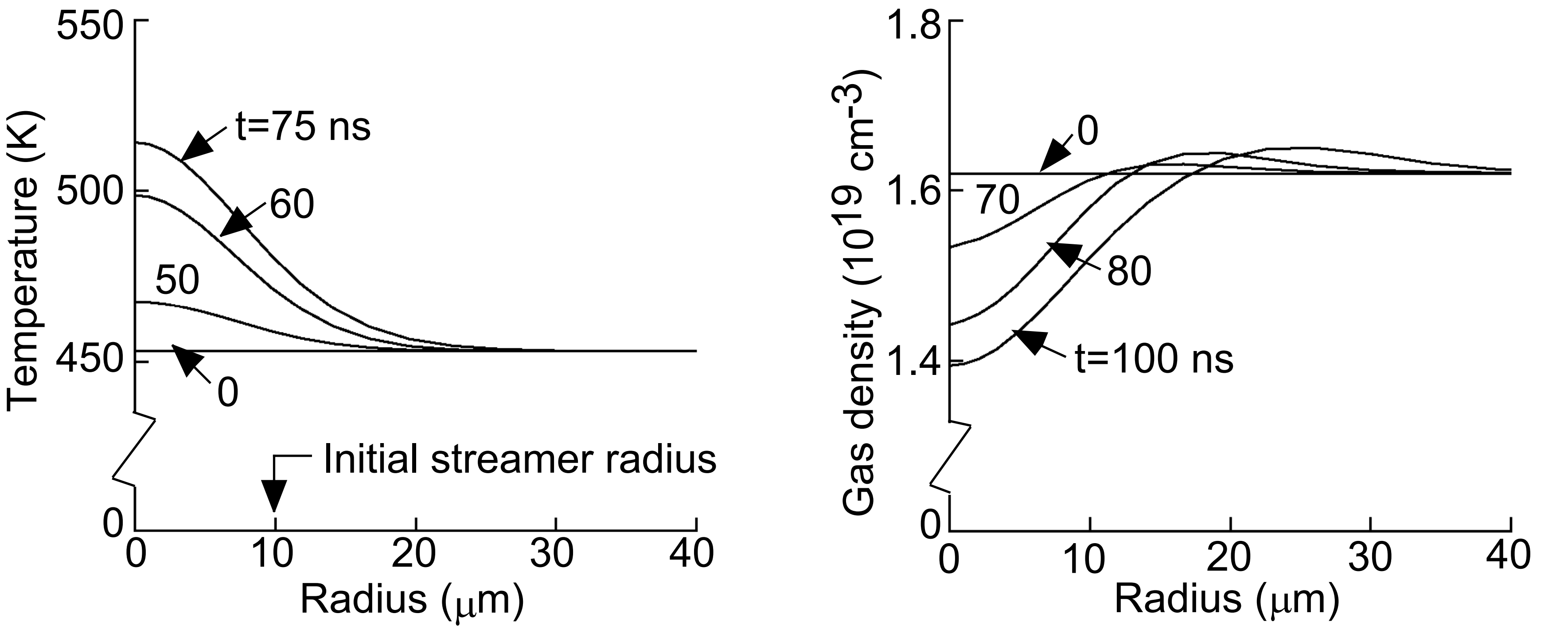


Initial streamer radius = 10μm

GAS TEMPERATURE AND DENSITY

- **Energy deposition in the streamer results in a rise in temperature which in turn produces a pressure gradient initiating radial advection.**

- **Due to the radial advection, a front of high mass density is formed outside the streamer. Because of this, a reversal of pressure gradient occurs, which results in refilling of the streamer region.**



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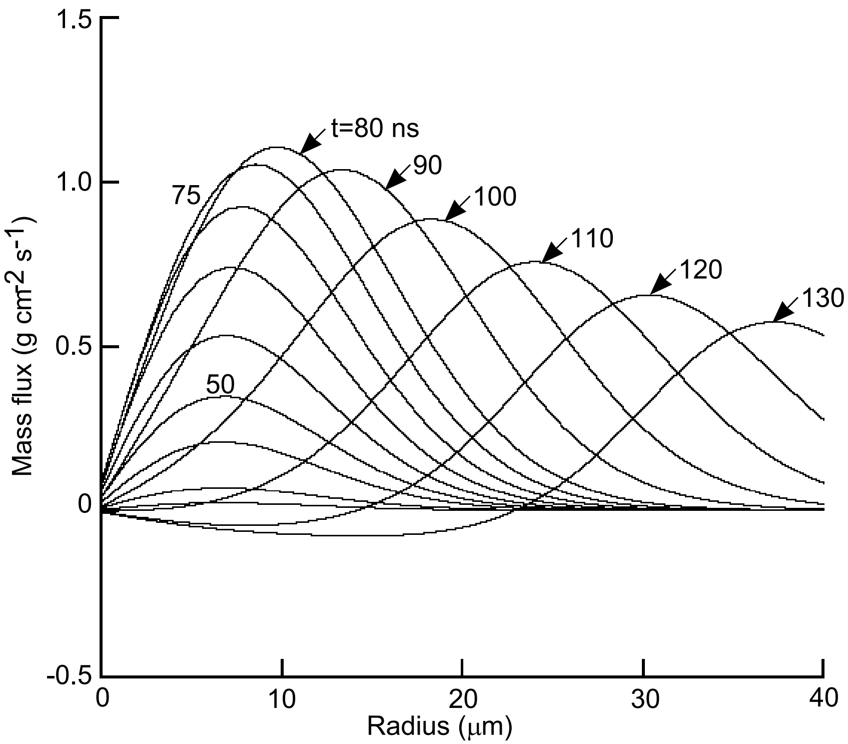
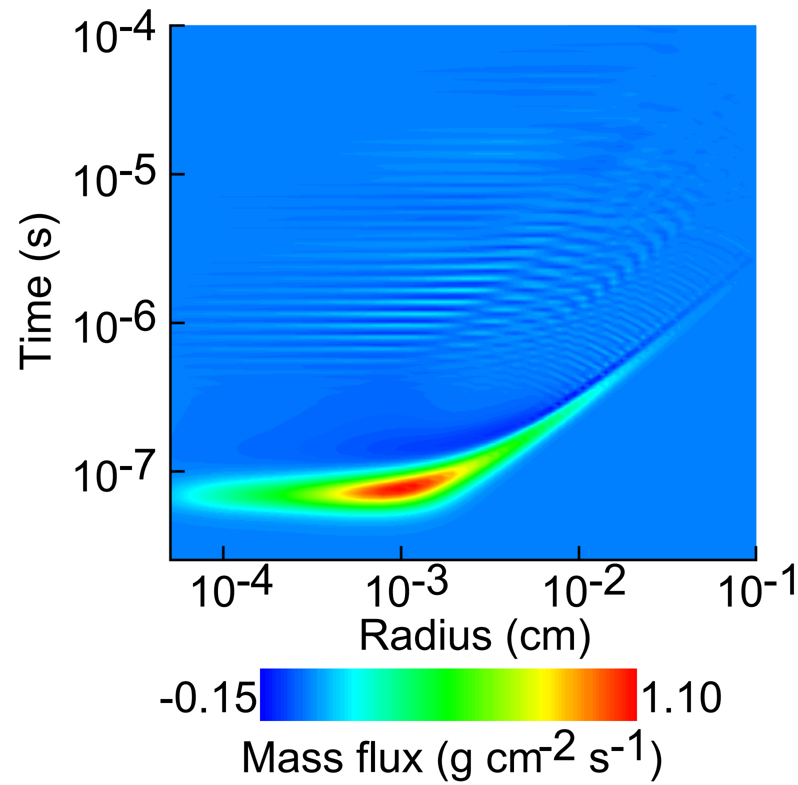
ADVECTION

- The initial increase in temperature in the streamer region initiates radial advection pushing mass outside of the streamer.

- After the current pulse, the peak mass flux decreases. The increased density in regions outside the streamer causes reversal of pressure gradient and reverses the flux direction.





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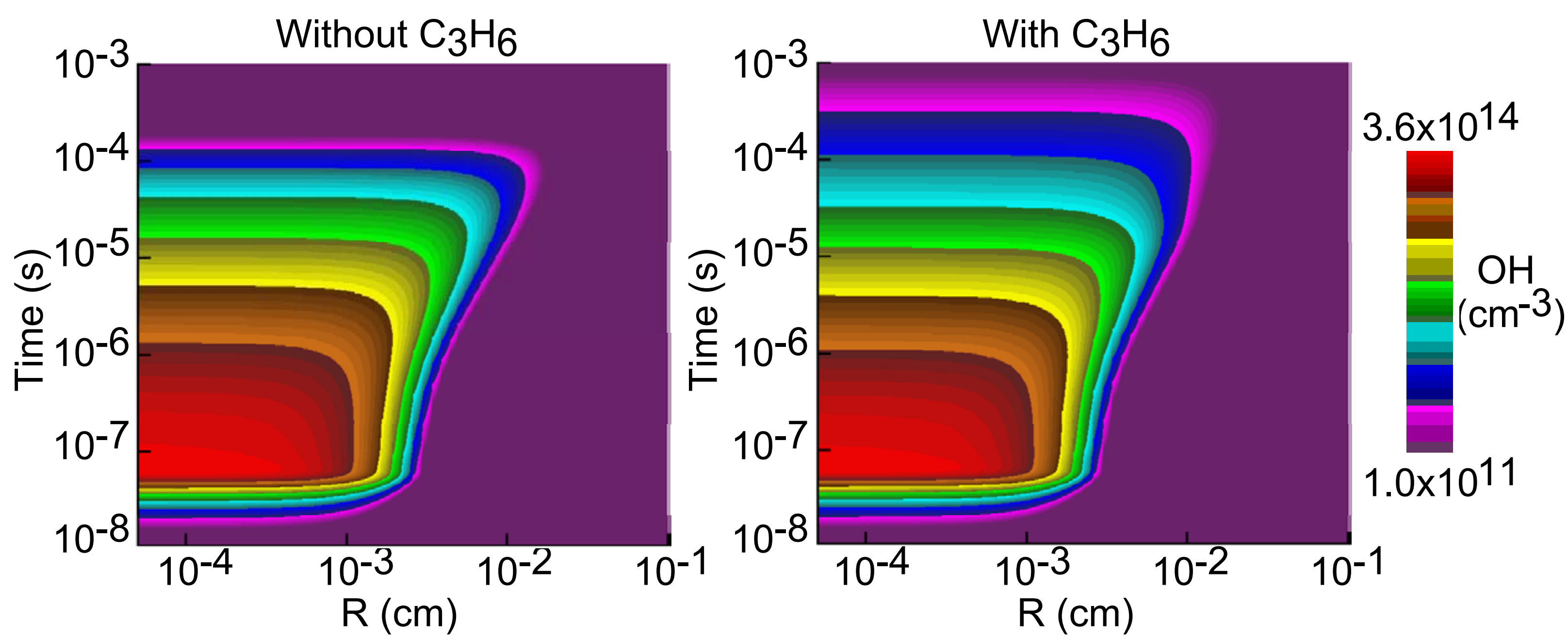
INITIATOR RADICALS – OH: WITH/WITHOUT C_3H_6

- **Initially ($t < 1\ \mu s$), OH is produced by the electron impact dissociation of H_2O and at later times, is produced by the reaction of NO with HO_2.**

$$e + H_2O \rightarrow H + OH + e \qquad e + H_2O \rightarrow H^- + OH$$
$$NO + HO_2 \rightarrow NO_2 + OH$$

- **Since UHC initiated reactions result in the production of HO_2 (which in turn produces OH), OH densities are sustained for longer times ($t > 0.1$ ms).**



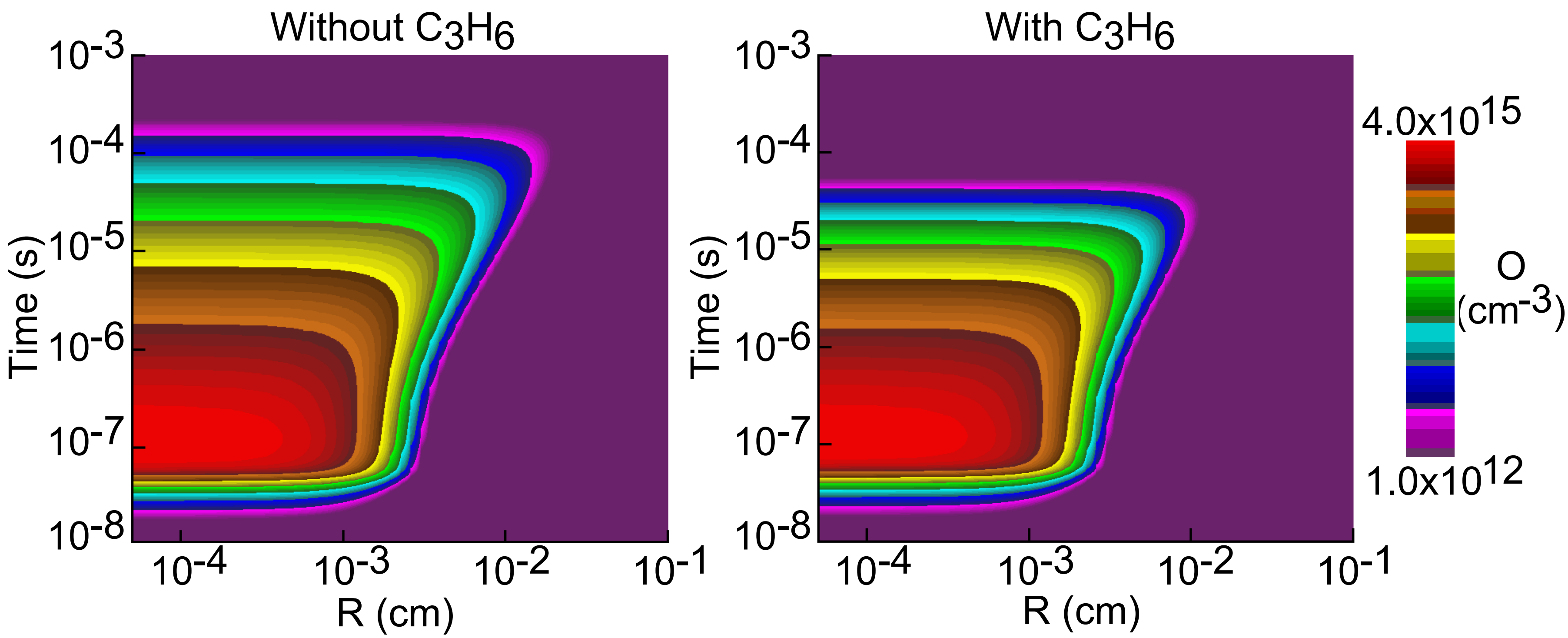
INITIATOR RADICALS - O: WITH/WITHOUT C_3H_6

- **O is produced through the electron impact dissociation of O_2 and is mainly consumed by O_2 in the absence of UHCs to form O_3.**

$$e + O_2 \rightarrow O + O + e \qquad O + O_2 + M \rightarrow O_3 + M$$

- **O is sustained for shorter periods in the presence of C_3H_6 because of the extra channels of consumption.**

$$O + C_3H_6 \rightarrow \text{Methyl Oxirane} + \text{Ethanal}$$



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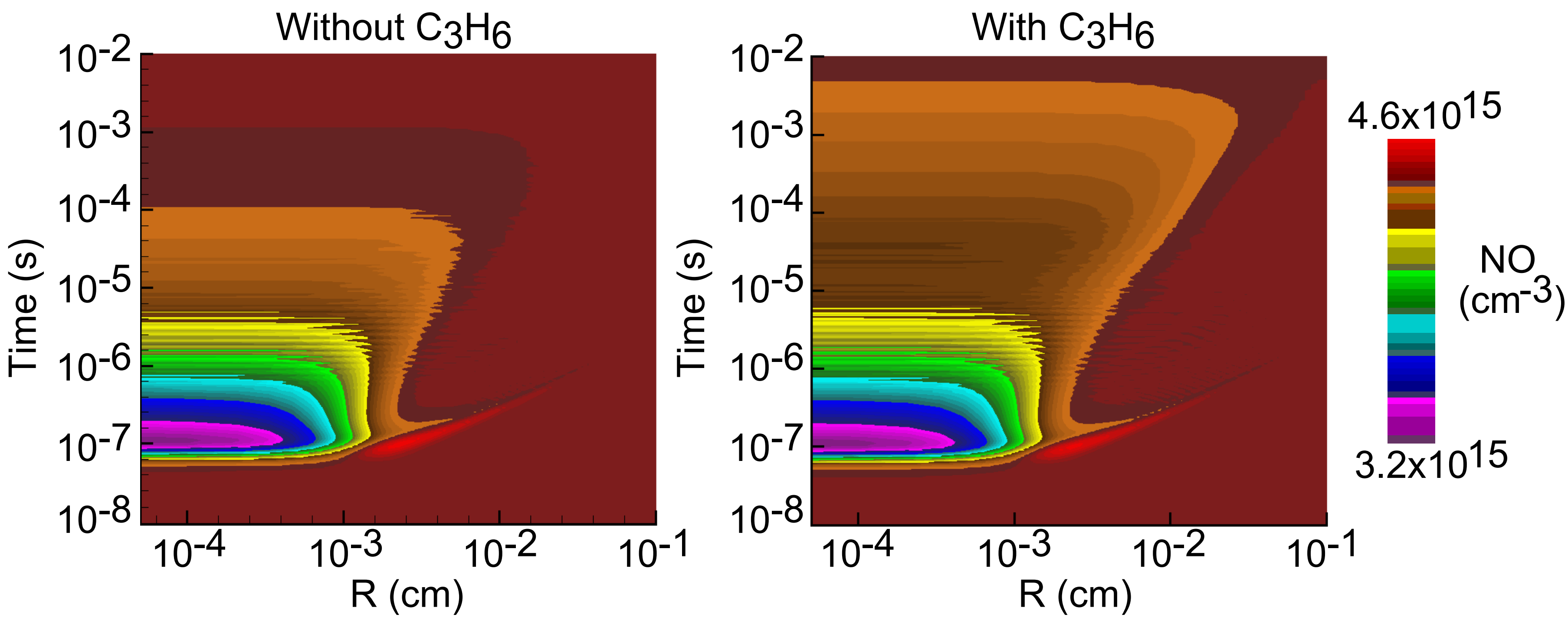
NO – WITH/WITHOUT C_3H_6

- **Initially (t<300 ns), depletion in NO densities occur within the streamer region because of the mass flux to the outside. At later times (t > 500 ns), the density in the outer regions increase causing reversal of pressure gradient which forces NO back into the streamer region.**

- **In the presence of propene, more NO is removed by reaction with peroxies.**

NO + peroxy radicals $\rightarrow$ NO_2 + alkoxy radicals.



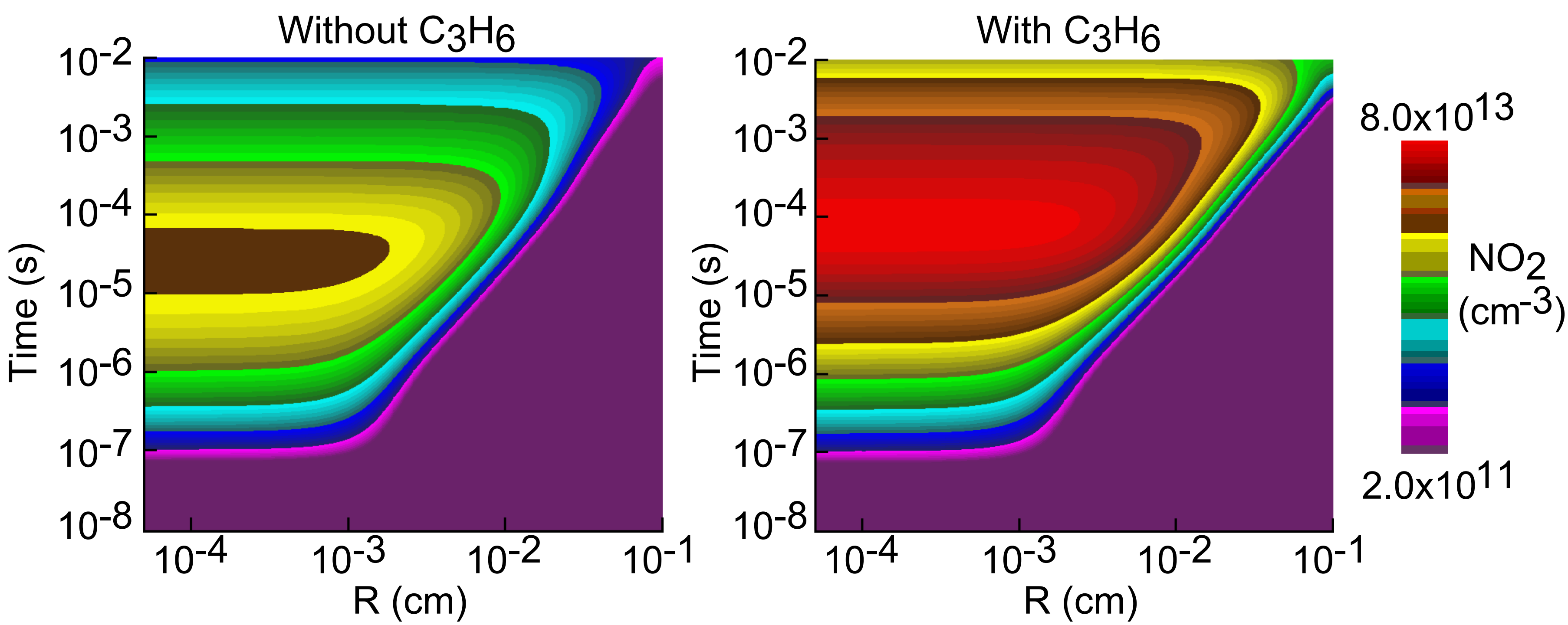
NO_2 – WITH/WITHOUT C_3H_6

- In the absence of UHCs, NO_2 is produced mainly by the reaction of HO_2 with NO.

$$NO + HO_2 \rightarrow NO_2 + OH$$

- In the presence of propene, increased conversion of NO to NO_2 occurs through the reaction of NO with peroxies.

$$NO + \text{peroxy radicals} \rightarrow NO_2 + \text{alkoxy radicals.}$$



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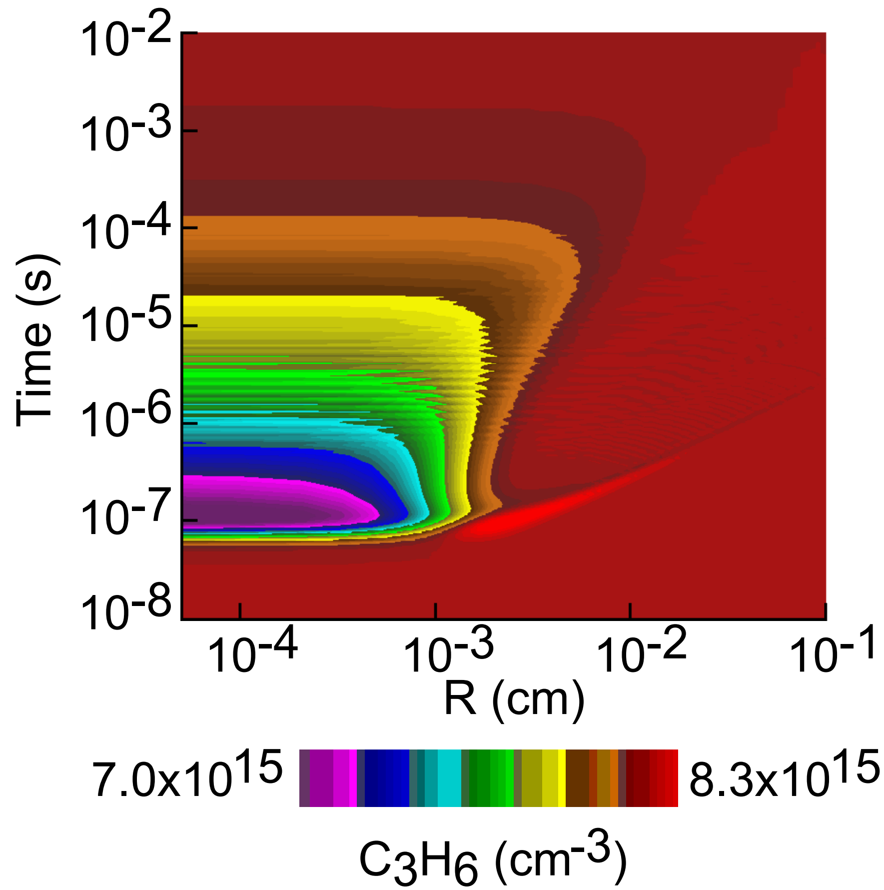
C_3H_6 DENSITIES – SPATIAL AND TEMPORAL EVOLUTION

- **The initiation reaction with C_3H_6 is by O and OH.**

$O + C_3H_6 \rightarrow$ Methyl Oxirane
$\rightarrow$ Ethanal
$\rightarrow C_2H_5 + HCO$
$\rightarrow CH_2CHO + CH_3$
$OH + C_3H_6 \rightarrow CH_3CH_2CH_2OH + CH_3CH(OH)CH_3$

- **Due to the initial shock wave produced in the streamer, C_3H_6 from within the streamer moves outside creating regions of higher density.**
- **The increase in density outside the streamer results in the reversal of pressure gradient causing mass to move back into the microstreamer region.**



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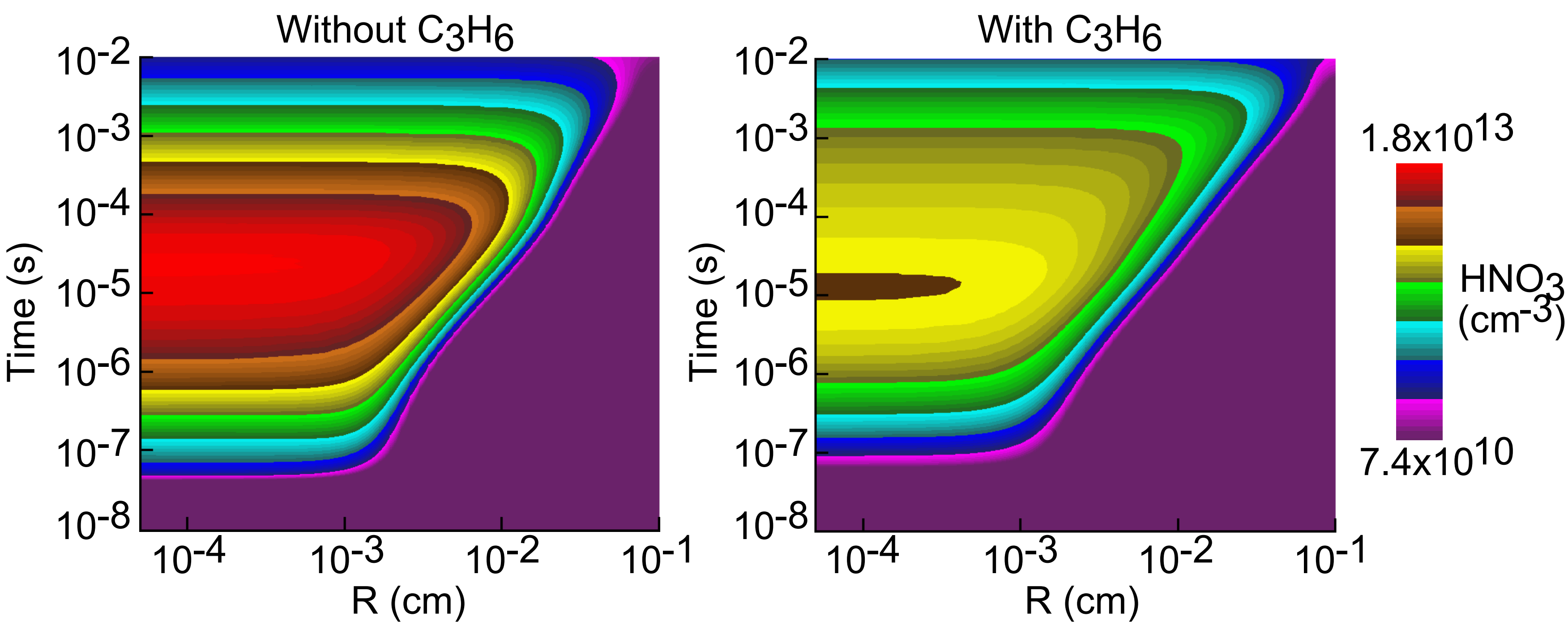
PRODUCTS OF NO_x REMEDIATION – HNO_3

- **HNO_3 is produced by the reaction of NO_2 with OH and HO_2 with NO.**

$$HO_2 + NO + M \rightarrow HNO_3 + M$$
$$OH + NO_2 + M \rightarrow HNO_3 + M$$

- **In the presence of UHCs, OH and HO_2 are competitively consumed by the UHCs and hence, the production of HNO_3 is lesser.**



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CONCLUDING REMARKS

- A one-dimensional plasma chemistry simulation coupled with diffusion, advection and circuit model has been developed.
- Spatial variations in temperature and density produce advection resulting in movement of mass into and out of the microstreamer.
- Transport of NO from outer zones into the streamer region and that of N from the microstreamer to outer regions result in increased remediation of NO.
- Transport of C_3H_6 from the streamer region to regions outside the streamer results in decreased remediation of NO within the streamer.
- The presence of C_3H_6 results in added consumption of O and OH in the microstreamer due to which transport of these radicals to outer regions is reduced.