THE HYDROCARBON CLOCK: A TOOL TO DISTINGUISH BETWEEN MIXING AND REACTION

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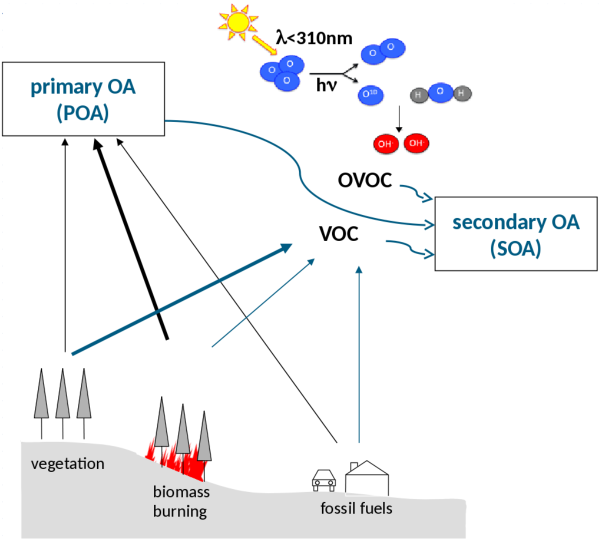
JÜLICH
Forschungszentrum

Organic Compounds - Formation Fate and Impact on Troposphere



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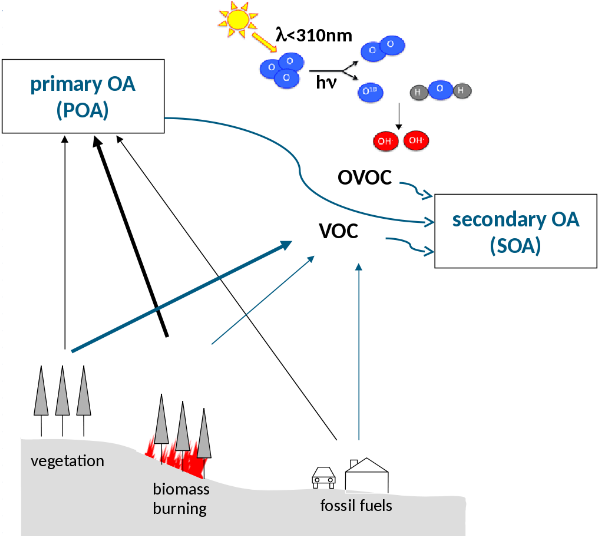
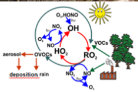
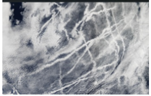






Definitions

VOC: organic compounds with $T_B < 520K$

Methane is usually not included in VOC due to its

- high emission rates
- low reactivity compared to most other VOC

sometimes 'NMVOC'

Other definition based on vapor pressure at room T

- VOC (gas phase only) $p_i > 10^{-2} Pa$
- SVOC (both gas and particle phase) $10^{-6} < p_i < 10^{-2} Pa$
- non-volatile (particle phase only) $p_i < 10^{-6} Pa$

Important VOC categories by chemical composition

Non-methane hydrocarbons NMHC

- alkanes (ethane, propane, butanes, pentanes...), alkenes (ethene, propene), alkynes (acetylene)
- aromatic compounds (benzene, toluene, xylenes, ethylbenzene...)
- isoprene, terpenes (alkenes!)

Halogenated VOC

- methyl halides (methyl chloride, methyl bromide, dichloromethane, trichloromethane, tetrachloromethane, trichloroethane)
- chloroflurocarbons (CFC), hydrochloroflurocarbons (HCFC), hydrofluorocarbons (HFC)
- halons (bromine containing CFC or HCFC)

Oxygenated VOC (OVOC)

- carbonyls (formaldehyde, acetaldehyde, acetone)
- alcohols (methanol, ethanol)
- acids (formic acid, acetic acids)

VOC source types

Anthropogenic ”man-made”

- emissions from cars and trucks, chemical industry, use of solvents, production and distribution of fuels, natural gas, crude oil, domestic heating

Biogenic

- emissions from foliage (trees and bushes), grasslands, soil, oceans (90 %)

Pyrogenic (Biomass Burning)

- forrest and savannah fires, use of biofuels (domestic heating, cooking), charcoal making, burning of agricultural waste, forest clearing

VOC chemistry

Loss processes

- photolysis
- deposition
- transport into the stratosphere
- BUT: PHOTOCHEMISTRY IS DOMINANT

O_xH radicals, ozone, Cl radical, NO_3

OH radical chemistry

- average global concentration 10^6 molecules cm^{-3}
- strong diurnal cycle
  midday maximum in summer up to several 10^7 molecules cm^{-3}
  nighttime OH is very low, often effectively zero

Complex feedbacks

- VOC reactions form oxidants
- oxidants play key role in formation of reactants
- reactant concentrations determine VOC reaction rates

Basic reaction kinetics

Pseudo-1st-order reaction

- $RH + \cdot OH \rightarrow R\cdot + H_2O$ second order
- considering [OH] constant / excess → pseudo-1st-order

Reaction rate, rate constant

$$\frac{-dRH}{dt} = k[RH][OH] \tag{1}$$

$$\frac{1}{[OH]_0 - [RH]_0} ln \frac{[OH][RH]_0}{[OH]_0[RH]} = kt \tag{2}$$

$$[OH]_0 >> [RH]_0, [OH]_0 \approxeq [OH] \rightarrow \frac{1}{[OH]} ln \frac{[RH]_0}{[RH]} = kt \tag{3}$$

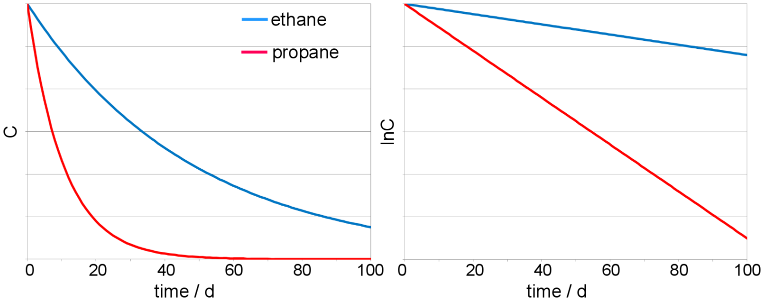
$$[RH] = [RH]_0 e^{-k[OH]t} \tag{4}$$

with k[OH] const. → first order

Graphing pseudo-1st-order reactions

Ethane and Propane

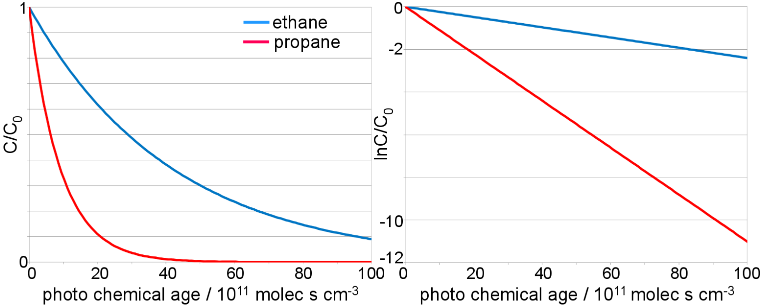
- k_{ethane} = 2.5 10^{-13} cm^3 molec $^{-1}$ s $^{-1}$ IUPAC
- $k_{propane}$ = 1.1 10^{-12} cm^3 molec $^{-1}$ s $^{-1}$ IUPAC



Graphing pseudo-1st-order reactions: in the lab

- from equation 3

$$ln\frac{[RH]_0}{[RH]} = k[OH]t \quad (5)$$



Half-lives of pseudo-1st-order reactions

Definition

- The half-life $t_{\frac{1}{2}}$ is the time in which the initial concentration decreases by half of its original value

Calculating half lives

$$[RH]_{\frac{1}{2}} = \frac{1}{2}[RH]_0 \quad (6)$$

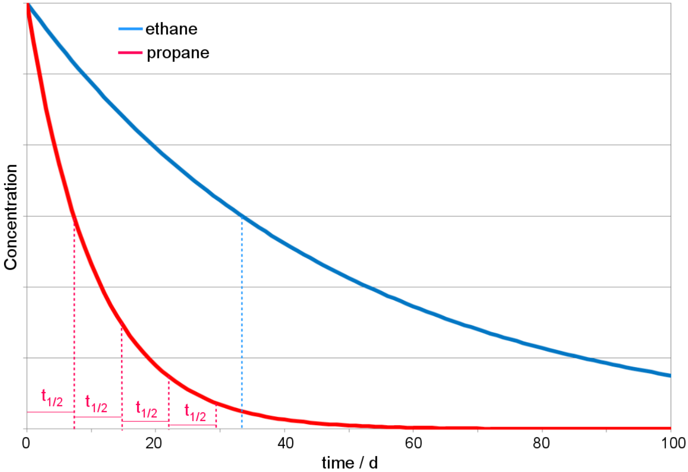
from equation 4:

$$\frac{[RH]_{\frac{1}{2}}}{RH]_0} = \frac{1}{2} = e^{-k[OH]t} \quad (7)$$

$$ln0.5 = -k[OH]t_{\frac{1}{2}} \quad (8)$$

$$t_{\frac{1}{2}} = \frac{ln2}{k[OH]} \quad (9)$$

Half-lives of pseudo-1st-order reactions: in the lab

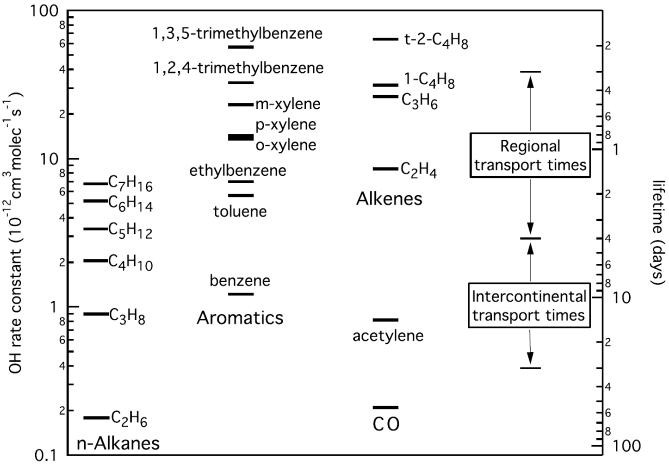


$t_{\frac{1}{2}}$ constant

- independent of initial concentration
- not the case with other reaction orders
- the higher the rate the lower the half-life

Rate constants and corresponding atmospheric lifetimes

$[OH] = 10^6 molec \cdot cm^{-3}$



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VOC life time and transport (1)

Very low reactivity $\tau >$ decades

Nearly uniform distribution in troposphere, loss often dominated by transport into the stratosphere, significant accumulation even for low emission rates, little seasonal variability. Example: CFC

Medium to low reactivity $\frac{1}{2}$ year$< \tau <$ decades

Well distributed within hemispheres, often substantial gradients between hemispheres, some transport into stratosphere, limited accumulation, strong seasonal cycles within hemispheres. Examples: methyl chloride, methyl bromide, carbonyl sulfide, HCFC

Medium reactivity month $< \tau < \frac{1}{2}$ year

Continental scale impact, often strong hemispheric gradients and strong seasonal cycle, very little transport into stratosphere. Examples: ethane, dichloromethane, tetrachloroethene

VOC life time and transport (2)

High reactivity day $< \tau <$ month

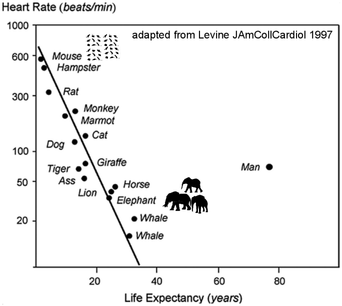
Local to regional impact, high spatial and temporal variability.

Examples: propane, benzene, toluene, acetone, methanol, formic acid, acidic acid, dimethylsulfide

Very high reactivity hours $< \tau <$ day

Local impact, very high spatial and temporal (diurnal) variability

Examples: ethene, propene, isoprene, terpenes, formaldehyde, acetaldehyde



Aging in an isolated air parcel

NHMC pairs

- Simultaneous consideration of two NMHC in an isolated air parcel removes the necessity of knowing the absolute magnitude of the NMHC concentration at the initial emission time
- Comparison of estimates of the photo chemical age from two different NMHC ratios provides a test of the quantitative utility

One or two different NMHC ratios

$$[OH]t = -\frac{1}{k_A} ln \frac{[A]}{[A]_0} \tag{10}$$

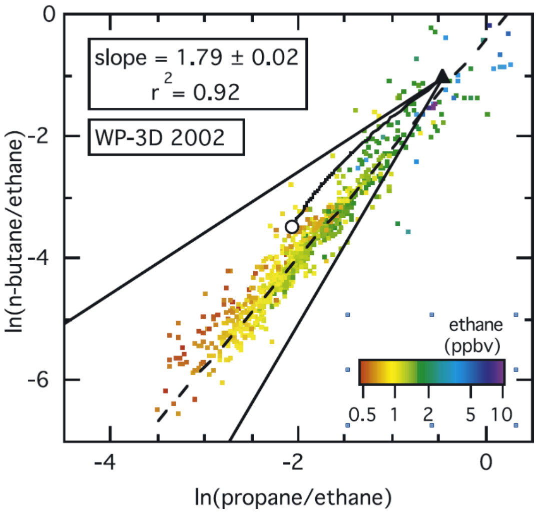
$$[OH]t = -\frac{1}{k_A - k_B} \left(ln \frac{[A]}{[B]} - ln \frac{[A]_0}{[B]_0} \right) \tag{11}$$

$$ln \frac{[A]}{[C]} = \frac{k_C - k_A}{k_C - k_B} ln \frac{[B]}{[C]} + M \tag{12}$$

where M depends on emission ratios and rate constants

$$M = ln \frac{[A]_0}{[C]_0} - \frac{k_C - k_A}{k_C - k_B} ln \frac{[B]_0}{[C]_0} \tag{13}$$

Aging of three hydrocarbons over eastern North Pacific



predicted slope 2.61 for aging of an isolated air parcel

- lower ethane concentrations generally correlate with lower ratios → aging
- data are within the aging of an isolated air parcel/mixing of fresh emissions boundaries

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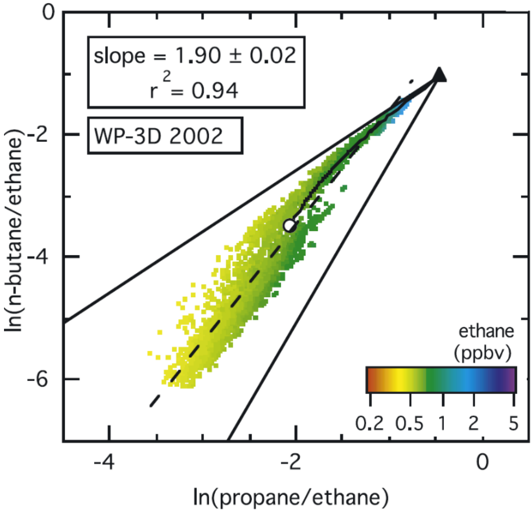
Impact of mixing among air parcels

- To hinder failure of the simple relationship between NMHC concentrations given by equation 12, a continuous, variable emission flux, $[A]'(t_E)$, is introduced into the final sampled air parcel
- Each differential emission, $[A]'(t_E)dt_E$, has its own, well-defined emission time, t_E. and represents the concentration of the NMHC that was emitted at time t_E and remains in the air parcel when sampled at time t_M

$$[A]'(t_E) = [A]'_0(t_E)e^{-\int_{t=t_E}^{t_M} k_A[OH]dt} \quad (14)$$

- A hemisphere scale chemical transport model is required for the solution of equation 14, that decouples chemistry from transport.
- LPDM FLEXPART $\rightarrow$ age spectra of NMHC using CO age spectra

Evolution of NMHC ratios in the troposphere using FLEXPART



slope is still lower than 2.61 → aging + mixing

- separation of colors towards mixing or aging might be explained by lowersmaller mixing impact when a single large injection of NMHC occurs

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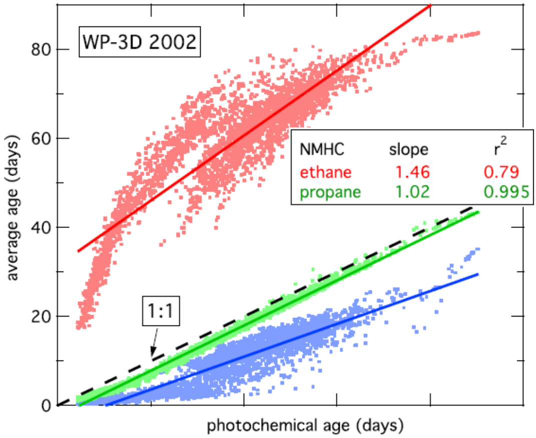
Measurements vs. Model



- average age of each alkane correlates reasonably well with the photochemical age
- slopes different than unity
- the approximations and correlations will be better in air parcels where the concentrations of the species of interest were all injected in a narrow period of time in the past; that is, when a sharply peaked age spectra exists

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Summing-up...

VOC impact on atmosphere

Definitions, categories

Reactivity

Hydrocarbon clock

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VOC are the key to atmospheric chemistry

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the higher the reaction rate, the lower the lifetime
higher spatial and temporal variability for shorter-lived species

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the concept of identical $\int [OH] dt$ has to be replaced by individual values for VOC with different reactivity

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additional information is needed → stable isotopes?