ATMOSPHERIC PRESSURE PLASMA PROCESSING OF POLYPROPYLENE*

Rajesh Dorai [1] and Mark J. Kushner [2]

University of Illinois
[1] Department of Chemical and Biomolecular Engineering, dorai@uiuc.edu
[2] Department of Electrical and Computer Engineering, mjk@uiuc.edu
Urbana, IL 61801

http://uigelz.ece.uiuc.edu

November 2002

* Work supported by the 3M Company and the National Science Foundation (CTS99-74962)

AGENDA

- Introduction to plasma surface modification of polymers
- Description of the model for gas phase and surface kinetics
- Processing of polypropylene in humid air plasmas
- Concluding remarks

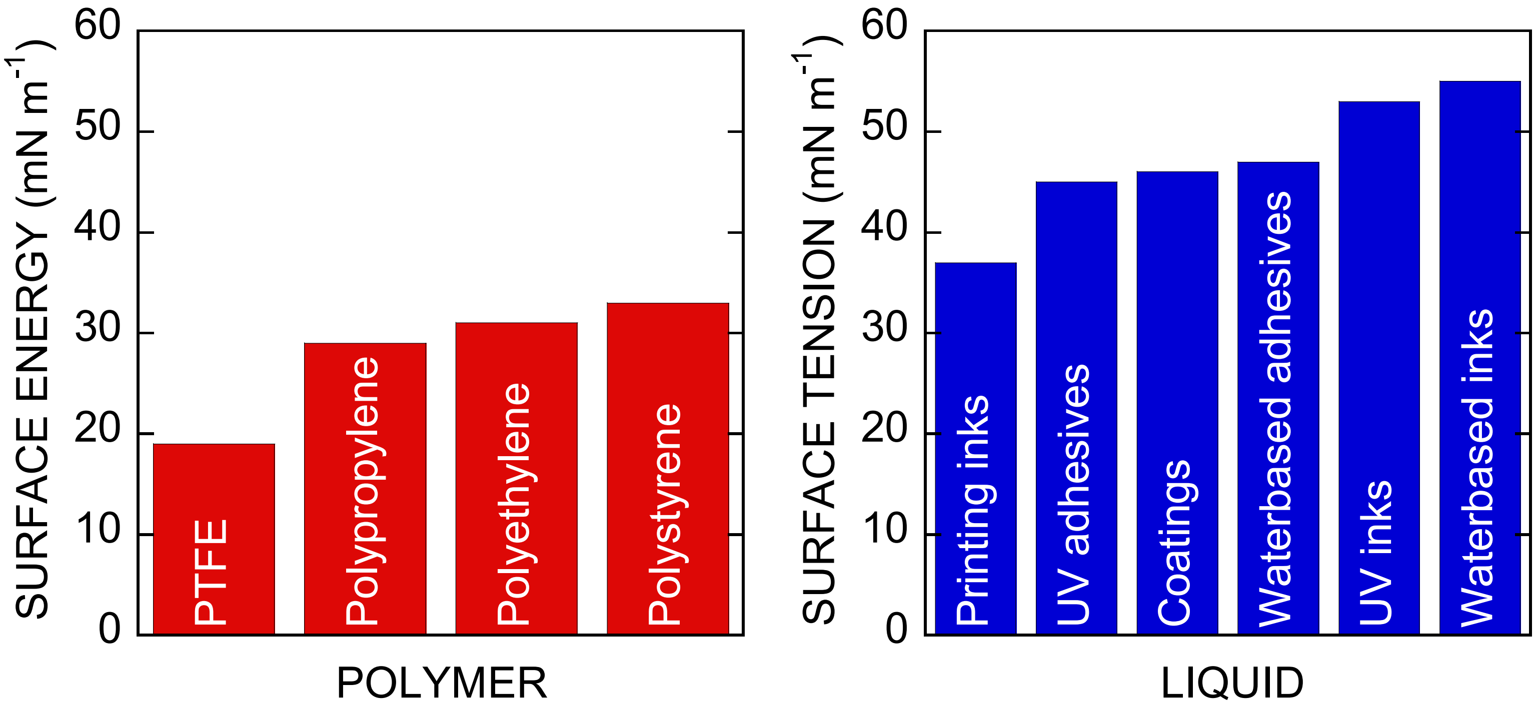
University of Illinois
Optical and Discharge Physics

PLASMA SURFACE MODIFICATION OF POLYMERS

- Polymers typically require surface activation to improve their wetting and adhesion properties.
- Atmospheric pressure plasmas (typically coronas) are used for the ease of generation of gas-phase radicals which react with and modify the polymer surface.

SURFACE ENERGY AND WETTABILITY OF POLYMERS

- **Most polymers, due to their low surface energies, are hydrophobic.**
- **For good adhesion between a liquid and a polymer, the surface energy of the polymer should exceed the surface tension of the liquid by ≈ 2-10 mN m^{-1}.**



University of Illinois
Optical and Discharge Physics

COMMERCIAL CORONA PLASMA EQUIPMENT

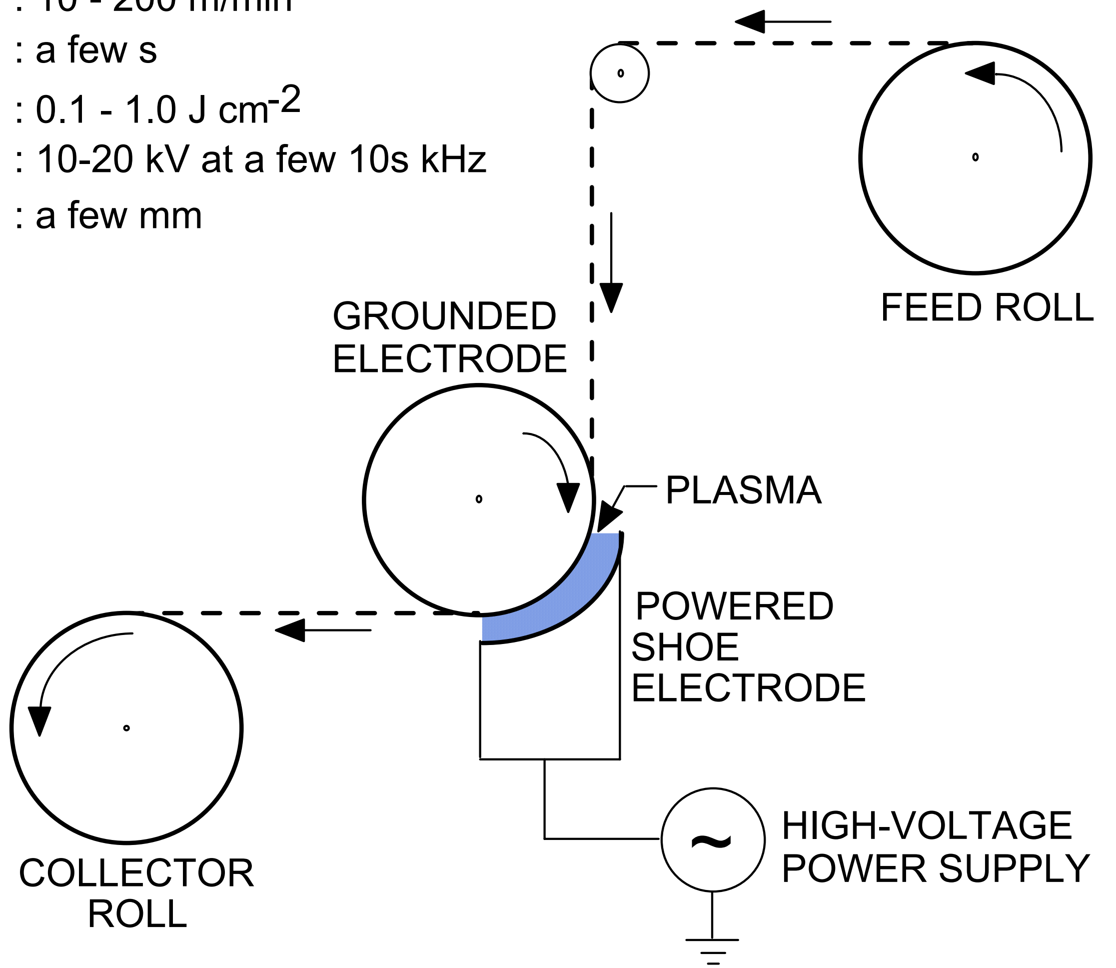
(Tantec Inc.)

University of Illinois
Optical and Discharge Physics

POLYMER TREATMENT APPARATUS

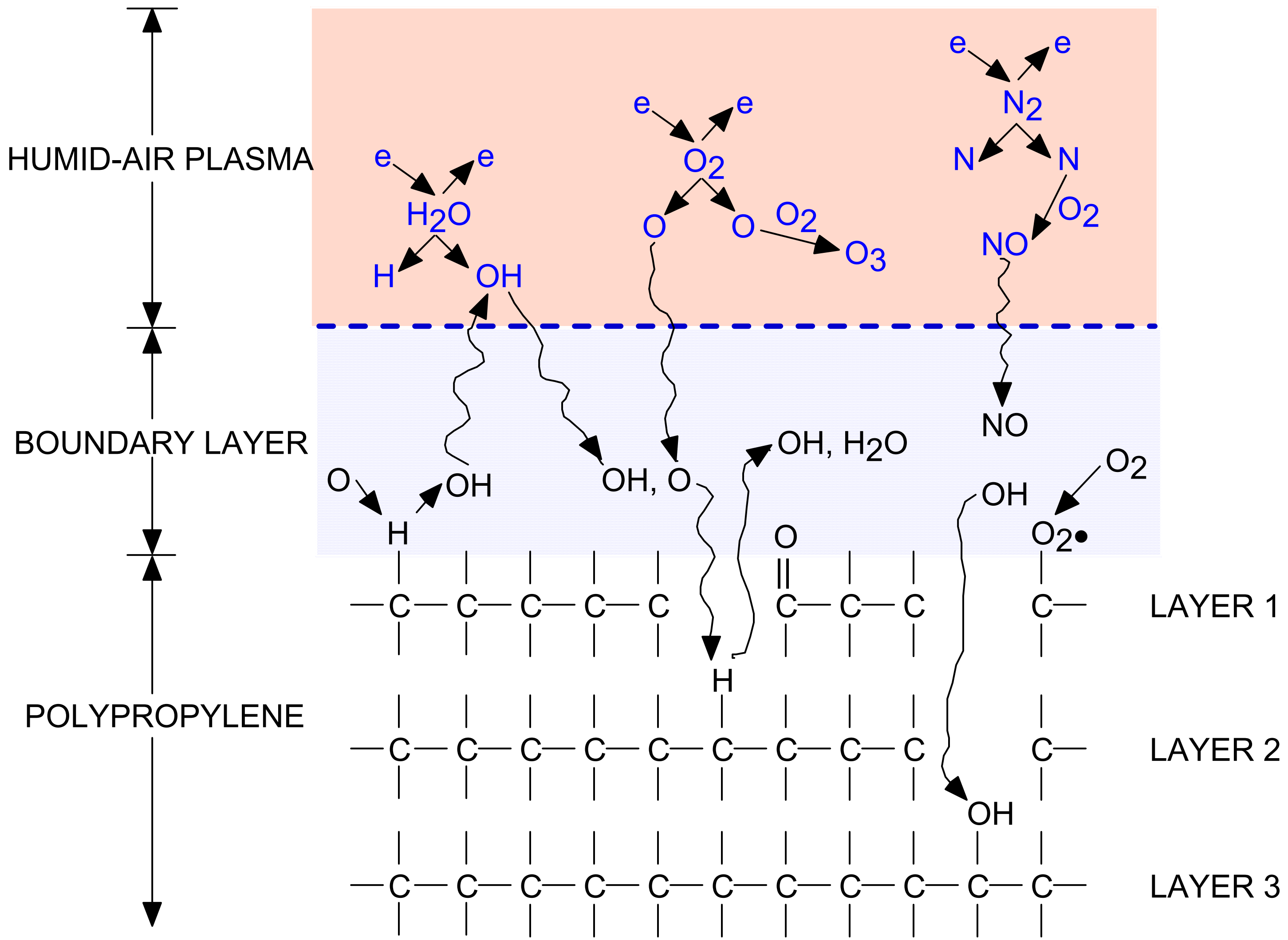
- TYPICAL PROCESS CONDITIONS:

Web speed	: 10 - 200 m/min
Residence time	: a few s
Energy deposition	: 0.1 - 1.0 J cm^{-2}
Applied voltage	: 10-20 kV at a few 10s kHz
Gas gap	: a few mm



University of Illinois
Optical and Discharge Physics

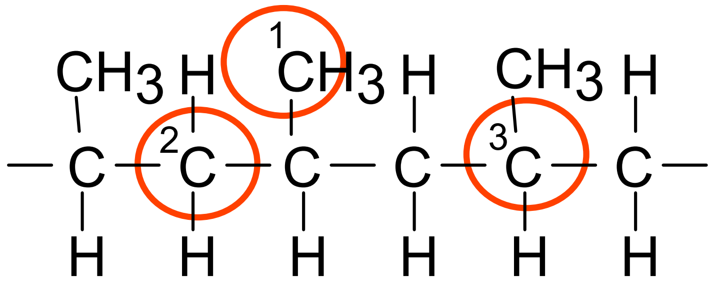
REACTION PATHWAY



University of Illinois
Optical and Discharge Physics

POLYPROPYLENE (PP) - STRUCTURE

- **Polypropylene polymer:**



1 - Primary C

2 - Secondary C

3 - Tertiary C

- **Three types of carbon atoms in a PP chain:**
  - **Primary C – attached to only one another carbon;**
  - **Secondary C – attached to two carbon atoms; and**
  - **Tertiary C – attached to three carbon atoms.**

- **The reactivity of an H-atom depends on the type of C bonding.**

- **Reactivity scales as: $H_T > H_S > H_P$ (H_T = tertiary H; H_S = secondary H; H_P = primary H)**

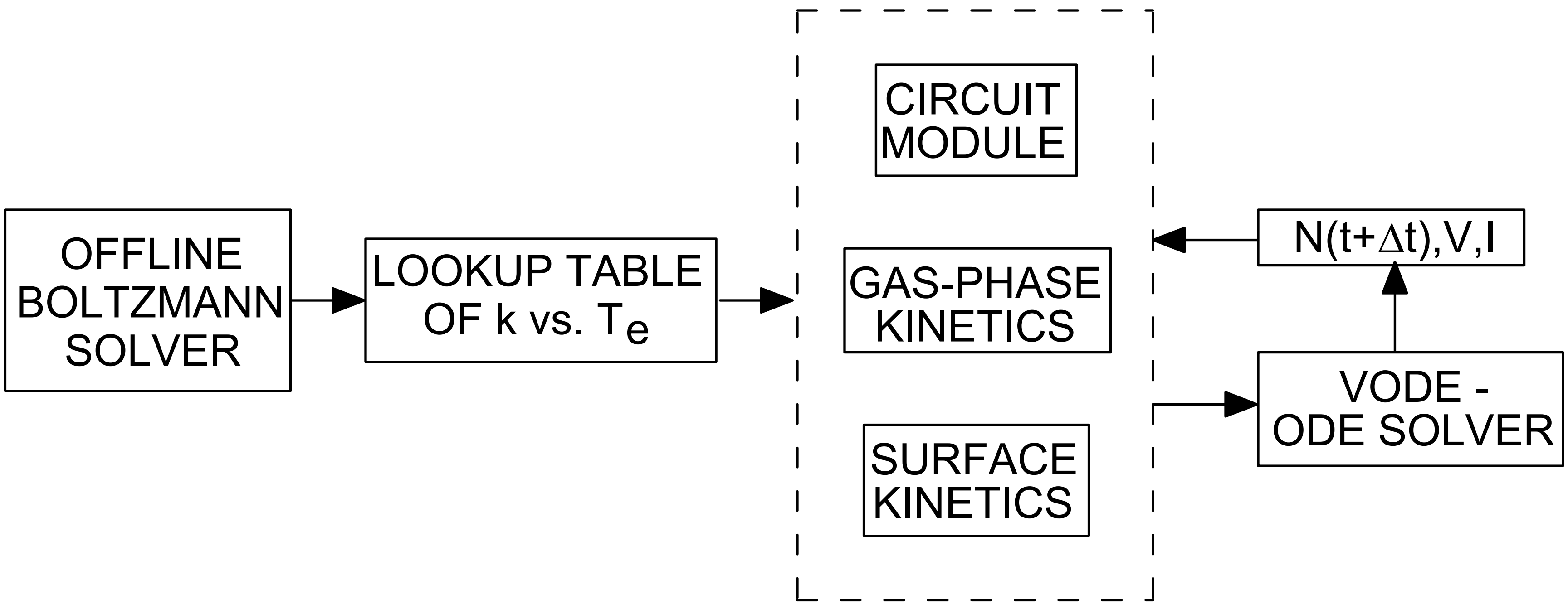
FUNCTIONALIZATION OF THE PP SURFACE

- Untreated PP is hydrophobic (repels water).
- The increase in surface energy of PP after corona treatment is attributed to the functionalization of the polymer surface with hydrophilic groups (attract water).
- An air-corona-processed PP film contains hydrophilic functional groups such as:
  - Carbonyl (-C=O)
  - Peroxy (-C-O-O)
  - Alcohols (C-OH)
  - Acids ((OH)C=O)
- The process parameters are energy deposition and relative humidity (RH).
- At sufficiently high energy deposition, erosion of the polymer occurs.

University of Illinois
Optical and Discharge Physics

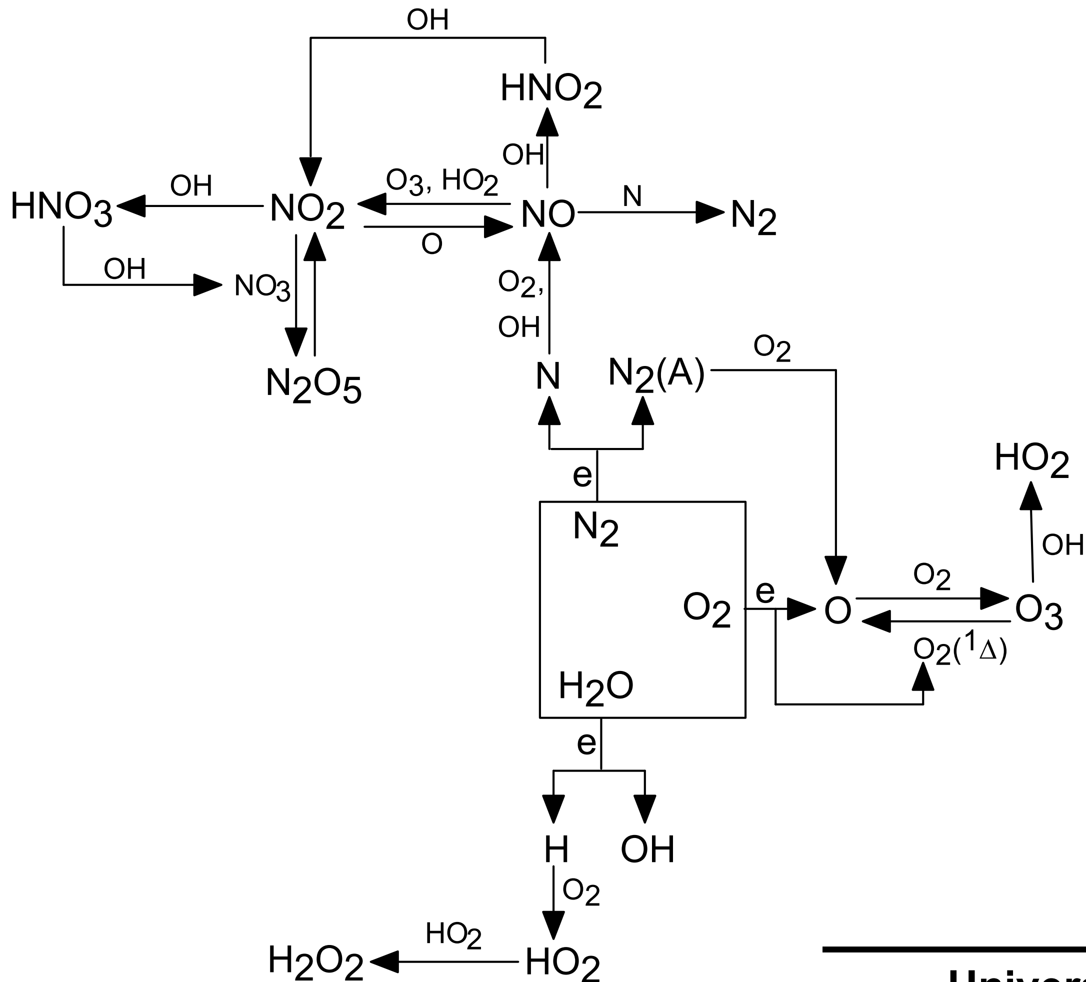
DESCRIPTION OF THE MODEL: GLOBAL_KIN

- **Modules in GLOBAL_KIN:**
  - **Circuit model**
  - **Homogeneous plasma chemistry**
  - **Species transport to PP surface**
  - **Heterogeneous surface chemistry**



REACTION MECHANISM FOR HUMID-AIR

- Gas phase products of humid-air corona treatment include O_3, N_2O, N_2O_5, HNO_2, HNO_3.



University of Illinois
Optical and Discharge Physics

RAJESH_AVS_02_09

SPECIES TRANSPORT TO THE POLYMER SURFACE

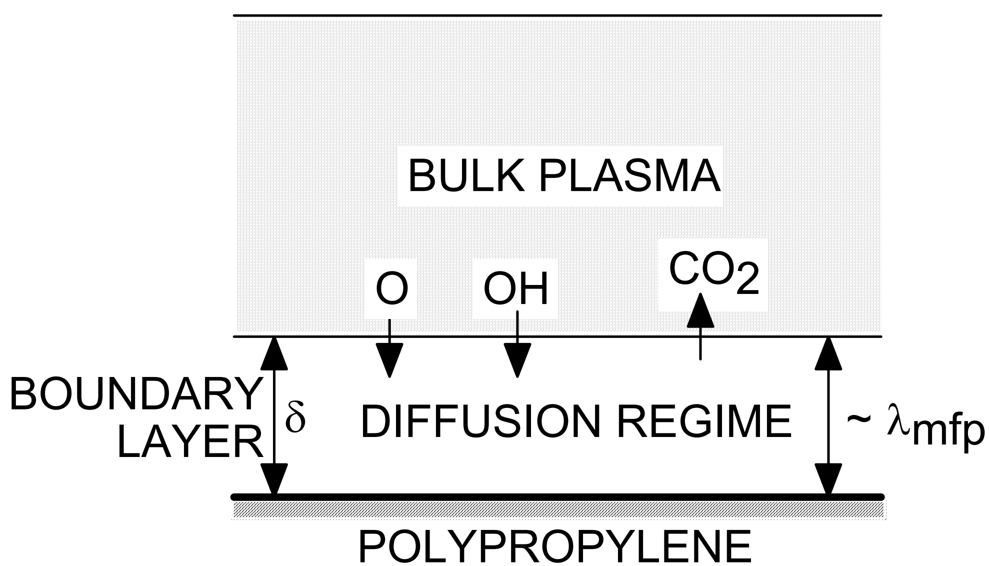
- **Species in the bulk plasma diffuse to the PP surface through a boundary layer (d ~ a few $\lambda_{mfp} \approx \mu$m).**

- **Flux of the radicals reaching the surface is,**

$$\phi = \frac{n v_{th}}{4}$$

, *n* = density, v_{th} = thermal speed.

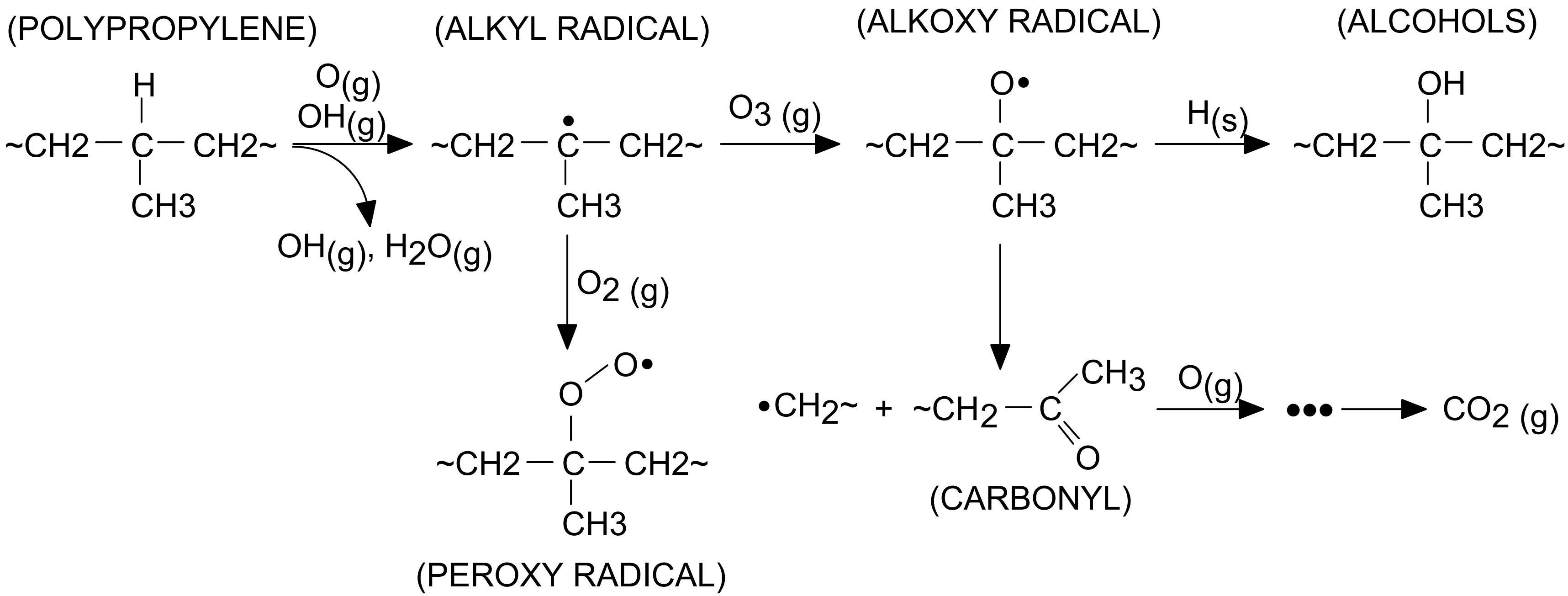
- **Radicals react on PP based on a site balance model.**



University of Illinois
Optical and Discharge Physics

REACTIONS AT PP SURFACE

- **O and OH abstract H from PP to produce alkyl radicals.**
- **Reactions of O_3 and O_2 with alkyl radicals produce peroxy and alkoxy radicals, which further react to form alcohols and carbonyl species.**



University of Illinois
Optical and Discharge Physics

BASE CASE: n_e, T_e

- **Ionization is dominantly of N_2 and O_2,**

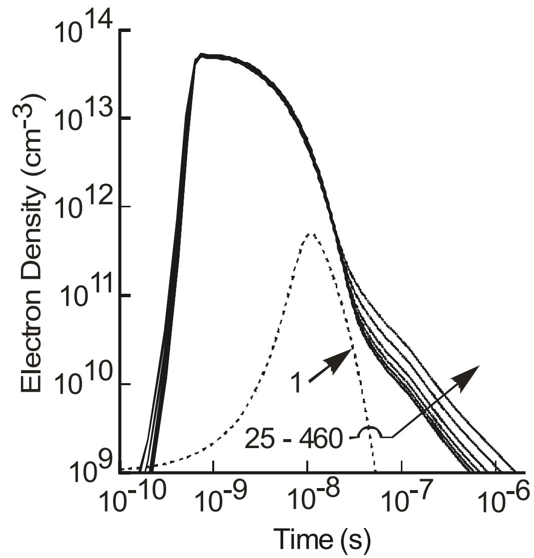
$$e + N_2 \rightarrow N_2^+ + e + e,$$
$$e + O_2 \rightarrow O_2^+ + e + e.$$

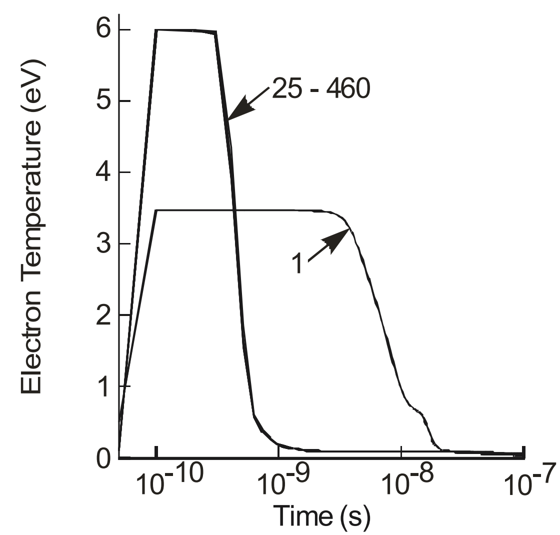
- **Once the gap voltage decreases below sustaining, electrons decay by attachment (primarily to O_2).**

- **The differences between the 1st and later pulses are due to the incomplete charging of the dielectrics on the electrodes.**

- **$N_2/O_2/H_2O$ = 79/20/1, 300 K, 15 kV at 9.6 kHz.**

- **Edep = 0.8 J cm^{-2}, Web speed = 250 cm/s.**



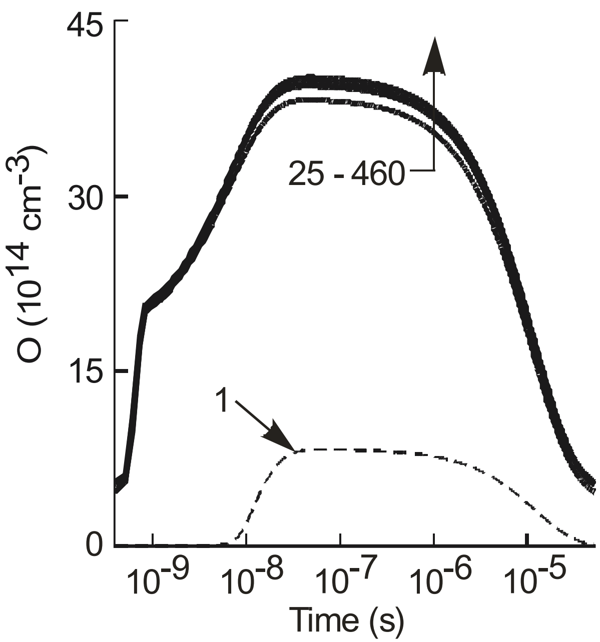


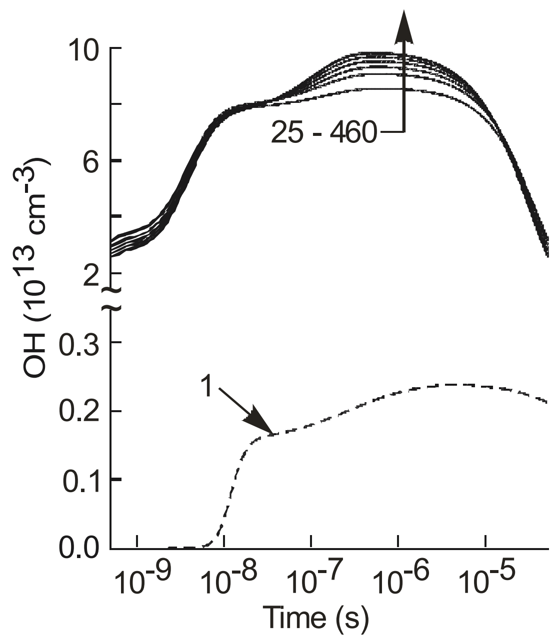
GAS-PHASE RADICALS: O, OH

- Electron impact dissociation of O_2 and H_2O produces O and OH.
- O is consumed in the gas phase primarily to form O_3,

$$O + O_2 + M \rightarrow O_3 + M.$$

- After 100s of discharge pulses, the radicals attain a periodic steady state.

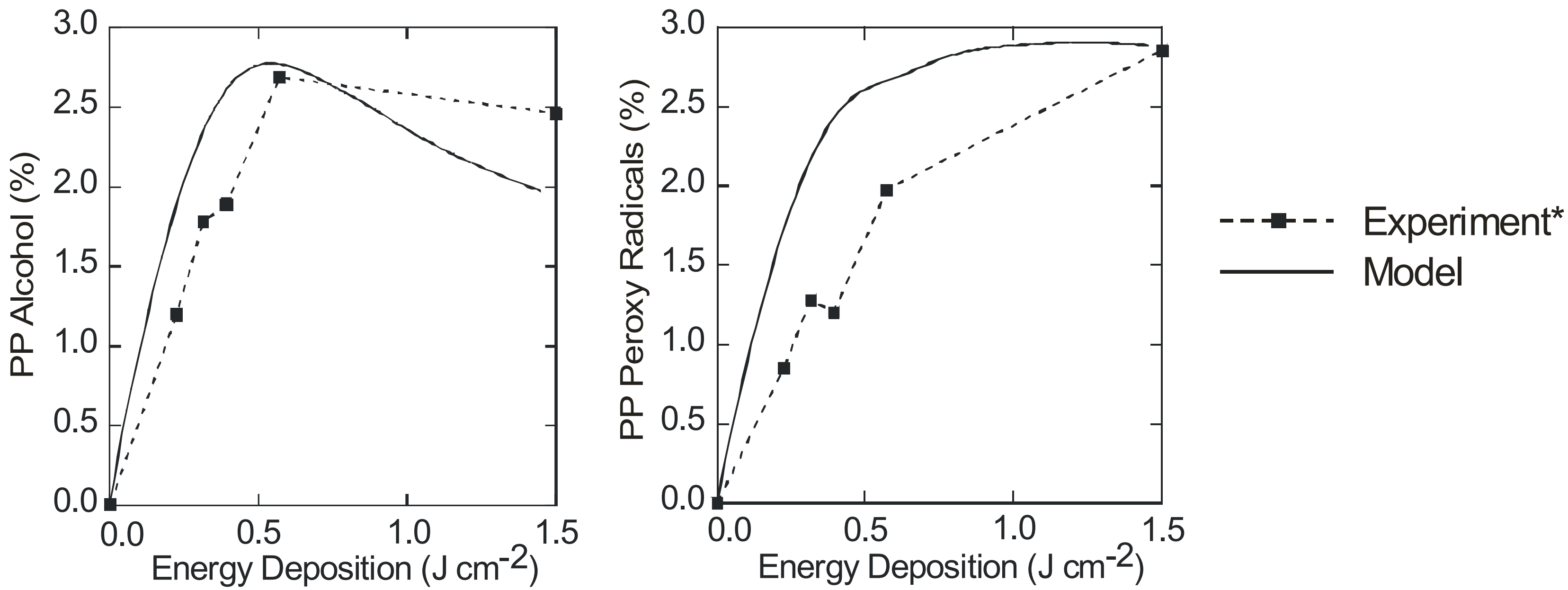




University of Illinois
Optical and Discharge Physics

MODEL VS. EXPERIMENT

- Surface concentrations of alcohols, peroxy radicals achieve near steady state with a few J cm^{-2}.
- Alcohol densities decreased at higher energy deposition due to decomposition by O and OH to regenerate alkoxy radicals.



Air at 300 K, 1 atm, 30% RH

*** L-A. Ohare *et al.*, Surf. Interface Anal. 33, 335 (2002).**

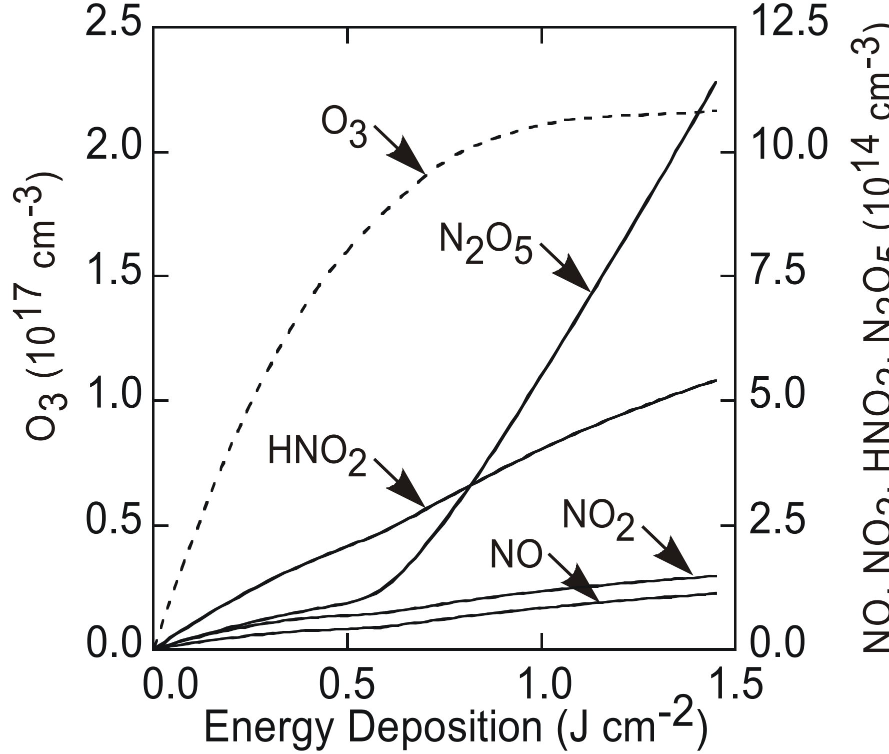
GAS-PHASE PRODUCTS: O_3, N_XO_Y, HNO_X

- O_3 is produced by the reaction of O with O_2,

$$O + O_2 + M \rightarrow O_3 + M.$$

- N-containing products include NO, NO_2, HNO_2 and N_2O_5,

$$N_2 + O \rightarrow NO + N,$$
$$NO + O + M \rightarrow NO_2 + M,$$
$$NO + OH + M \rightarrow HNO_2 + M,$$
$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M.$$



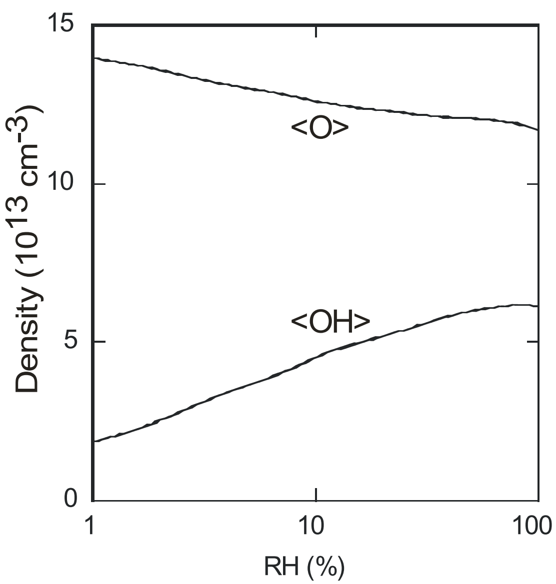
University of Illinois
Optical and Discharge Physics

EFFECT OF RH: PP FUNCTIONALIZATION

- With increasing RH, more OH is produced.
- Due to the high reactivity of OH, more PP alkyl radicals are generated.
- As a result, the densities of peroxy radicals increase,

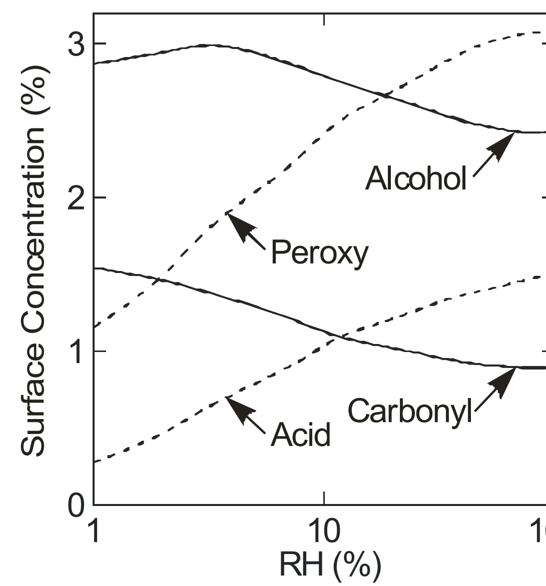
$$PP\text{-}H + OH_{(g)} \rightarrow PP\bullet + H_2O_{(g)} \qquad PP\bullet + O_{2(g)} \rightarrow PP\text{-}O_2\bullet\ .$$

- Alcohol and carbonyl densities decrease at higher RH due to increased consumption by OH to form alkoxy radicals and acids.



$$PP\text{-}OH + OH_{(g)} \rightarrow PP\text{-}O\bullet + H_2O_{(g)}$$

$$PP{=}O\bullet + OH_{(g)} \rightarrow (OH)PP{=}O$$

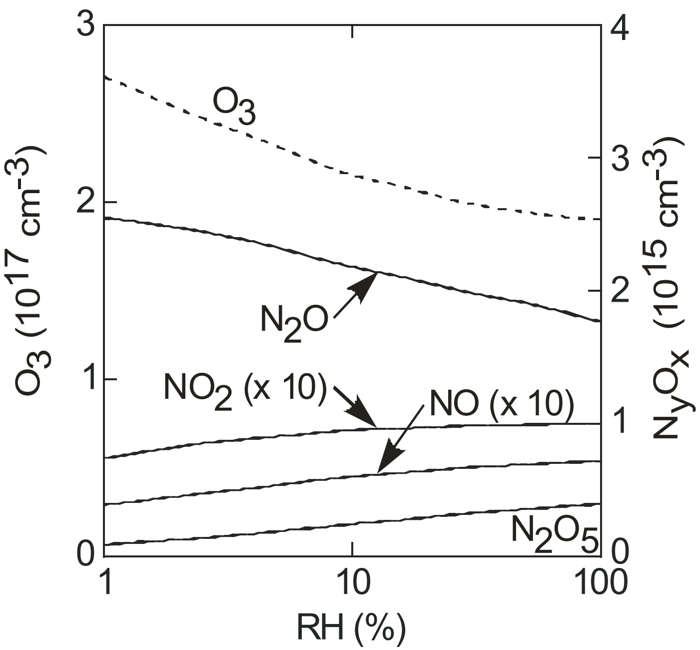


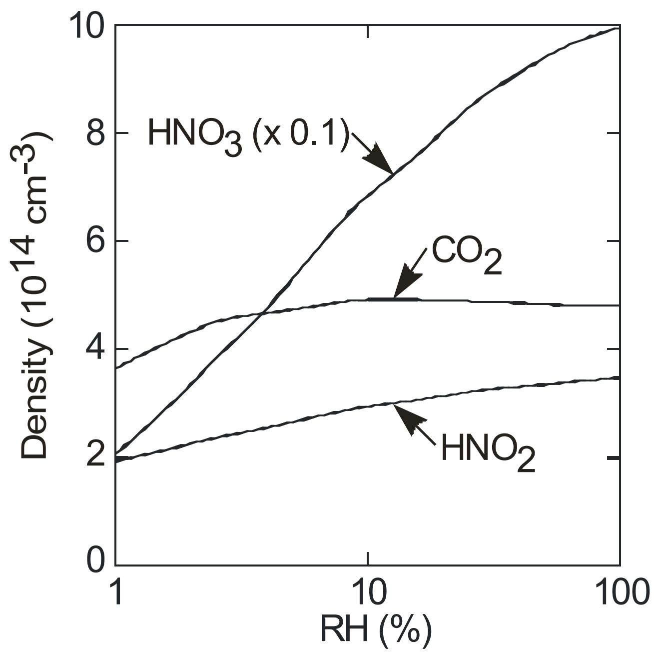
University of Illinois
Optical and Discharge Physics

EFFECT OF RH: GAS-PHASE PRODUCTS

- **Higher RH results in decreasing O atom densities and so the production of O_3 decreases.**
- **Due to the increased production of OH with RH, larger densities of HNO_2 and HNO_3 are produced.**

$$N + OH \rightarrow NO + H, \quad NO + OH \rightarrow HNO_2, \quad NO_2 + OH \rightarrow HNO_3.$$





University of Illinois
Optical and Discharge Physics

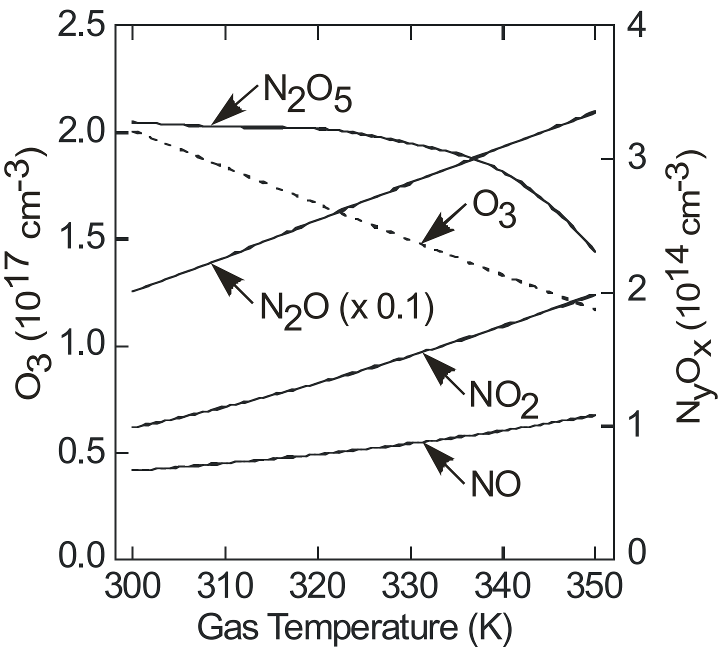
EFFECT OF TEMPERATURE: GAS-PHASE PRODUCTS

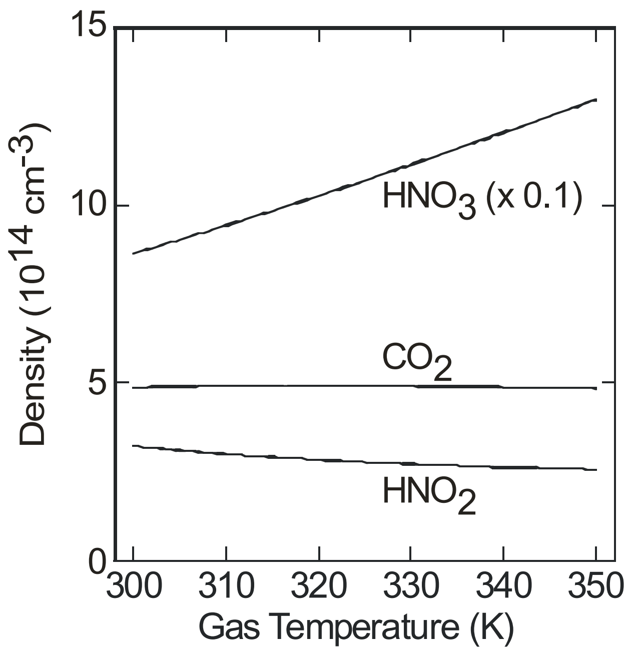
- With increasing gas temperature, consumption of O_3 increases.
- Most of the NO is lost by reduction to N_2 and oxidation to NO_2,

$$NO + N \rightarrow N_2 + O, \qquad NO + O_3 \rightarrow NO_2 + O_2.$$

- N_2O_5 is a maximum at intermediate temperatures,

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M, \qquad N_2O_5 \rightarrow NO_2 + NO_3.$$





University of Illinois
Optical and Discharge Physics

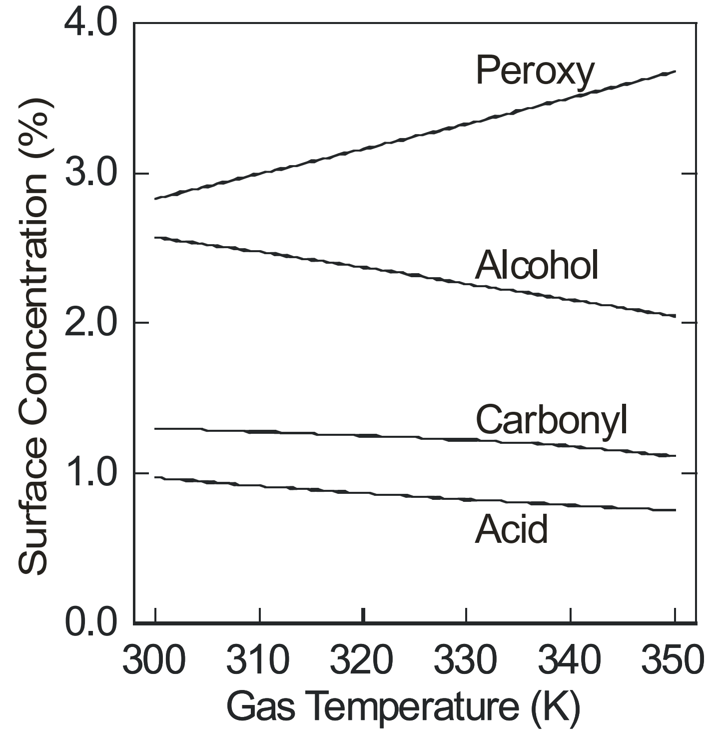
EFFECT OF T_{GAS}: PP FUNCTIONALIZATION

- With increasing gas temperature, the production of O_3 decreases leading to lower alkoxy production,

$$PP\bullet + O_{3(g)} \rightarrow PP\text{-}O\bullet + O_{2(g)}.$$

- … and decreased production of alcohols, carbonyl, and acids,

$$PP\text{-}O\bullet + PP\text{-}H \rightarrow PP\text{-}OH + PP\bullet$$
$$PP\text{-}O\bullet \rightarrow PP{=}O$$
$$PP{=}O \rightarrow PP{=}O\bullet$$
$$PP{=}O\bullet + OH \rightarrow (OH)PP{=}O\bullet$$



- Decreased consumption of alkyl radicals by O_3 enables increased consumption by O_2 increasing the density of peroxy radicals.

University of Illinois
Optical and Discharge Physics

SUMMARY

- A surface reaction mechanism for PP has been developed and validated against experiments.
- With increasing energy deposition the surface concentrations of alcohol, acid, carbonyl, and peroxy groups increase.
- However, significant densities of environmentally sensitive gases such as O_3 (10^{17} cm^{-3}) and HNO_3 (10^{16} cm^{-3}) are generated.
- Increasing RH resulted in increased surface concentrations of peroxy and acid groups and decreased alcohols and carbonyls.
- Operating at larger RH resulted in reduced production of O_3.
- Surface concentrations of alcohol, carbonyl, and acid groups decreased with temperature while those of peroxy groups increased.