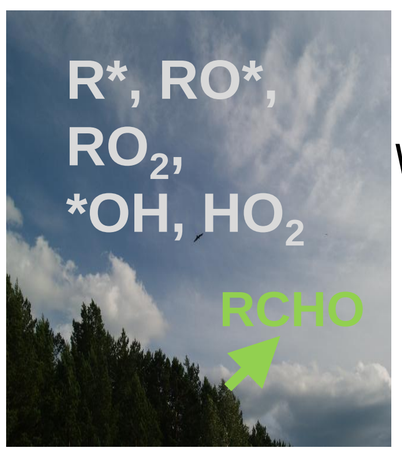
Unraveling the Mechanism of Gas-to-Particle Conversion in Lower Troposphere: Trap or Trace?



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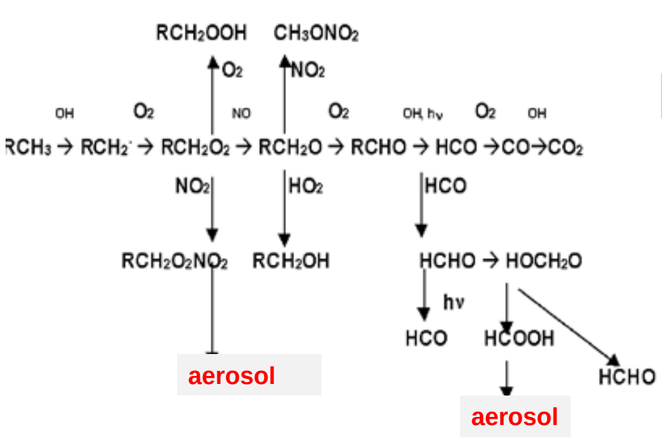
Atmospheric photonucleation of organic compounds, mainly alkenes and aldehydes, is a permanent source of atmospheric organic particulate matter both under background conditions and in the presence of typical urban air pollutants (eg. NO, NO_2, O_3, etc.). Freshly formed particles are several ten nanometers in size (inhalable fraction) and carry reactive functional groups on their surface. Particles formed in furfural photonucleation have –OH and –COOH groups, known to cause diverse biological effects in humans and animals.

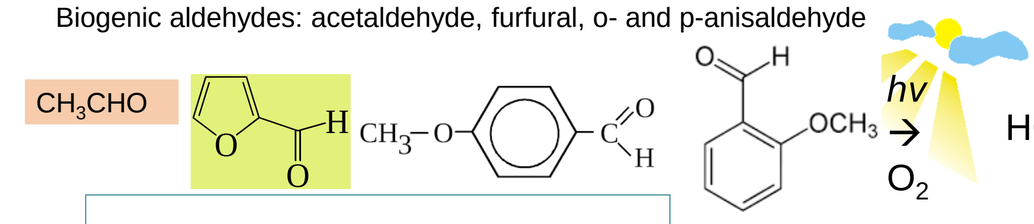
Dultseva G.G., Dubtsov S.N., Dultsev F.N., Kobzeva T.V., Nekrasov D.V. Analysis of the surface functional groups of organic nanoparticles formed in furfural vapour photonucleation using a rupture event scanning technique, Analytical Methods, 2017, V. 9, P. 5348-5355. DOI: 10.1039/c7ay01437f.

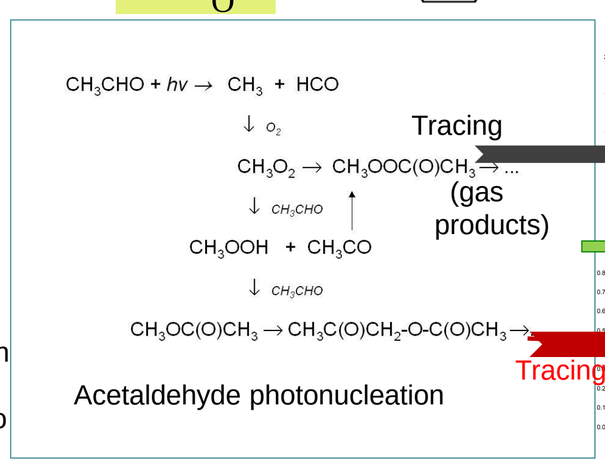
Objectives: to develop a versatile strategy for the reliable determination of reaction routes associated with short-lived free radicals in atmospheric photonucleation of aldehydes and to apply this approach to biogenic aldehydes: acetaldehyde, furfural and substituted aromatic aldehydes emitted by vegetation into atmosphere.

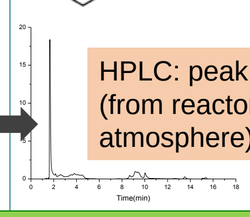


General sequence of photooxidation processes usually starts with hydrogen atom abstraction by short-lived reactive species (hydroxyl radical, nitrate radical or oxygen atom), or radical addition to a double bond. Thus formed carbon-centered radicals are immediately transformed into peroxy radicals through the addition of O_2. Further atmospheric fate of organic radicals on their route to organic nanosized particulate matter is still unknown in detail.

Biogenic aldehydes: acetaldehyde, furfural, o- and p-anisaldehyde

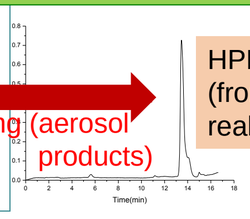




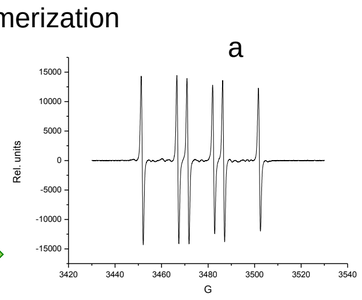


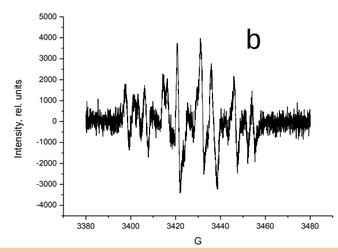
HPLC: peak of the dimer (from reactor and from real atmosphere)

Trapping (free radicals)



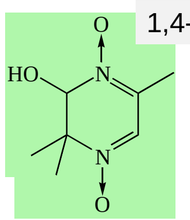
HPLC: peak of the tetramer (from reactor and from real atmosphere)

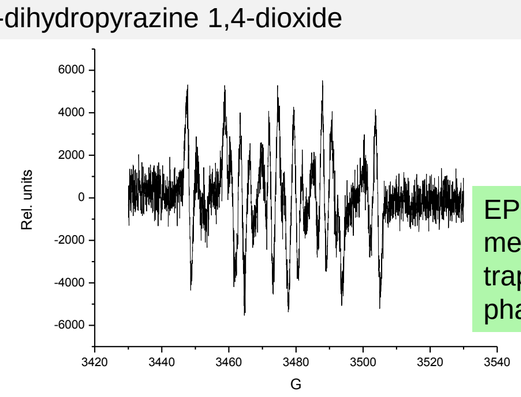




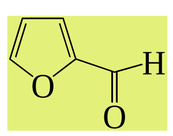
EPR: Spin adduct of methoxy (a) and methylperoxy (b) radicals (spin trap: 1,4-dihydropyrazine 1,4-dioxide, trapping from the gas phase)

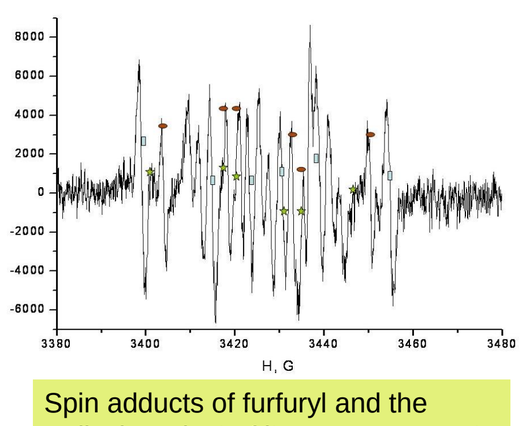
Spin trap: 1,4-dihydropyrazine 1,4-dioxide



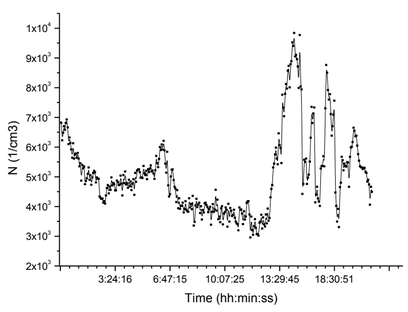


EPR: Spin adduct of methoxyphenyl radical, trapping from the gas phase





Spin adducts of furfuryl and the radical product of its rearrangement (spin trap: pentamethyl-3-imidazoline-3-oxide, trapping from the gas phase)



Example: real atmospheric diurnal variation of the number concentration of organic aerosol (inhalable fraction, size ~ 100 - 700 nm)

Kinetic modeling of the generation of condensable products in aldehyde photooxidation shows that diurnal variations of OH, HO_2 (daytime) and NO_3 (nighttime) concentrations exhibit peaks preceding those observed in real atmosphere in diurnal variations of particulate matter.

Dultseva, G.G., Nemova, E.F., Dubtsov, S.N., Plokhotnichenko, M.E. (2020). Aerosol generating potential of the products of atmospheric photooxidation of biogenic organic compounds. Atmospheric and Oceanic Optics, 2020, Vol. 33. No. 5, p. 545-548.

Carboxylic acids are the products of atmospheric oxidation of alkanes, alkenes, aldehydes, etc. and, when formed, promote aerosol generation through acid-catalyzed polymerization of aldehydes.

Calculated concentrations of the condensable products (B) of photooxidation of A (initial concentration of each compound A is set at $3 \cdot 10^9 cm^{-3}$)

Organic class	Compound A	Product B cm^{-3}
Peracetic acid	CH_3COOOH	$1.2 \cdot 10^6$
Ethyl hydroperoxide	CH_3CH_2OOH	$7.6 \cdot 10^5$
Peroxide	$CH_3CH_2OOCH_2CH_3$	$9.1 \cdot 10^4$
Ethylnitrate	$CH_3CH_2O_2NO_2$	$6.8 \cdot 10^3$
Ethylnitrite	$CH_3CH_2ONO_2$	$4.5 \cdot 10^3$
Peroxyacetylnitrate	$CH_3C(O)OONO_2$	$2.7 \cdot 10^3$
Acetic acid	CH_3COOH	$5.2 \cdot 10^2$

Atmospheric processes generating short-lived free radicals:

$NO_2 + h\nu \rightarrow NO + O(^3P)$
$NO_2 + h\nu \rightarrow NO + O(^1D)$
$O(^1D) + H_2O \rightarrow 2OH$
$O(^3P) + O_2 \rightarrow O_3$
$RO_2 + NO \rightarrow RO + NO_2$

Peracid $CH_3C(O)OOH + h\nu \rightarrow CH_3COO\cdot + \cdot OH$
Hydroperoxide $CH_3CH_2OOH + h\nu \rightarrow CH_3CH_2O\cdot + \cdot OH$
Dialkylperoxide $CH_3CH_2OOCH_2CH_3 \rightarrow 2\ CH_3CH_2O\cdot$
Peroxy nitrite and nitrate $CH_3CH_2O_xNO_2 + h\nu \rightarrow CH_3CH_2O_x\cdot + NO_2$

Aerosol generating capacity: Peracids (RCOOOH) > Hydroperoxides (ROOH) > Peroxides (R_1OOR_2) > Peroxyacyl nitrates and nitrites (RO_xNO_2) > Carboxylic acids (RCOOH)

Conclusions

1. Spin trapping investigation of the radicals dominating in the gaseous reaction mixture during photonucleation of the aldehydes of environmental significance - acetaldehyde, furfural, o- and p-anisaldehyde - revealed the formation of free radicals: formyl, methoxyl, methoxyphenyl, substituted phenoxyl, furfuryl.
2. These radicals drive subsequent photopolymerization and photocondensation; these stages, together with radical rearrangements, lead to a variety of aerosol products of concern with respect to human health.
3. The presence of the radicals identified under laboratory conditions was traced in real atmosphere by detecting the products of their transformations.
4. To understand the mechanism of atmospheric photonucleation, the 'trap and trace' approach is necessary: trapping free radicals under laboratory conditions and tracing the products of their transformations under atmospheric conditions.