Investigation of the aqueous oxidation of terpenoic alcohols by OH as a potential source of secondary organic aerosols

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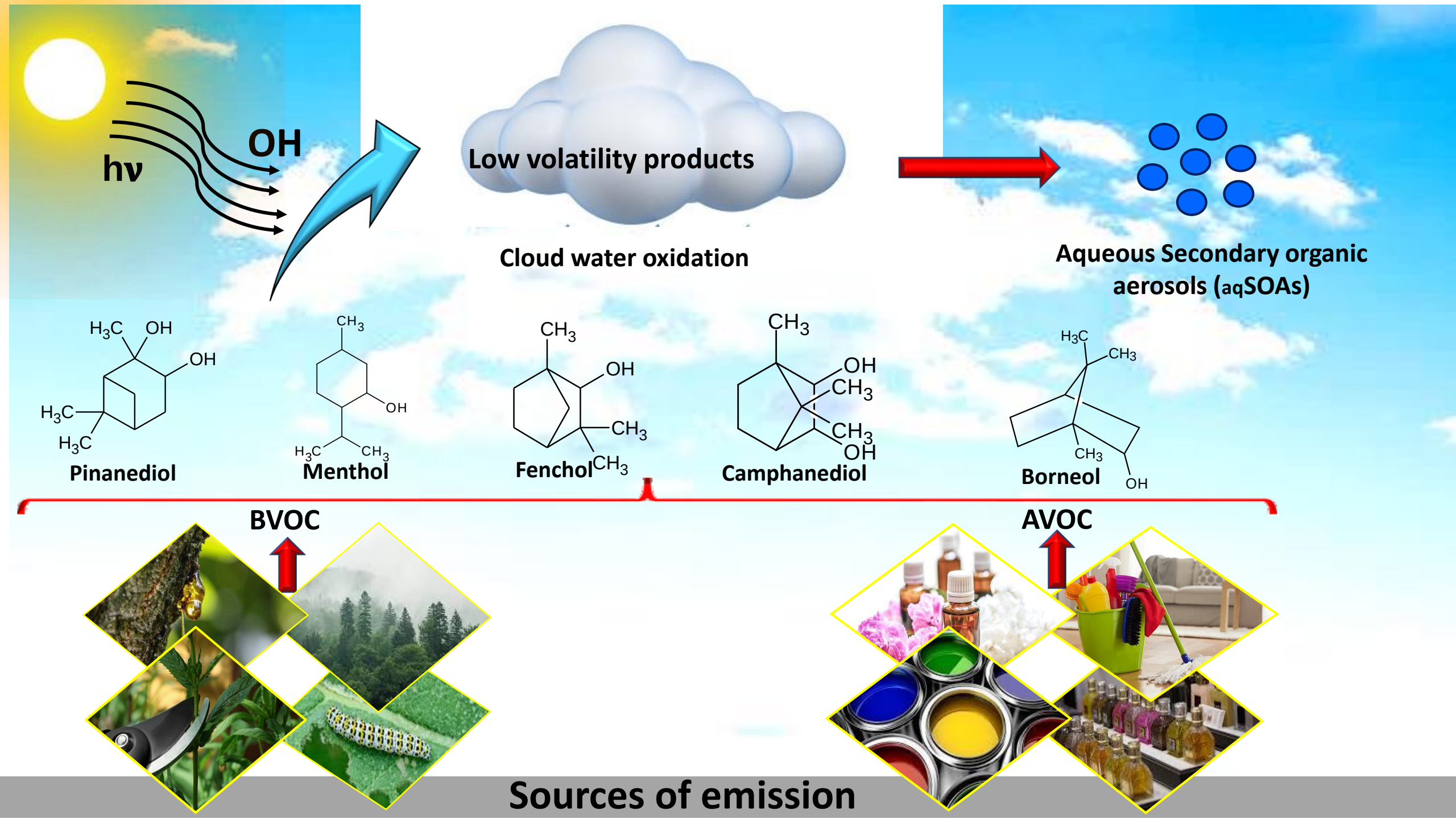
Some terminology:

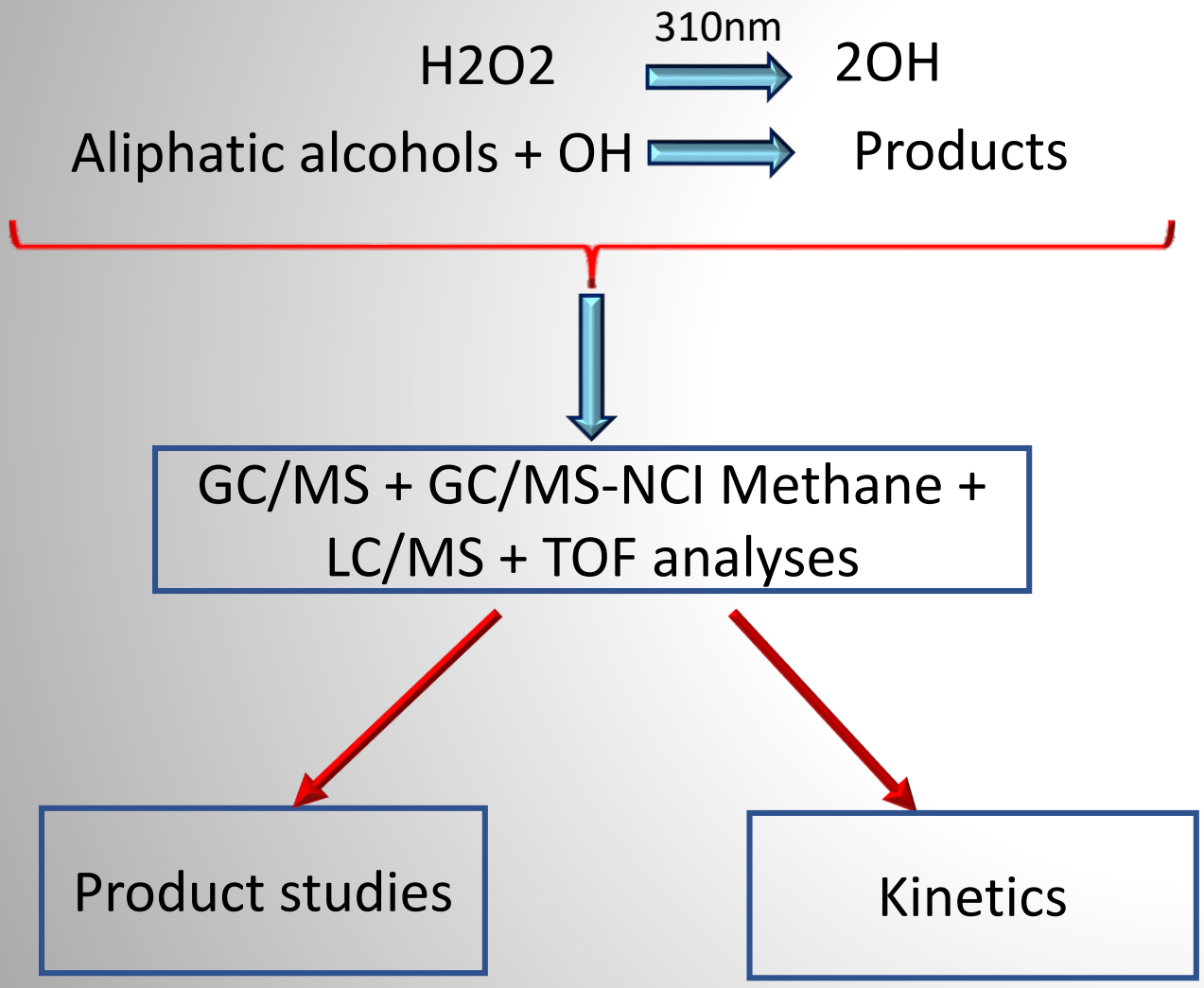
- Volatile Organic Compounds (VOCs) - An organic compounds that has a high vapor pressure depending on their individual boiling point (50-250C).

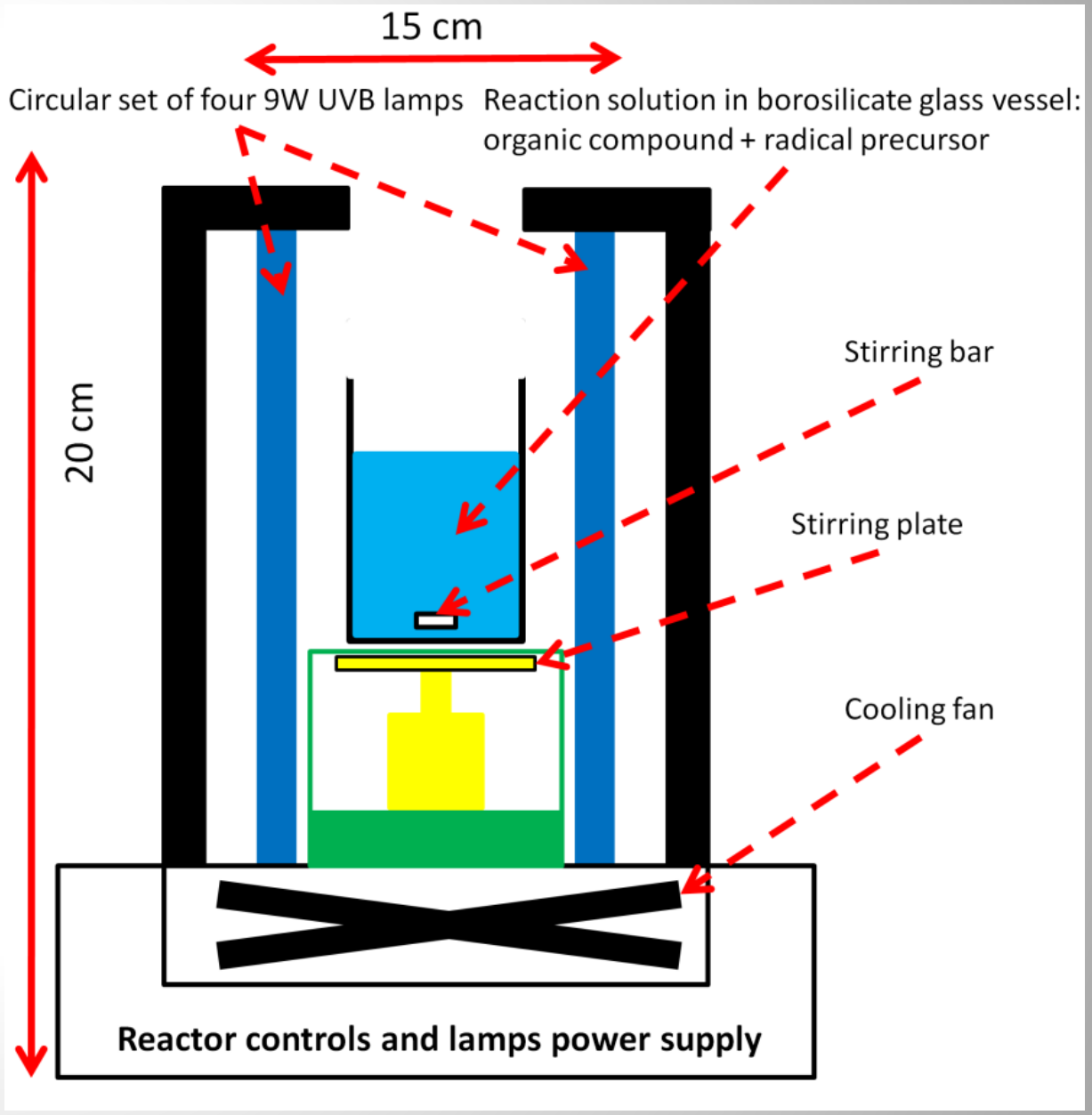
- Primary Organic Aerosols (POAs) – that directly emitted.

- Secondary Organic Aerosols (SOAs)- Organic aerosols that are formed from the reaction of gas or aqueous phase precursor molecules.


hν
OH
Low volatility products
Cloud water oxidation
Aqueous Secondary organic aerosols (aqSOAs)
Pinanediol
Menthol
Fenchol
Camphanediol
Borneol
BVOC
AVOC
Sources of emission

Aqueous photoreactor

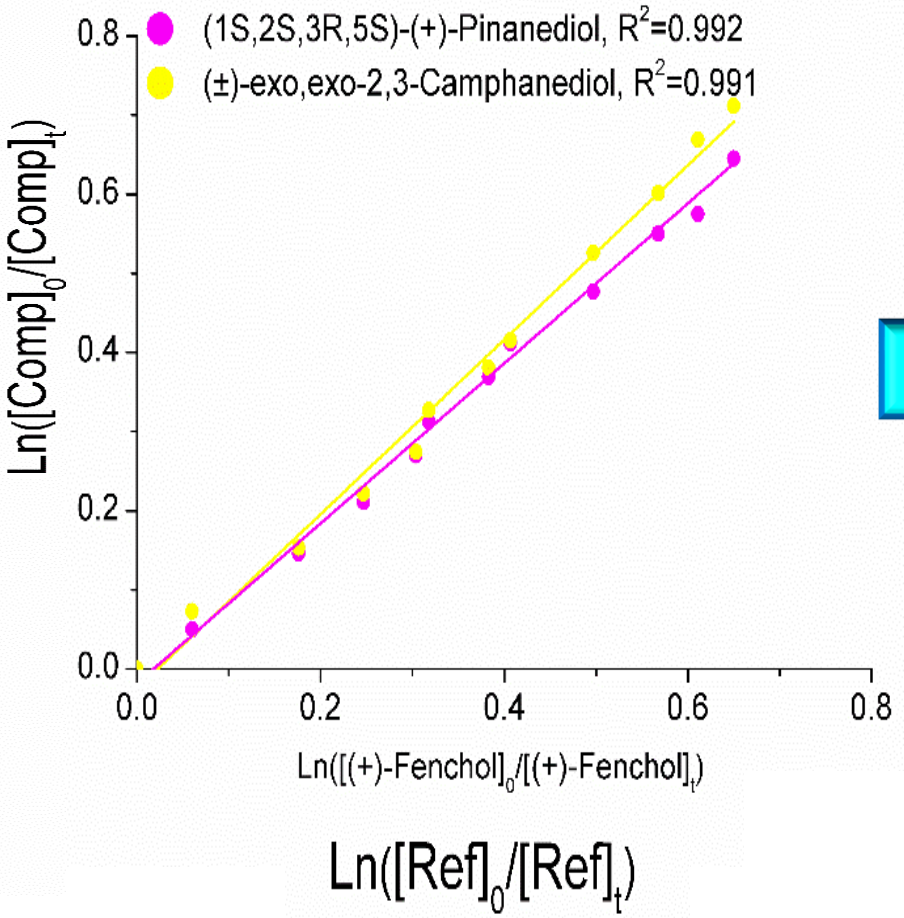




kinetics measurement for Terpenoic alcohol at different temperatures

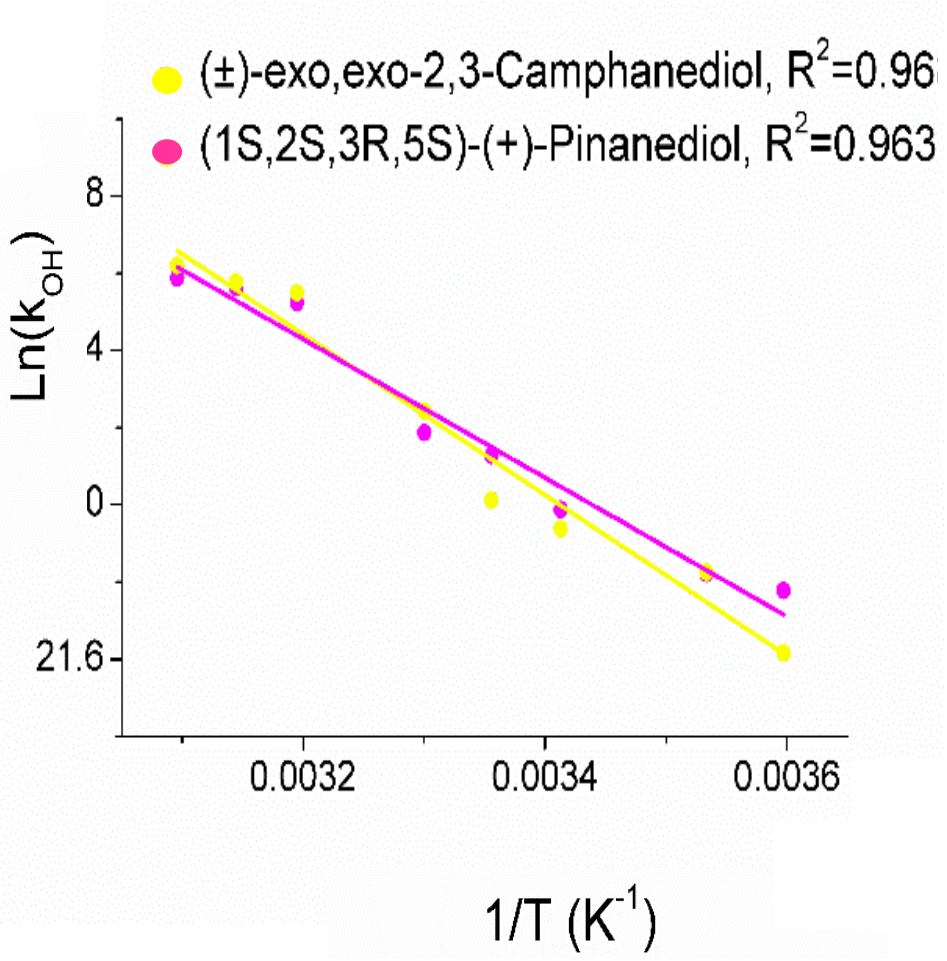
Kinetics; relative rate method

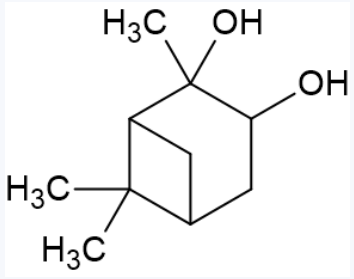
$$\mathrm{Ln}\left(\frac{[\mathrm{Analyte}]_0}{[\mathrm{Analyte}]_t}\right) = \frac{k_{\mathrm{Analyte}}}{k_{\mathrm{Reference}}}\,\mathrm{Ln}\left(\frac{[\mathrm{Reference}]_0}{[\mathrm{Reference}]_t}\right)$$



Activation parameters

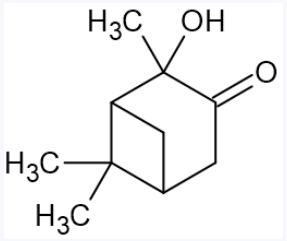
$$K = Ae - E\,a/R\,T$$



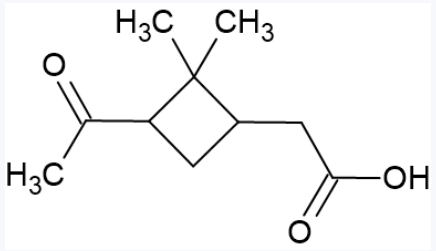


2,3-Pinanediol

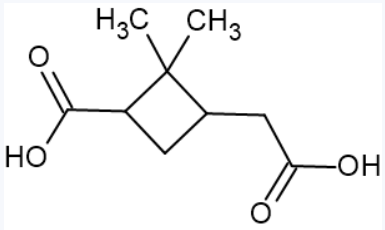
+ OH_{aq} → **Products**



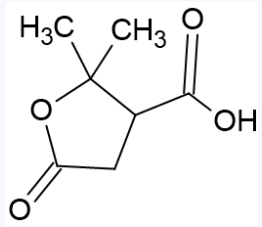
2-hydroxy-3-Pinanone



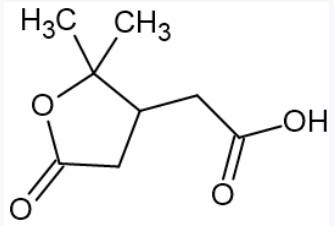
Pinonic acid



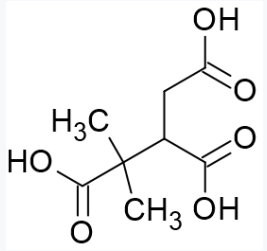
Pinic acid



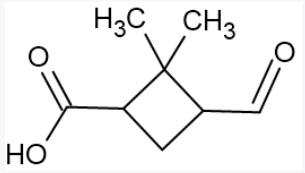
Terebic acid



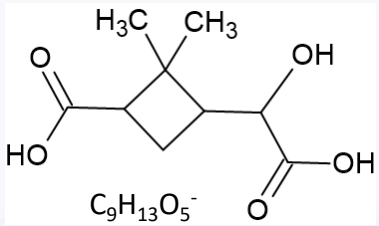
Terpenylic acid



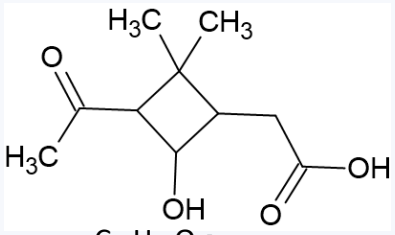
MBTCA



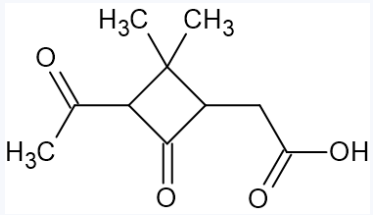
$C_8H_{11}O_3^-$
m/z:155.07



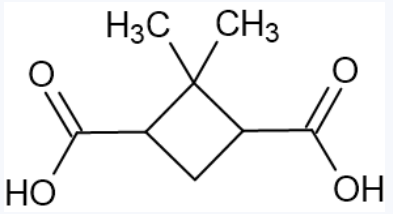
$C_9H_{13}O_5^-$
m/z:201.07



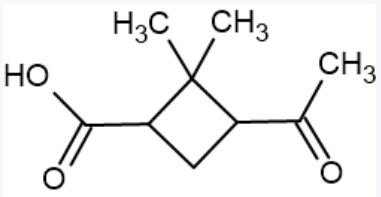
$C_{10}H_{15}O_4^-$
m/z:199.09



$C_{10}H_{13}O_4^-$
m/z:197.08

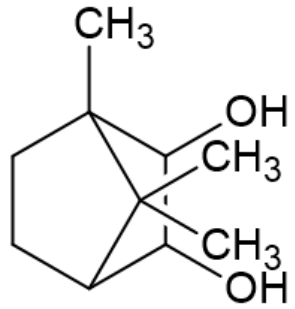


Norpinic acid



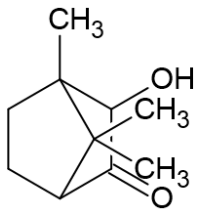
Norpinonic acid

Aqueous oxidation of 4-nitrophenol by hydroxyl radicals; products, mechanism and light absorptivity, B. Witkowski, P. Jain, and T. Gierczak, Atmospheric Chemistry and Physics, 22, 5651–5663, 2022 https://doi.org/10.5194/acp-22-5651-2022



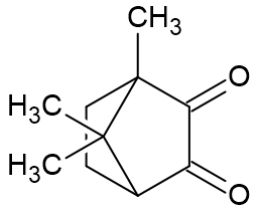
2,3-Camphanediol

+ OH_{aq} → **Products**

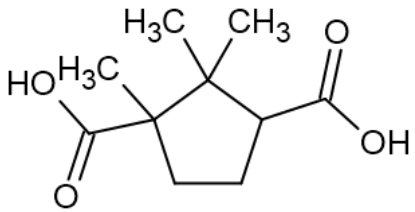


$C_{10}H_{16}O_2$

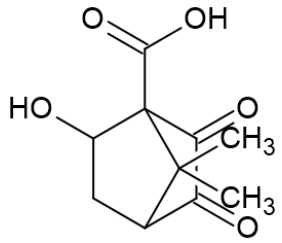
m/z:168.23



Camphorquinone

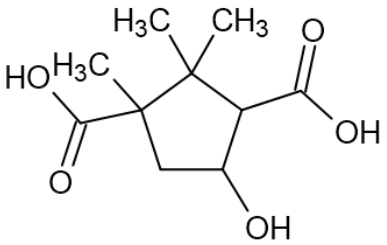


Camphoric acid



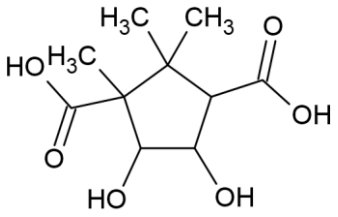
$C_{10}H_{12}O_5$

m/z:212.19



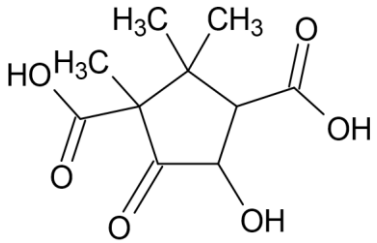
$C_{10}H_{16}O_5$

m/z:216.23



$C_{10}H_{16}O_6$

m/z:232.23

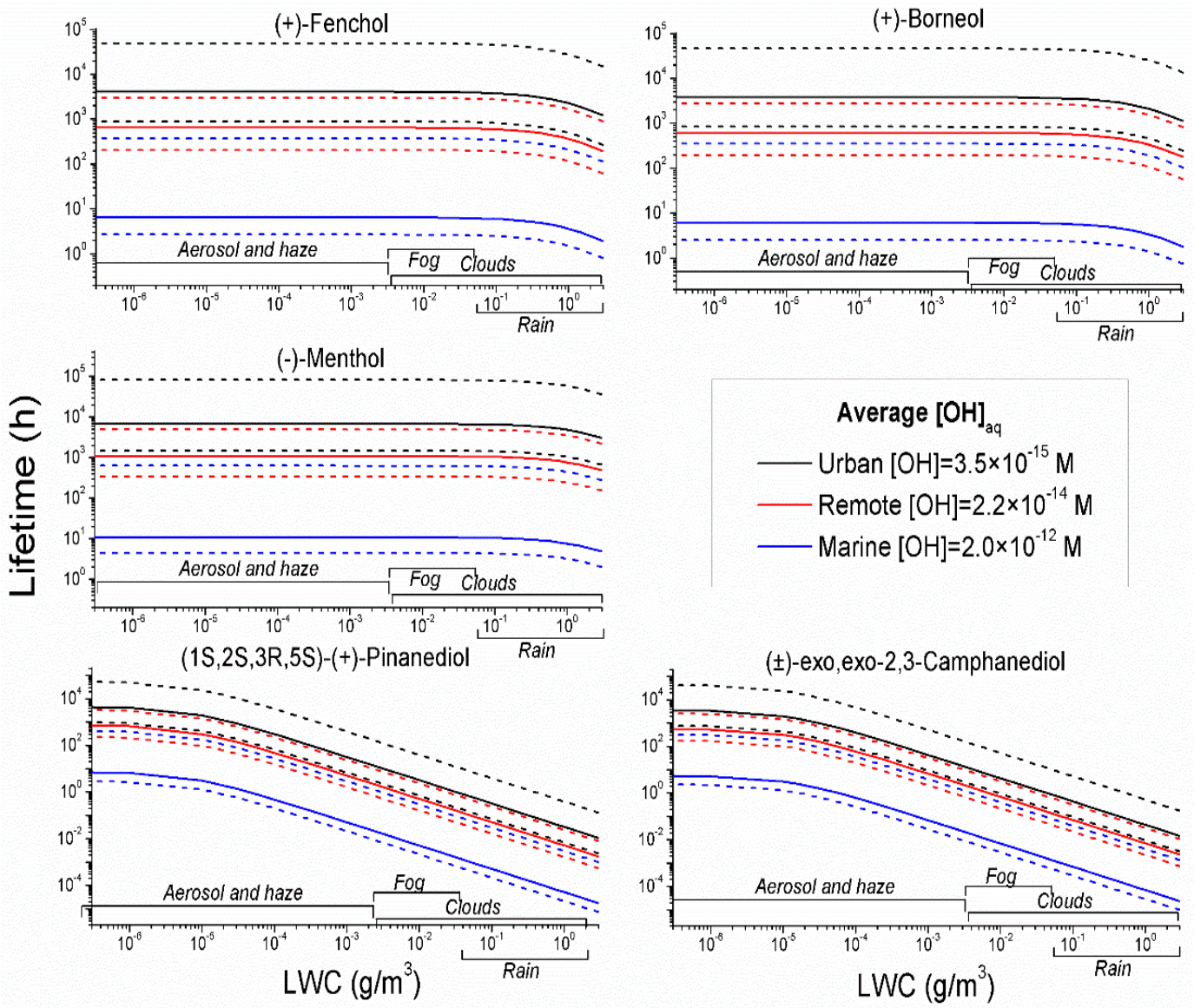


$C_{10}H_{14}O_6$

m/z:230.21

Aqueous OH kinetics of alcohols emitted from natural and industrial sources; new quantitative structure-activity relationship model and atmospheric lifetimes, B. Witkowski, P.Jain, J. Szlęk, B. Wileńska and T. Gierczak, Chemosphere, under revison

Atmospheric lifetimes of Terpenoic alcohols



$$t = \frac{1}{\left(\frac{k_{OH_g}}{H_{OH}^{cc}} + k_{OH_{aq}} H_{AA}^{cc} \omega\right)[OH]_{aq}}$$

Where,

t=Lifetime due to oxidation by the OH (gas and aqueous phase)

k_{OH_g}= Reaction rate coefficient in the gas phase ($M^{-1}s^{-1}$)

H_{OH}^{cc} = Dimensionless Henry's law constant for the OH (764)

$k_{OH_{aq}}$ = Reaction rate coefficient in the aqueous phase ($M^{-1}s^{-1}$)

H_{AA}^{cc}= Dimensionless Henry's law constant for Terpenoic alcohol

ω = Liquid-water content (m^3/ m^3)

Aqueous OH kinetics of saturated C6-C10 dicarboxylic acids under acidic and basic conditions between 283 and 318 K; new structure-activity relationship parameters, B. Witkowski, J. Chi, P. Jain, K. Błaziak and T.Gierczak, Atmospheric Environment, Volume 267(2021) 118761 http://doi.org/10.1016/j.atmosenv.2021.118761