# ENVE 576 Indoor Air Pollution Fall 2016

#### Week 5: September 20, 2016

Gaseous pollutants: Reactive deposition and heterogeneous/ homogeneous chemistry

> Dr. Brent Stephens, Ph.D. Department of Civil, Architectural and Environmental Engineering Illinois Institute of Technology <u>brent@iit.edu</u>

> > Built Environment Research Group www.built-envi.com

Built Environment Research @ III

Advancing energy, environmental, and sustainability research within the built environment

# Scheduling update

Course Topics and Tentative Schedule						
Week	Date	Lecture Topics	Reading*	Assignment:		
		Introduction to topic/field				
1	Aug 23	<ul> <li>Indoor and outdoor atmospheres</li> </ul>	1-5			
		Fundamental air principles				
		Reactor models				
		<ul> <li>Steady-state and dynamic</li> </ul>				
2	Aug 30	<ul> <li>Ventilation and air exchange rates</li> </ul>	Reading*         Assignment:           1-5			
		Human exposure patterns				
		<ul> <li>Inhalation and intake fractions</li> </ul>				
		Overview of indoor pollutants/constituents				
		<ul> <li>Particulate matter</li> </ul>				
3	Sep 6	<ul> <li>Gas-phase compounds</li> </ul>	9	9 HW #1 due		
		⇒ Organic and inorganic				
		Biological				
4	Sem 12	Gaseous pollutants	10.12			
4	Sep 15	<ul> <li>Sources and emissions models</li> </ul>	10-15			
		Gaseous pollutants and indoor chemistry				
		<ul> <li>Adsorption/desorption</li> </ul>				
5	Sep 20	<ul> <li>Reactive surface deposition</li> </ul>	14-18			
	_	<ul> <li>Homogenous chemistry</li> </ul>				
		<ul> <li>Reaction byproduct formation</li> </ul>				
		Indoor aerosols				
	Sec. 27	<ul> <li>Single particle physics and dynamics</li> </ul>		11111 #2 days		
0	Sep 27	<ul> <li>Particle size distributions</li> </ul>	19-21	HW #2 due		
		<ul> <li>Respiratory deposition</li> </ul>				
	i	· · · · ·	1			

# **Final project topics**

Name	Project topic
Boyer, Jeffrey L.	
Faramarzi, Afshin	
Liang, Dejun	
Liu, Xiaoqi	
Ma, Peiling	
Meng, Zhenyu	
Rice, Lindsey E.	
Shao, Zhihui (Kevin)	
Wang, Yintong	
Zeng, Yicheng	
Zhang, Peng (indoorenvir)	
Zhang, Xu	
Zhu, Guozhu	
Angulo Duato, Ana Claudia	

#### Remember:

- Teams of up to 2
- Project topic justification due October 4<sup>th</sup>

### **Review from last time**



# Measured impacts of sorption in real rooms

• Injection + adsorption + flush out period + desorption in a bathroom



#### Measured impacts of sorption in real rooms

• Measured and modeled adsorption, flush out, and desorption



#### A note on A/V



# **REACTIVE DEPOSITION**

Heterogeneous chemistry

#### **Indoor environment: Mass balance**



# **Reactive deposition: Why is it important?**

- In lecture 1, we mentioned surface area to volume ratios
  - Average A/V outdoors ~ $0.01 \text{ m}^2/\text{m}^3$  (Nazaroff et al., 2003)
  - Average A/V indoors ~3 m<sup>2</sup>/m<sup>3</sup>
  - Varies ~2-5 m<sup>2</sup>/m<sup>3</sup> in residences and varies by material



Hodgson et al., 2005 LBNL Report "Quantifying object and material surface areas in residences"

#### **Reactive deposition**

- Because of large surface area to volume ratios indoors
  - Surface chemistry can be very important



- Why bother with surface chemistry?
  - Lowers indoor concentration (potentially beneficial)
  - Some by-product formation (potentially harmful)
  - Possible degradation of materials (seldom anything but bad)

#### **Reactive deposition**

• Refer to notes on the board

Summary of mass balance terms (ignoring indoor sources)

$$\frac{dC}{dt} = P\lambda C_{out} - \lambda C - \frac{v_d A}{V}C$$

C = concentration in air inside space of interest (mg/m<sup>3</sup>)  $C_{out} = \text{concentration outside of space (mg/m<sup>3</sup>)}$  V = chamber volume (m<sup>3</sup>)  $\lambda = \text{air exchange rate through space (1/hr)}$  P = penetration factor (-) A = material area (m<sup>2</sup>) $v_d = \text{deposition velocity to material (m/hr)}$ 

$$C_{ss} = \frac{P\lambda C_{out}}{\lambda + \frac{v_d A}{V}} = \frac{P\lambda C_{out}}{\lambda + k_{dep}}$$

 $k_{dep}$  = deposition loss rate coefficient to all materials (1/hr)

# **Reactive deposition: Surface vs. Transport**

- Deposition velocity  $(v_d)$  is often <u>surface-uptake-limited</u> indoors
  - Not always
  - Depends on reactivity of material and fluid dynamics in indoor environment
  - Think in a series of resistances:

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{1}{v_s} = \frac{1}{v_t} + \frac{4}{\gamma \langle v \rangle}$$
$$v_d = \frac{v_s v_t}{v_s + v_t}$$

 $v_s$  = surface-limited deposition velocity (m/hr)  $v_t$  = transport-limited deposition velocity (m/hr)  $\gamma$  = reaction probability (-)  $\langle v \rangle$  = Boltzmann velocity (m/hr)

$$k_{dep} = \frac{v_d A}{V}$$

 $v_d$  and  $\gamma$ 



Fig. 1. Average ozone deposition velocity as a function of reaction probability from laminar forced convection flow parallel to a flat plate, with free stream velocity  $U_{\infty} = 0.1 \text{ m s}^{-1}$ , plate length L = 2 m, ozone diffusivity  $\mathcal{D} = 1.82 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ . The analytical predictions are obtained from equation (31).

### **Reaction probability: Measured** $\gamma$

#### • For ozone (O<sub>3</sub>) on different materials

Reference  $v_{d}(\text{cm s}^{-1})^{*}$ v\* Material  $v_{i}(\text{cm s}^{-1})^{\dagger}$ Simmons and Colbeck, 19901 FEP Teflon  $5.5 \times 10^{-7}$ 0.005 1.5 Dirty glass 0.026 1.37  $2.9 \times 10^{-6}$ Clean glass 0.048 1.37  $5.5 \times 10^{-6}$ 3.8 × 10 <sup>- 5</sup> Gray tiles (new) 0.31 3.45 Red tiles (new) 0.32 1.49  $4.5 \times 10^{-5}$ 0.39  $4.8 \times 10^{-5}$ Gravel 3.45 Concrete slab 0.58 3.13  $7.9 \times 10^{-5}$ 0.32 1.59  $4.4 \times 10^{-5}$ Outdoor concrete  $2.2 \times 10^{-4}$ Bricks (new) 1.03 2.13 Old bricks 1.22 3.13  $2.2 \times 10^{-4}$ Sutton et al., 1976§ Polyethylene sheet 8% rel. humidity 0.006  $7 \times 10^{-7}$ 0.470% rel. humidity 0.012 0.4 $1.4 \times 10^{-6}$  $>2 \times 10^{-4} - 1.9 \times 10^{-6}$ Sabersky et al., 1973 Cotton muslin 0.109-0.015 0.1Lamb's wool  $> 2 \times 10^{-4} - 4.6 \times 10^{-7}$ 0.106-0.004 0.1 $> 2 \times 10^{-4} - 1.9 \times 10^{-6}$ Neoprene 0.097-0.015 0.1Plywood 0.030-0.005 0.1 $4.7 \times 10^{-6} - 5.8 \times 10^{-7}$  $5.1 \times 10^{-6} - 5.5 \times 10^{-8}$ 0.032-0.0005 Nylon 0.1 $3.5 \times 10^{-6} - 1.2 \times 10^{-6}$ Polyethylene sheet 0.024-0.010 0.1 $1.1 \times 10^{-6} - 6.3 \times 10^{-7}$ Linen 0.009-0.005 0.1 $7.0 \times 10^{-7} - 5.5 \times 10^{-8}$ Lucite 0.006-0.0005 0.1 $1.1 \times 10^{-7} \cdot 5.5 \times 10^{-8}$ Aluminium 0.001-0.0005 0.10.001-0.0005  $1.1 \times 10^{-7} - 5.5 \times 10^{-8}$ Plate glass 0.1Mueller et al., 1973 Aluminium 5% rel. humidity 0.00044 0.1 $4.9 \times 10^{-8}$  $7.0 \times 10^{-7} - 1.3 \times 10^{-7}$ 40-50% r.h. 0.006-0.0012 0.187% rel. humidity  $2.4 \times 10^{-6}$ 0.0176 0.1Stainless steel \*\* 0.015-0.008  $1.7 \times 10^{-6} - 9 \times 10^{-7}$ 0.4Cox and Penkett, 1972tt Aluminium 32% rel. humidity 0.00698 0.19 7.7 × 10<sup>-8</sup> 83% rel. humidity 0.00206 0.19  $2.3 \times 10^{-7}$ 

Table 1. Ozone reaction probabilities from chamber decay experiments

#### **Reaction probability: Measured** $\gamma$

#### • For ozone $(O_3)$ , sarin, and $SO_2$ on different materials

Species	Material	$\gamma^{\mathbf{a}}$
Sarin	Silanized glass, 0-60% RH	$1.6 \times 10^{-8}$
	Plastic coated wallpaper	$2.1 \times 10^{-8}$
	Rough spruce, 50-60% RH	$1.9 \times 10^{-8}$
	Chalking paint on concrete	$5.1 \times 10^{-7}$
SO <sub>2</sub>	Gloss paint, 32% RH	$1.5 \times 10^{-7}$
	Gloss paint, 84% RH	$5.0 \times 10^{-6}$
	Aluminum, 78% RH	$5.7 \times 10^{-6}$
	Softwood	$3.1 \times 10^{-4}$
	Hardwood, 65% RH	$6.2 \times 10^{-4}$
	PVC wall covering, 60% RH	$3.9 \times 10^{-5}$
Ozone	Dirty glass	$2.9 \times 10^{-6}$
	Clean glass	$5.5 \times 10^{-6}$
	Bricks (new and old)	$2.2 \times 10^{-4}$
	Outdoor concrete	$4.4 \times 10^{-5}$
	Concrete slab	$7.9 \times 10^{-5}$
	Plywood <sup>f</sup>	$4.7 \times 10^{-6} - 5.8 \times 10^{-7}$
	Plate glass <sup>f</sup>	$1.1 \times 10^{-7} - 5.5 \times 10^{-8}$
	Aluminum <sup>f</sup>	$1.1 \times 10^{-6} - 5.5 \times 10^{-8}$
	Aluminum, 5% RH	$4.9 \times 10^{-8}$
	Aluminum, 40-50% RH	$7.0 \times 10^{-7}$ $-1.3 \times 10^{-7}$
	Aluminum, 32% RH	$7.7 \times 10^{-8}$
	Aluminum, 83% RH	$2.3 \times 10^{-7}$
	Latex paint, <10% RH <sup>f</sup>	$2 \times 10^{-6} - 7 \times 10^{-7}$
	Latex paint, ~80% RHf	$2 \times 10^{-5} - 1 \times 10^{-6}$
	Glass	$< 1 \times 10^{-6}$
	Vinyl wallpaper	$5 \times 10^{-6}$
	Paper wallpaper	$1 \times 10^{-6}$
	Galvanized sheet steel	$1.1 \times 10^{-6}$

Reaction probability  $(\gamma)$  for sarin, SO<sub>2</sub>, and ozone on selected building materials

# **Reaction probability: Measured** $\gamma$

• For ozone (O<sub>3</sub>) on different materials



# Notes on reaction probability

- Can γ change over time?
   Yes
- Why?
  - Wipe out reaction sites over time (decreases  $\gamma$ )
  - Humidity effects (water chemistry)
    - RH can increase  $\gamma$
  - Regeneration of reaction sites
    - Diffusion within material matrix changes concentration gradient
      - Increases  $\gamma$

• Chamber testing for ozone  $(O_3)$  on different materials



# Measured $v_d$

• Chamber testing for ozone  $(O_3)$  on different materials



Fig. 5. Geometric mean ozone deposition velocities for last 5 h of disinfection stage.

Poppendieck et al., 2007 Atmos Environ

# Measured $v_d$

#### • For ozone (O<sub>3</sub>) on different materials

Material	RH (%)	Temp. (K)	$v_{\rm d}~({\rm cm~s^{-1}})$	$v_d$ , aged (cm s <sup>-1</sup> )	vt (cm s <sup>-1</sup> )	$\frac{v_{\rm s}}{({\rm cm}{\rm s}^{-1})}$	$v_s$ , aged (cm s <sup>-1</sup> )	Author
(a) Values of $v_s$ for $O_3$ cal	culated from the lite	rature, inferring v, where neces	sarv					
Lacquered ash	50	294±2	$0.0007 \pm 0.0008$		0.7	0.0007		Klenø et al. (2001)
Oiled ash	50	294±2	$0.003 \pm 0.0007$		0.7	0.003		Klenø et al. (2001)
Oiled beech parquet	50	294±2	$0.0078 \pm 0.0027$		0.7	0.0079		Klenø et al. (2001)
Plywood	50	295	0.030	0.005 <sup>a</sup>	0.75	0.031	0.005 <sup>a</sup>	Sabersky et al. (1973)
Aluminium	87	299	0.0294		0.1	0.042		Mueller et al. (1973)
Aluminium	32	_	0.000698		0.19 <sup>b</sup>	0.00070		Cox and Penkett (1972)
Aluminium	83	_	0.00206		0.19	0.0021		Cox and Penkett (1972)
Carpet nylon fibre latex backing	50	294±2	$0.032 \pm 0.0043$		0.7	0.034		Klenø et al. (2001)
Cotton muslin	50	295	0.109	0.015 <sup>a</sup>	0.75	0.128	0.015 <sup>a</sup>	Sabersky et al. (1973)
Linen	50	295	0.0095	0.0055 <sup>a</sup>	0.75	0.0096	0.0055 <sup>a</sup>	Sabersky et al. (1973)
Nylon	50	295	0.032	0.0005 <sup>a</sup>	0.75	0.033	0.0005 <sup>a</sup>	Sabersky et al. (1973)
Wool (lamb)	50	295	0.107	0.004 <sup>a</sup>	0.75	0.12	0.004 <sup>a</sup>	Sabersky et al. (1973)
Linoleum	50	294+2	$0.007 \pm 0.004^{e}$	$0.004 \pm 0.005^{f}$	0.7	0.0071°	0.004 <sup>f</sup>	Klenø et al. (2001)
Paper wall paper	50	_	4% <sup>d</sup>	_	c	0.042		Reiss et al. (1994)
Painted gypsum board (urethan modified alkyd binding agent)	50	294±2	$0.03 \pm 0.0052$		0.7	0.031		Klenø et al. (2001)
Painted gypsum board (acrylic binding agent)	50	294±2	$0.042 \pm 0.0023$		0.7	0.044		Klenø et al. (2001)

# Measured $v_d$

#### • For nitrogen dioxide (NO<sub>2</sub>) on different materials

Material	RH (%)	Temp. (K)	$v_{\rm d}~({\rm cms^{-1}})$	$v_{\rm t}  ({\rm cm  s^{-1}})$	$v_{\rm s}  ({\rm cm  s^{-1}})$	Author
(a) Values of $v_s$ for NO <sub>2</sub> cal	lculated from the literature, in	ferring v <sub>t</sub> when	re necessary			
Lacquered plywood	50	292	0.00639	3.7	0.0064	Miyazaki (1984)
Painted wood	58	295.5	0.003	3.7	0.003	Miyazaki (1984)
Aluminium	30	304	0.0006	0.13	0.00060	Leaderer et al. (1986)
Aluminium	60	304	0.002	0.13	0.0020	Leaderer et al. (1986)
Painted stainless steel	65	293	0.00083	3.7	0.00083	Miyazaki (1984)
Particle board	50		0.0124	1	0.013	Spicer et al. (1989)
Wool carpet	50		0.0856	1	0.094	Spicer et al. (1989)
Wool carpet	50	294.5	0.0919	3.7	0.094	Miyazaki (1984)
Vinylchloride treated floor- sheet	45	291	0.0022	3.7	0.0022	Miyazaki (1984)
Vinylchloride treated	70	292.5	0.00278	3.7	0.00278	Miyazaki (1984)
floorsheet						
Plastic tile	52	294	0.00333	3.7	0.00333	Miyazaki (1984)
Cotton bathmat	41	291	0.0211	0.13	0.025	Miyazaki (1984)
Cotton bathmat	55	293.5	0.0542	3.7	0.057	Miyazaki (1984)
Cotton bathmat	67	294	0.055	3.7	0.058	Miyazaki (1984)
Curtain (material not stated)	30	296.5	0.00083	3.7	0.00083	Miyazaki (1984)
Cotton terry cloth	50		0.0047	1	0.0047	Spicer et al. (1989)
Cotton/polyester bedspread	50		0.0386	1	0.040	Spicer et al. (1989)
Wool/polyester fabric	50		0.0047	1	0.0047	Spicer et al. (1989)
Plasterboard	44	295.5	0.0169	3.7	0.017	Miyazaki (1984)
Plasterboard	59	293.5	0.02	3.7	0.020	Miyazaki (1984)
Plasterboard	67	293.5	0.0272	3.7	0.027	Miyazaki (1984)
Sandstone	80	295	0.02	1	0.020	Behlen et al. (1996)
Used brick	50		0.059	1	0.063	Spicer et al. (1989)

Grøntoft and Raychaudhuri, 2004 Atmos Environ

## Measured $v_d A/V$ in real environments

#### • $k_{dep}$ for ozone (O<sub>3</sub>) in different environments

Indoor environment		Reference
Aluminum Room (11.9 m <sup>3</sup> )	3.2	Mueller et al., 1973
Stainless Steel Room (14.9 m <sup>3</sup> )	1.4	Ibid.
Bedroom (40.8 m <sup>3</sup> )	7.2	Ibid.
Office (55.2 m <sup>3</sup> )	4.0	Ibid.
Home (no forced air)	2.9	Sabersky et al., 1973
Home (forced air)	5.4	Ībid.
Department Store	4.3	Thompson et al., 1973
Office (24.1 m <sup>3</sup> )	4.0	Allen et al., 1978
Office (20.7 m <sup>3</sup> )	4.3	Ibid.
Office/Lab	4.3	Shair and Heitner, 1974
Office/Lab	3.2	Ibid.
Office/Lab	3.6	Ibid.
13 Buildings, 24 Ventilation Systems	3.6	Shair, 1981; assumes $A/V = 2.8 \text{ m}^{-1}$
Museum	4.3	Nazaroff and Cass, 1986
Museum	4.3	Ibid.
Office/Lab	4.0	Weschler et al., 1989
Office/Lab	3.2	Ibid.
Office	2.5	Ibid.
Lab	2.5	Ibid.
Cleanroom	7.6	Ibid.
Telephone Office	0.8–1.0	Weschler et al., 1994; large office, small A/V
43 Homes	$2.8 \pm 1.3$	Lee et al., 1999

Table 3 Rate Constants (h<sup>-1</sup>) for the Removal of Ozone by Surfaces in Different Indoor Environments

#### Measured $v_d A/V$ in real environments

•  $k_{dep}$  for ozone (O<sub>3</sub>) in one room with different HVAC operation



Sabersky et al., 1973 Environ Sci Technol

Mueller et al., 1973 Environ Sci Technol

# **Measured** $v_d A/V$ in real environments

*k<sub>dep</sub>* for ozone (O<sub>3</sub>) in the same environment w/ different fan speeds and materials



**Fig. 5.** Ozone decay rates for bedroom with 4.4 m<sup>2</sup> of paperless gypsum wallboard (PLGWB) PRM placed on a vertical wall.

### **Reactive deposition: Byproduct formation**

- Reactive deposition to surfaces removes indoor pollutants
  - Can also generate others in the form of reaction by-products

 $R_{byproduct} = Y_i v_d A C f_{conversion}$ 

 $R_{byproduct,i} = by-product i production rate (moles/hr)$   $Y_i = molar yield of i (moles i per moles of gas consumed)$  $f_{conversion} = conversion factor (e.g., \frac{10^{-6}}{MW} to convert from \frac{\mu g}{m^3} to \frac{moles}{hour})$ 

# **Byproduct formation: mass balance**

• Mass balance on reactive pollutant (e.g., ozone)

$$\frac{dC}{dt} = P\lambda C_{O_3,out} - \lambda C_{O_3} - \frac{v_d A}{V} C_{O_3}$$

• Mass balance on byproduct *i* 

$$\frac{dC_i}{dt} = P\lambda C_{i,out} - \lambda C_i + Y_i \frac{v_{d,O_3}A}{V} f_{conversion} C_{O_3}$$

# Example heterogeneous byproduct formation

living room carpet

• Ozone deposition velocity, yields, and secondary emission rates of aldehydes after ozone exposure in 4 homes

10







Ozone deposition velocity for each surface.

Wang and Morrison, 2006 Environ Sci Technol

# O<sub>3</sub> + people in a simulated aircraft cabin



FIGURE 1. Total levels, determined by PTR-MS, of the gaseous organic compounds in the cabin air during 14:00–16:00 for each of the 8 experiments with human subjects present. Also displayed, as stacked bars, are the sums of the positively identified "aldehydes, ketones & organic acids" and "alcohols & hydrocarbons".

# Example heterogeneous byproduct formation

 Skin oils have also recently been identified as being important for heterogeneous ozone chemistry



Fig. 4. Schematic of ozone reacting with squalene on exposed skin. The initial reaction produces both gas phase and surface-bound primary products. Ozone further reacts with surface bound primary products (see Table 3) to produce additional gas-phase products.

0

0,

squalene

# Example heterogeneous byproduct formation

• Skin oils have also recently been identified as being important for heterogeneous ozone chemistry







Initial: Reactants A and B Equilibrium: Reactants A and B. Product AB

# **HOMOGENEOUS CHEMISTRY**

Gas-phase to gas-phase reactions

#### Homogeneous chemistry

Homogeneous reactions also occur in indoor environments
 – Gas *i* + Gas *j* → Byproduct *k*

$$R_{\text{homogeneous}} = -k_{ij}C_iC_jV$$

 $R_{\text{homogeneous}} = \text{loss rate due to homogenerous reactions between } i \text{ and } j$ (moles/hr or  $\mu$ g/hr)  $k_{ij}$  = reaction rate constant (ppb<sup>-1</sup> hr<sup>-1</sup>)  $k_{ij}C_j$  = reaction rate (1/hr)

- Need at least 3 mass balances:
  - Two reactants + product(s)  $R_{byproduct,k} = (k_{ij}C_iC_j)Y_kf_{conversion}$
- For a reaction to be relevant indoors, it must occur on a relevant time scale
  - $k_j C_j$  (1/hr) needs to be on the same order as  $\lambda$  (1/hr)
    - · Reaction must be reasonably fast

### Homogenous chemistry: Mass balance

Summary of mass balance terms:

$$\frac{dC}{dt} = P\lambda C_{out} + \frac{E}{V} - \lambda C - \sum k_j C C_j$$

C = concentration in air inside space of interest (mg/m<sup>3</sup>) $C_{out} = \text{concentration outside of space (mg/m<sup>3</sup>)}$ V = chamber volume (m<sup>3</sup>) $\lambda = \text{air exchange rate through space (1/hr)}$  $C_{j} = \text{concentration of species j in indoor air (mg/m<sup>3</sup>)}$  $k_{j} = \text{reaction rate constant } (\frac{m^{3}}{mg hr} \text{ or } \frac{1}{ppb hr})$  $k_{j} = f(\text{temperature, reactants})$ 

# Homogenous chemistry: Mass balance

• Summary of mass balance terms (steady-state):

$$C_{ss} = \frac{P\lambda C_{out} + \frac{E}{V}}{\lambda + \sum k_j C_j} \qquad k_j = f(\text{temperature, reactants})$$
  
If:  $\sum k_j C_j << \lambda$  If:  $\sum k_j C_j \approx \lambda$ 

r /

Then: reactions are <u>not</u> important

Then: reactions are important

(reaction must occur reasonably fast)

• Mass balance for estimating by-production formation:

$$C_{byproduct,ss} = \frac{\sum y_p k_j C_j C}{\lambda}$$

 $y_p$  = byproduct yield

# Homogeneous chemistry

#### Ozone (O<sub>3</sub>) is an important driver of homogeneous chemistry

- Oxidation chemistry with unsaturated (C=C double bond) VOCs
- Weschler (2000) Indoor Air provides great review of ozone chemistry
  - · Including what reactants are important
- Important reactants include:
  - Terpenes (limonene, pinene, and others)
    - Household cleaners, scented products
  - Fatty acids (oleic acid, linoleic acid)
  - Squalene
- Important byproducts include:
  - Gas phase: aldehydes (including HCHO), carbonyls
  - Particle phase: secondary organic aerosols (low-vapor pressure species that self-nucleate to form small particles or condense on and increase the mass of existing particles)

- Byproducts from indoor chemistry can be respiratory or skin irritants

#### **Reaction byproducts: O<sub>3</sub> + VOCs from cleaning products**



# Gas phrase reaction byproducts (O<sub>3</sub> + VOCs)

Products (reported or inferred for indoor settings) derived from reactions between unsaturated organic compounds and ozone, hydroxyl radicals or nitrate radicals

Product		ict of react	Refs <sup>a</sup>	
	<b>O</b> <sub>3</sub>	OH	NO <sub>3</sub>	
Primary ozonides				a, d
Stabilized Crigee biradicals				d, p, q
Hydroxyl radical				l, o t, u
Alkyl radicals				a, d
Hydroxyalkyl radicals				а
Nitrooxyalkyl radicals			-	а
Hydroperoxy radical			-	l, n, v
Alkoxy radicals			-	a, d, n
Unidentified radical				b
α-Hydroxyhydroperoxides				a, c
Hydrogen Peroxide				h, i
Hydroperoxides				a, h, i, p, q
Peroxy-hemiacetals				p, q
Secondary ozonides				k, p, q
Epoxides				a
Hydroxy carbonyls				a
Dihydroxy carbonyls				а
Hydroxy nitrates				а
Carbonyl nitrates			-	а
Formaldehyde				a, d
Other aldehydes			-	a, d
Acetone				a, d
Other ketones				a, d
Formic acid				а
Other carboxylic acids				a
Organic nitrates				а
Multifunctional oxidation products with carbonyl, carboxylate and/or hydroxyl groups				d, e, f, r, x
Secondary organic aerosols via gas/particle partitioning of low volatility products				i, l, s, v, w

#### O<sub>3</sub> chemistry: Typical VOC concentrations + rate constants indoors

**Table 4** Volatile organic compounds commonly found indoors: typical indoor concentrations and rate constants for their reaction with ozone. N. B.: units of concentration are " $\mu g/m^{3}$ " rather than "ppb", reflecting units used by Brown et al. (1994) in their review of the literature

Common indoor organic	Brown et al., 1994; weighted average <sup>a</sup>	Daisey et al., 1994; geo. mean <sup>b</sup>	Shields et al., 1996; median <sup>c</sup>	Girman et al., 1999; range, median <sup>d</sup>	Rate constant <sup>e</sup>
	$\mu g \ m^{-3}$	$\mu g \ m^{-3}$	$\mu g \ m^{-3}$	$\mu g \ m^{-3}$	
Ethanol	50-100	36	_	_	$2.46 \times 10^{-10}$
Acetone	20-50	10.2	-	7.1-220, 29	$2.46 \times 10^{-10}$
2-Propanol	-	5.6	-	-	$2.46 \times 10^{-10}$
Toluene	20-50	9.8	6	1.6-360, 9	3.69×10 <sup>-12</sup>
1,1,1-Trichloroethane	20-50	24.3	_	0.6-450, 3.6	$2.46 \times 10^{-11}$
m- & p-Xylene	10-20	9.1	5	0.8-96, 5.2	$1.48 \times 10^{-11}$
Dichloromethane	10-20	1.4	_	0.5-360	$2.46 \times 10^{-11}$
Decamethylcyclopentasiloxane	-	-	40	_	2.46×10 <sup>-13</sup>
p-Dichlorobenzene	5-10	_	0.2	0.3-85	$1.72 \times 10^{-12}$
Ethyl acetate	5-10	1.1	_	0.2-65	$2.46 \times 10^{-10}$
n-Decane	5-10	2.9	6	0.3-50	2.46×10 <sup>-13</sup>
Branched C10	_	_	5	_	$2.46 \times 10^{-13}$
n-Undecane	1–5	7	9	0.6-58, 3.7	$2.46 \times 10^{-13}$
n-Dodecane	1-5	10.4	7	0.5-72, 3.5	2.46×10 <sup>-13</sup>
n-Pentadecane	1-5	-	13	_	2.46×10 <sup>-13</sup>
n-Hexadecane	<1	_	11	-	2.46×10 <sup>-13</sup>
n-Tetradecane	1–5	_	11	_	$2.46 \times 10^{-13}$
1,2,4-Trimethylbenzene	5-10	3.9	5	0.3-25	$3.20 \times 10^{-11}$
Octamethylcyclotetrasiloxane	-	_	10	_	2.46×10 <sup>-13</sup>
Ethylbenzene	5-10	2.2	2	0.3-30	3.69×10 <sup>-12</sup>
Nonanal	5-10	_	_	1.2-7.9, 3.1	$2.46 \times 10^{-10}$
2-Butanone	1-5	-	_	0.7–18	$2.46 \times 10^{-10}$
Benzene	5-10	3.2	_	0.6-17, 3.7	$1.72 \times 10^{-12}$
Tetrachloroethylene	5-10	2.7	4	0.3–50	$2.46 \times 10^{-11}$
o-Xvlene	5-10	3	2	0.3-38	$2.46 \times 10^{-10}$
n-Hexane	1-5	1.8	-	0.6-21, 2.9	2.46×10 <sup>-13</sup>
Camphene	10-20	-	-	-	2.21×10 <sup>-8</sup>
1,2-Dichloroethylene	10-20	-	-	-	6.05×10 <sup>-9</sup>
Isoprene	-	_	_	_	2.95×10 <sup>-7</sup>
d-Limonene	20-50	6.7	6	0.3-140, 7.1	$5.14 \times 10^{-6}$
a-Pinene	1–5	-	0.2	0.3-8.4	$2.14 \times 10^{-6}$
Styrene	1–5	1.7	1.5	0.2-6.7	5.31×10 <sup>-7</sup>

#### O<sub>3</sub> chemistry: Typical VOC concentrations + half-lifes indoors

Common indoor organics	50 ppb O3 half-life	50 ppb O3 half-life	100 ppb O3 half-life	100 ppb O3 half-life
	hours	days	hours	days
Ethanol	15700	650	7850	325
Acetone	15700	650	7850	325
2-Propanol	15700	650	7850	325
Toluene	1040000	43500	522000	21700
1,1,1-Trichloroethane	157000	6500	78300	3250
m-p-Xylene	260840	10868	130420	5434
Dichloromethane	156504	6521	78252	3261
Decamethylcyclopentasiloxane	15700000	652000	7820000	326000
p-Dichlorobenzene	2240000	93000	1120000	46500
Êthyl acetate	15700	650	7850	325
n-Decane	15700000	652000	7820000	326000
Branched C10	15700000	652000	7820000	326000
n-Undecane	15700000	652000	7820000	326000
n-Dodecane	15700000	652000	7820000	326000
n-Pentadecane	15700000	652000	7820000	326000
n-Hexadecane	15700000	652000	7820000	326000
n-Tetradecane	15700000	652000	7820000	326000
1,2,4-Trimethylbenzene	120000	5020	60200	2510
Octamethylcyclotetrasiloxane	15700000	652000	7820000	326000
Ethylbenzene	1040000	44000	520000	22000
Nonanal	15700	650	7850	325
2-Butanone	15700	650	7850	325
Benzene	2230000	93000	1120000	46500
Tetrachloroethylene	157000	6500	78300	3250
o-Xylene	15700	650	7850	325
n-Hexane	15700000	652000	7820000	326000
1,2-Dichloroethylene	636	27	318	13
Camphene	174	7.2	87	3.6
Isoprene	13	0.54	6.5	0.27
d-Limonene	0.75	0.03	0.37	0.02
a-Pinene	1.80	0.08	0.90	0.04
Styrene	7.25	0.30	3.62	0.15

Table 5 Half-lives for the reaction of ozone with volatile organic compounds commonly found in indoor air

# Other homogeneous chemistry

- Hydroxyl radical (·OH)
  - Formed during ozone-terpene chemistry
  - Strong oxidant and reacts with almost any hydrocarbon (very fast)
  - Concentrations typically ppt
  - Byproducts from oxidation are expected to be more irritating and corrosive than their precursors
     Weschler and Shields 1996 Environ Sci Technol
- Nitrate radical (NO<sub>3</sub><sup>-</sup>)
  - Forms as product of reaction between O<sub>3</sub> and NO<sub>2</sub>
  - Targets reactions with terpenes
  - Concentrations typically ppt

Weschler et al. 1992 Environ Sci Technol

#### **SOA: Secondary organic aerosols**



# **SOA formation from homogeneous chemistry**



# **SOA formation from homogeneous chemistry**



#### We can also have heterogeneous SOA formation

 $O_3$  + Surface-sorbed Terpenes  $\rightarrow$  Secondary Organic Aerosol



### Indoor chemistry in residences

Volatile organic compound conversion by ozone, hydroxyl radicals, and nitrate radicals in residential indoor air: Magnitudes and impacts of oxidant sources

• Monte Carlo modeling to predict O<sub>3</sub>, OH, and NO<sub>3</sub> concentrations and their impacts on reactions with common indoor VOCs in residences

 $C_{i} = \frac{p_{i}\lambda C_{i,o} + E_{i}/(V\Gamma_{i}) + R_{S,i}}{\lambda + \beta_{i} + R_{L,i}}$  Total VOC conversion rate by each oxidant =  $C_{ox} \sum_{j} (k_{j \cdot ox}C_{j})$ 

 Results suggest that total VOC conversion is dominated by reactions with O<sub>3</sub> (reacting mostly with D-limonene) AND with OH (which reacted with D-limonene, other terpenes, alcohols, aldehydes, and aromatics

# **SOA in residences**

Secondary organic aerosol in residences: predicting its fraction of fine particle mass and determinants of formation strength

- Monte Carlo modeling to predict indoor SOA mass formed in residences due to the oxidation of 66 reactive organic compounds by ozone or the hydroxyl radical
  - Used the RIOPA data set



# **SOA in residences**

Secondary organic aerosol in residences: predicting its fraction of fine particle mass and determinants of formation strength

- Results: SOA typically a small fraction of total indoor PM<sub>2.5</sub> mass conc.
  - Except in about 10% of the cases, SOA contributed to >30% of total indoor PM<sub>2.5</sub>
  - Highest in homes with high terpene emissions (mostly d-limonene)
     and high outdoor ozone



Before moving on to particulate matter in the next lecture ...

### **CONTROL OF GAS PHASE COMPOUNDS**

# **Control of VOCs and inorganic gases**

- There are a few important ways to control (i.e., remove) VOCs and inorganic gases:
  - 1. Source control
  - 2. Adsorption-based air-cleaning (e.g., activated carbon)
  - 3. Photocatalytic air-cleaning (e.g., UV/PCO)
  - We won't spend much time on these but we need to know they exist
    - You may incorporate into your final project too

## Source control/substitution

- Simple enough: this involves switching to low-emitting materials
  - We've discussed this already in some form



# Adsorption: activated carbon

- Microporous activated carbon adsorbents
  - Very high surface areas
    - e.g., 800-2000 m<sup>2</sup>/g







Measured in Center of Room



# UV+PCO

- Ultraviolet (UV) photocatalytic oxidation (PCO)
  - Honeycomb reactor coated with  $TiO_2$
  - Structure is irradiated with UV light
  - VOCs adsorb reversibly on the catalyst
  - React to form CO<sub>2</sub> and water
    - TiO<sub>2</sub> semi-conductor sensitizes light-induced reactions ٠

http://hdestaillats.lbl.gov/research.htm

TIO<sub>2</sub>

particle

hν

h



0.

#### **Next few lectures**

- HW 2 is assigned now; due in 1 week
- Next few lectures: Indoor aerosols