Aromatics as Precursors of Urban Particles

I. Barnes

Venice/Italy 25-27 October, 2004

- Significant impact on photooxidant formation in urban areas (Derwent *et al*. 90/98)

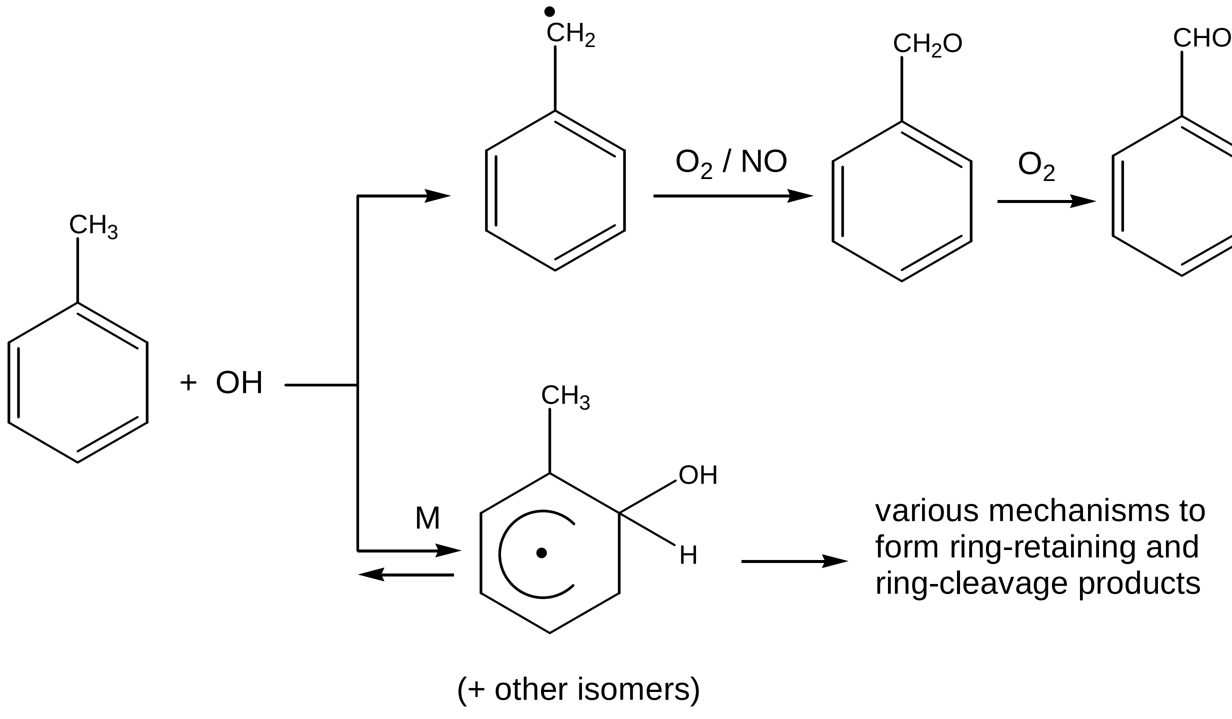
- Benzene is carcinogenic and irradiation of hydrocarbon mixtures containing aromatic hydrocarbons produces species with mutagenic properties (Kleindienst *et al*. 1992)

- Of the 32 most prevalent non-methane hydrocarbons observed in urban air 7 are aromatic hydrocarbons

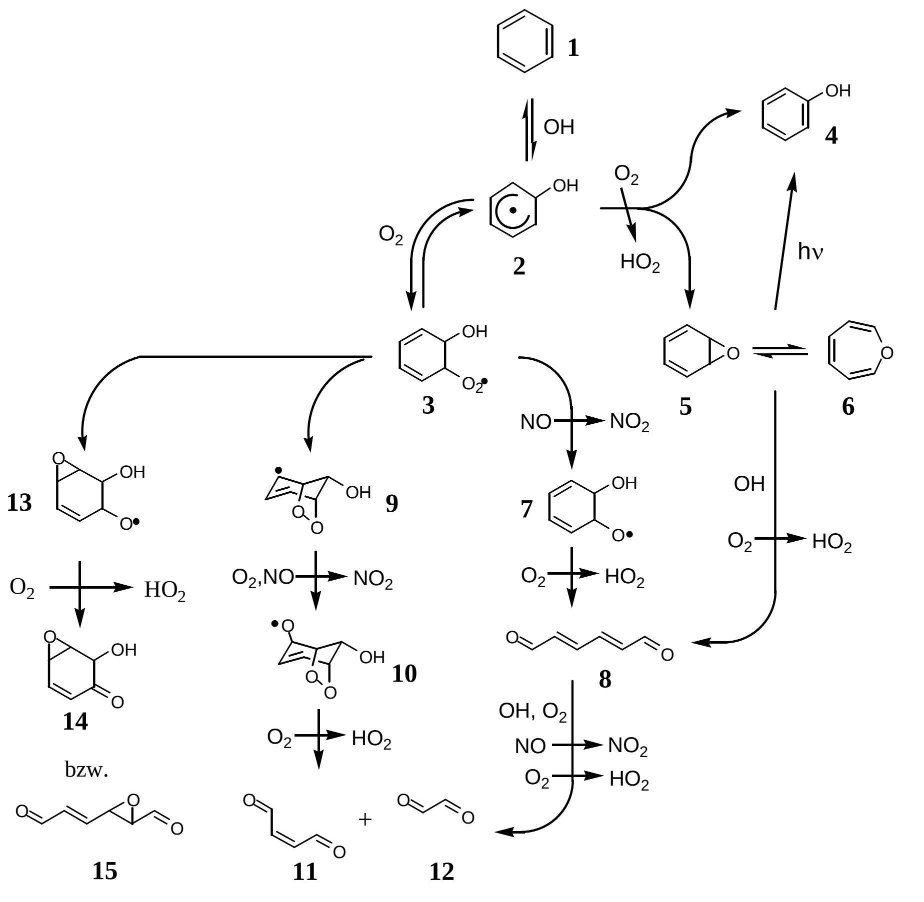
- Toluene is often the most abundant aromatic compound in urban air accounting for approximately 6% of the observed NMHC

- major sources are combustion systems and solvent use
- Typical ambient concentrations of alkylated benzenes in cities:
  - low 25 ppbC high 590 ppbC
- Aromatic hydrocarbon photooxidation is alleged to make a significant contribution to secondary organic aerosol (SOA) formation in urban air

Aromatic HCs: OH photooxidation mechanism



Aromatic HCs: OH photooxidation mechanism



Secondary organic aerosol (SOA) observed from the photooxidation of some 21 aromatic hydrocarbons

benzene,

toluene, *m*,*o*-*p*-xylenes, ethylbenzene

m,*o*,*p*-ethyltoluenes, n-propylbenzene, p-diethylbenzene

1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene

1,4-dimethyl-4-ethylbenzene, 1,4-dimethyl-2-ethylbenzene

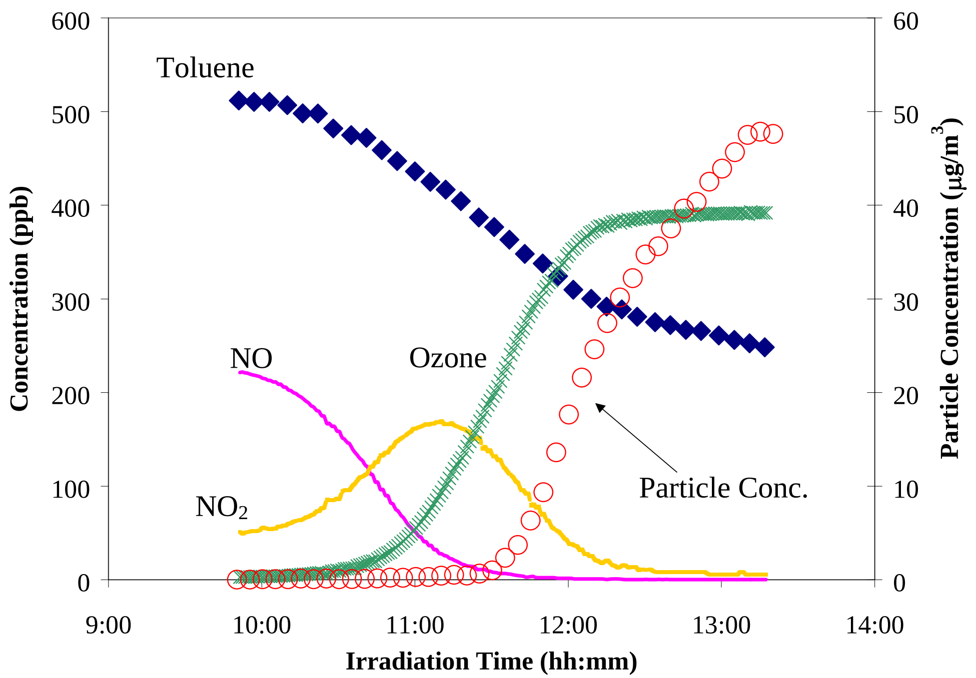
1,2,4,5- and 1,2,3,5-tetrametylbenzene

1-methyl-3-*n*-propylbenzene

Secondary organic aerosol (SOA) - yield observations

- there appear to be high- and low-yield aromatics
- high-yield aromatic species tend to be those containing one or fewer alkyl substituent groups
- low-yield aromatic species are aromatics which contain two or more alkyl substituent groups

Aromatic HCs: Aerosol Formation (SOA)



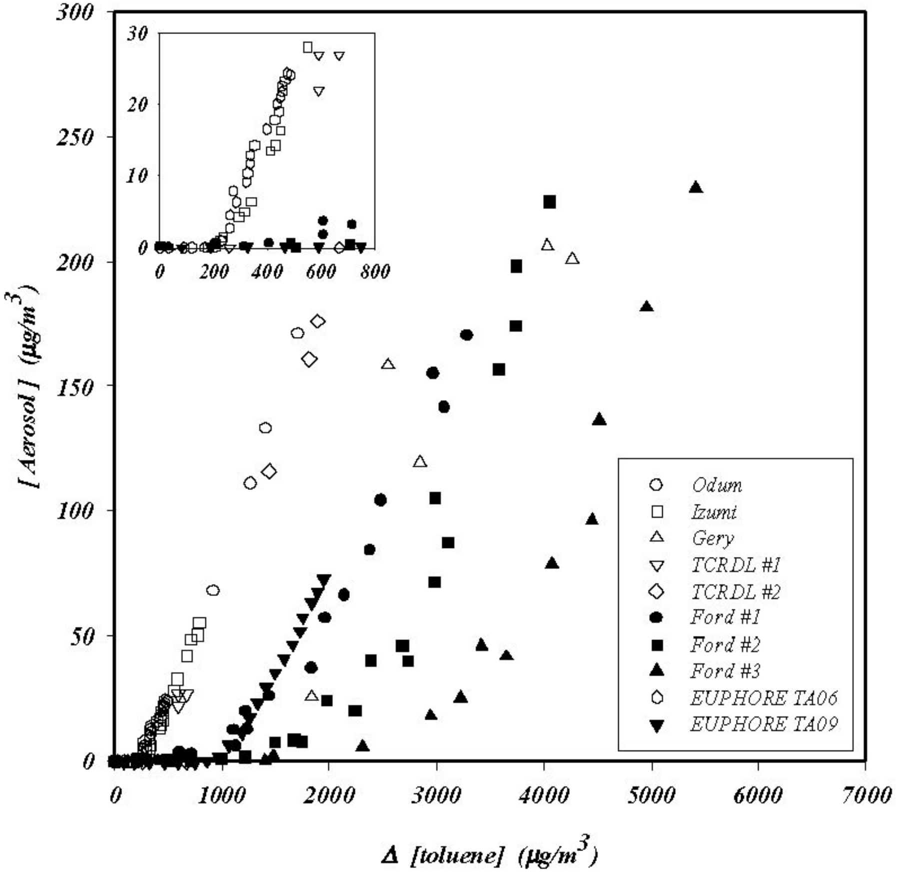
Irradiation of 500 ppb toluene + 300 ppb NO_x in the Euphore chamber

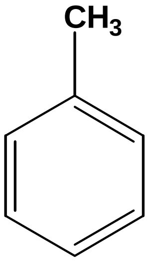
Concentration-time profiles of toluene, NO, NO_2, ozone and the total aerosol mass concentration

K. Wirtz, M. Martín-Reviejo, C. Maldonado, E. Borrás, T. Vera

Euphore Report 2001

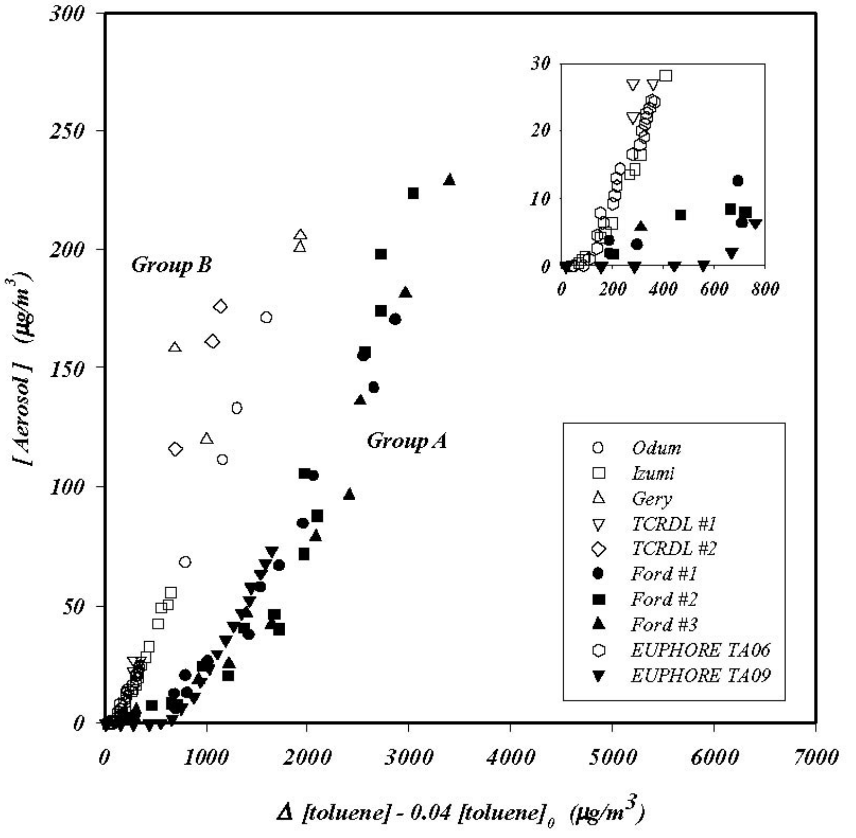
Aromatic HCs: Aerosol Formation OH + toluene

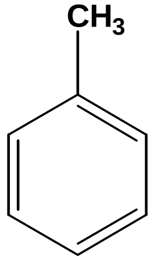




Hurley *et al*. (2001)Environ. Sci. Technol. 35, 1358-1366.

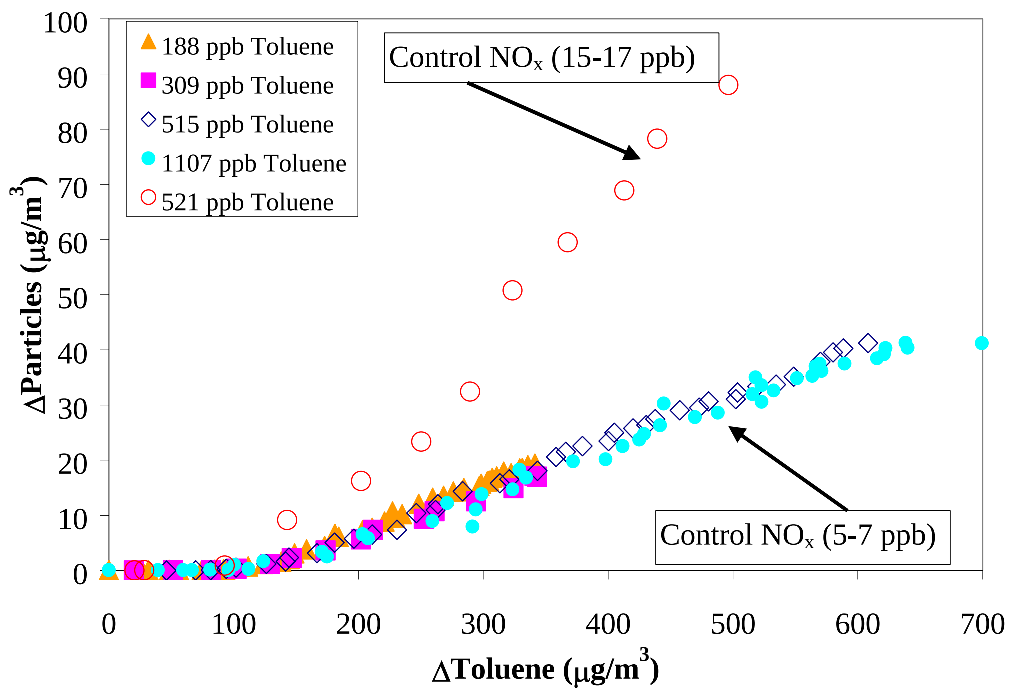
Aromatic HCs: Aerosol Formation OH + toluene





Hurley et al. (2001)Environ. Sci. Technol. 35, 1358-1366.

Aromatic HCs: Aerosol Formation (SOA)

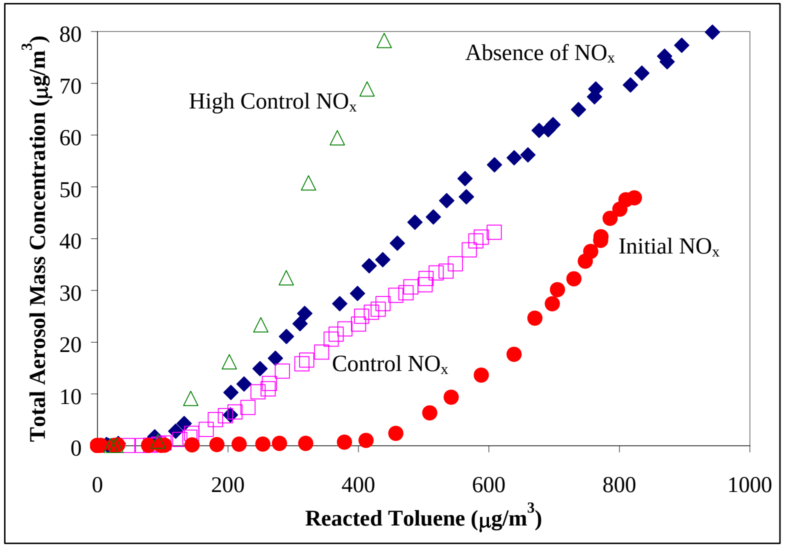


Total aerosol mass concentration in µg/m^3 as a function of reacted toluene for experiments with different initial toluene concentrations.

K. Wirtz, M. Martín-Reviejo, C. Maldonado, E. Borrás, T. Vera

Euphore Report 2001

Aromatic HCs: Aerosol Formation (SOA) OH + toluene



Aerosol mass concentrations against reacted toluene for different NO_x-regimes.

K. Wirtz, M. Martín-Reviejo, C. Maldonado, E. Borrás, T. Vera

Euphore Report 2001

High initial NO concentrations (classical smog) produce a long delay in the onset of particle formation

Aerosol yields in the absence of NO_x are slightly higher than the standard control NO_x (5-7 ppb of NO_x), but lower than the high control NO_x (15-17 ppb of NO_x).

- aerosol is secondary in nature
- appear to be many different pathways to aerosol precurors
- level of NOx is an important parameter
- relative importance of OH, O_3 or NO_3 reactions (and possibly photolysis) in aerosol formation unclear

Studies on:

toluene, *m*-xylene, *p*-xylene, ethylbenzene, *m*-ethyltoluene, *p*-ethyltoluene, trimethylbenzenes

- quartz filter and/or impinger derivation collection
- GC/MS analysis

Aromatic HCs: Aerosol Molecular Composition - literature

D. R. Cocker, B. T. Mader, M. Kalberer, R. C. Flagan and J. H. Seinfeld

The effect of water on gas-particle partioning of secondary organic aerosol: II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems

Atmospheric Environment 35 (2001) 6073-6085

T. E. Kleindienst, D. F. Smith, W. Li, E. O. Edney, D.J. Driscoll, R. E. Speer and W. S. Weathers

Secondary organic aerosol from the photooxidation of aromatic hydrocarbons in the presence of dry submicron ammonium sulfate aerosol

Atmospheric Environment 33 (1999) 3669-3681

H . J. L. Forstner, R. C. Flagan and J. H. Seinfeld

Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: molecular composition.

Environment Science and Technology 31 (1997) 1346-1358

M. Jang and R. M. Kamens

Characterization of secondary aerosol from the photooxidation of toluene in the presence of Nox and 1-propene.

Environment Science and Technology 35 (2001) 3626-3639

Aromatic HCs: Aerosol Molecular Composition - literature

OSOA / EXACT - EU projects

T. E. Kleindienst, T. S. Conver, C. D. McIver, and E. O. Edney
Determination of secondary organic aerosol products from the photooxidation of toluene and their implications in ambient PM2.5
J. Atmos Chem. 47 (2004) 79-100

Aromatic HCs: SOA Molecular Composition

- over 60 compounds identified
- both ring-retaining and ring-fragmentation products detected among aerosol products
- identified compounds are mostly small with relatively high vapour pressures
- identified compounds only represent a small fraction of aerosol mass

Major compound classes:

- multi-functional oxygenates
- saturated and unsaturated anhydrides
- multifunctional mono- and dicarboxylic acids

    - *their presence in the aerosol arises is thought to arise largely from gas/particle partitioning*

Aromatic HCs: SOA Molecular Composition - polymers

Identifcation of Polymers as Major Components of Atmospheric Organic Aerosols

M. Kalberer,* D. Paulsen, M. Sax, M. Steinbacher, J. Dommen, A. S. H. Prevot, R. Fisseha, E. Weingartner,V. Frankevich, R. Zenobi, U. Baltensperger*

Science, **303**, 1659-1662, 2004

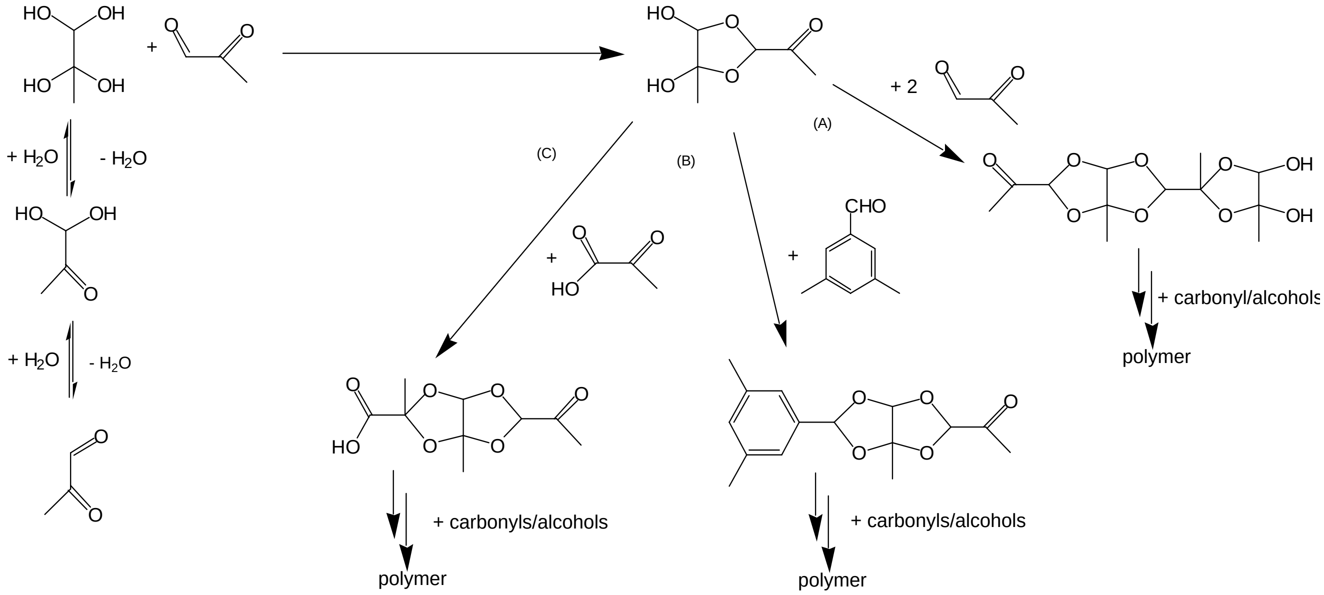
- found for the photooxidation of trimethylbenzene that a substantial fraction of the organic aerosol mass is composed polymers

- after ageing for 20 h about 50% of the particle mass consists of polymers (molecular mass up to 1000 daltons)

- the polymerization is proposed to occur from reactions of carbonyls and their hydrates

Aromatic HCs: SOA Molecular Composition – Polymer formation

Possible mechanism



Aromatic HCs: SOA Molecular Composition – Polymers

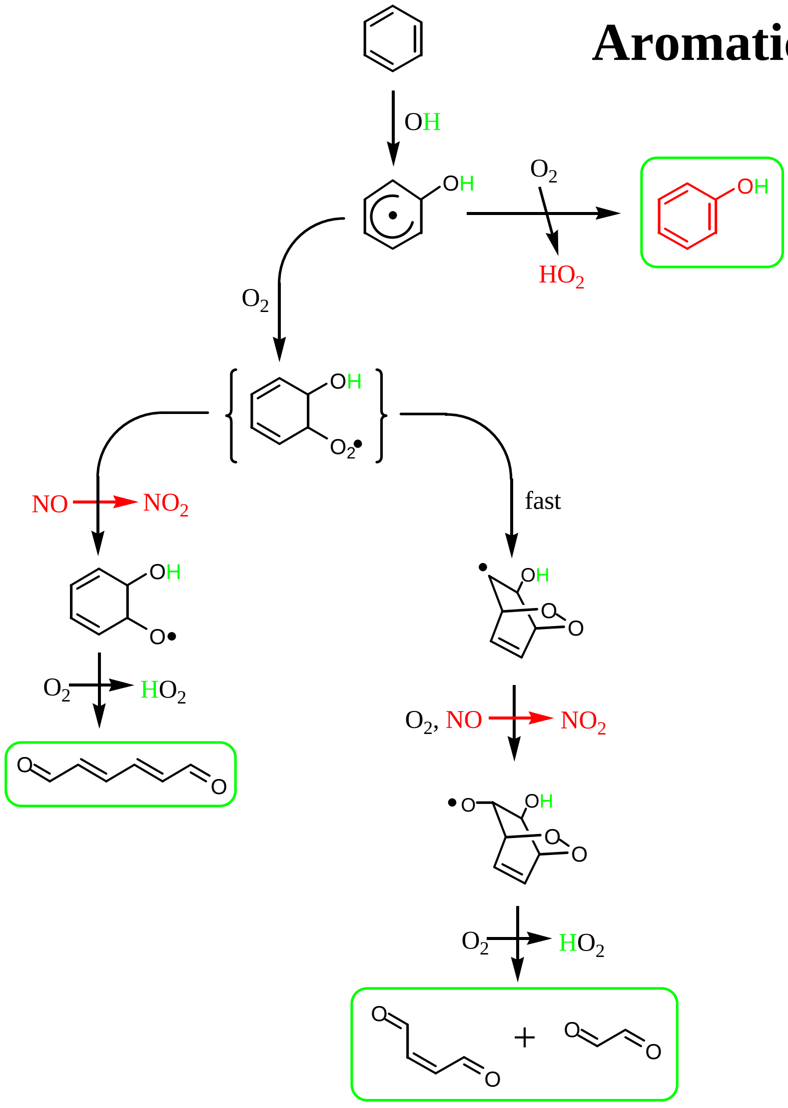
Polymerization has been shown to occur within the aerosol for TMB SOA (at least in chambers)

High concentrations of inorganic acids not required

There may be other processes yielding polymers
(any carbonyl forming process)

Still many open questions, e.g.
- polymerization rate in atmospheric aerosols?
- is polymerization reversible at high RH?
- what compounds and conditions favor polymerization?

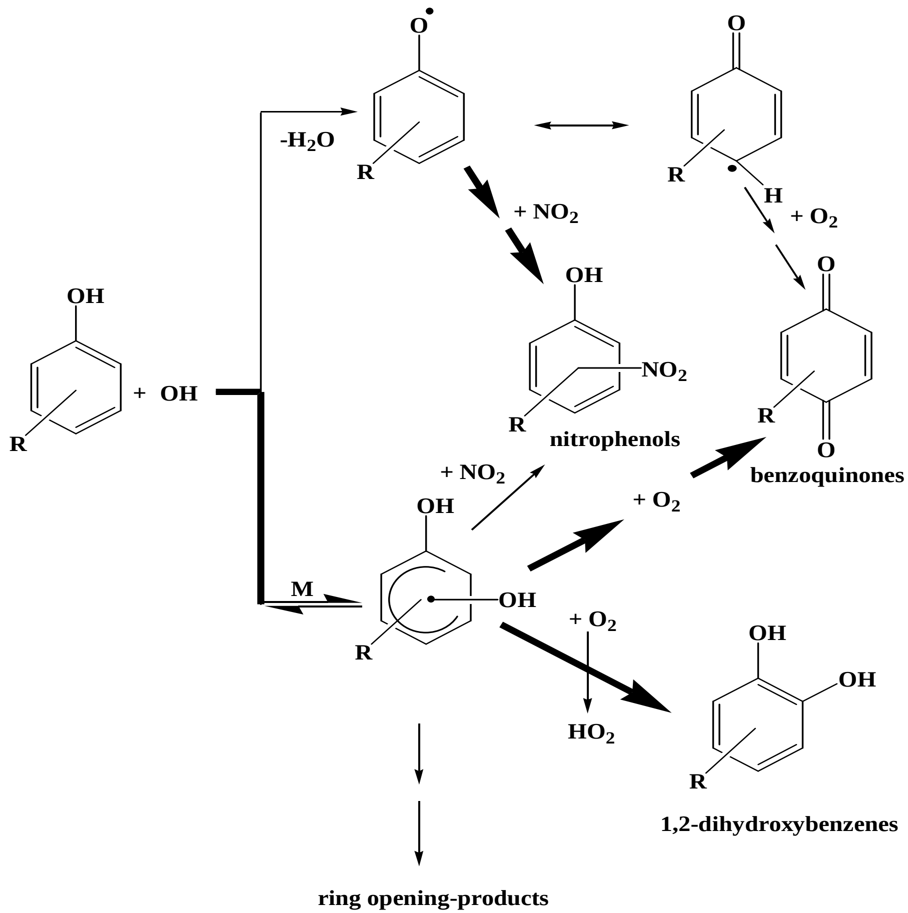
Aromatic HCs: oxidation mechanism



Aromatic HCs: SOA formation OH + Phenols

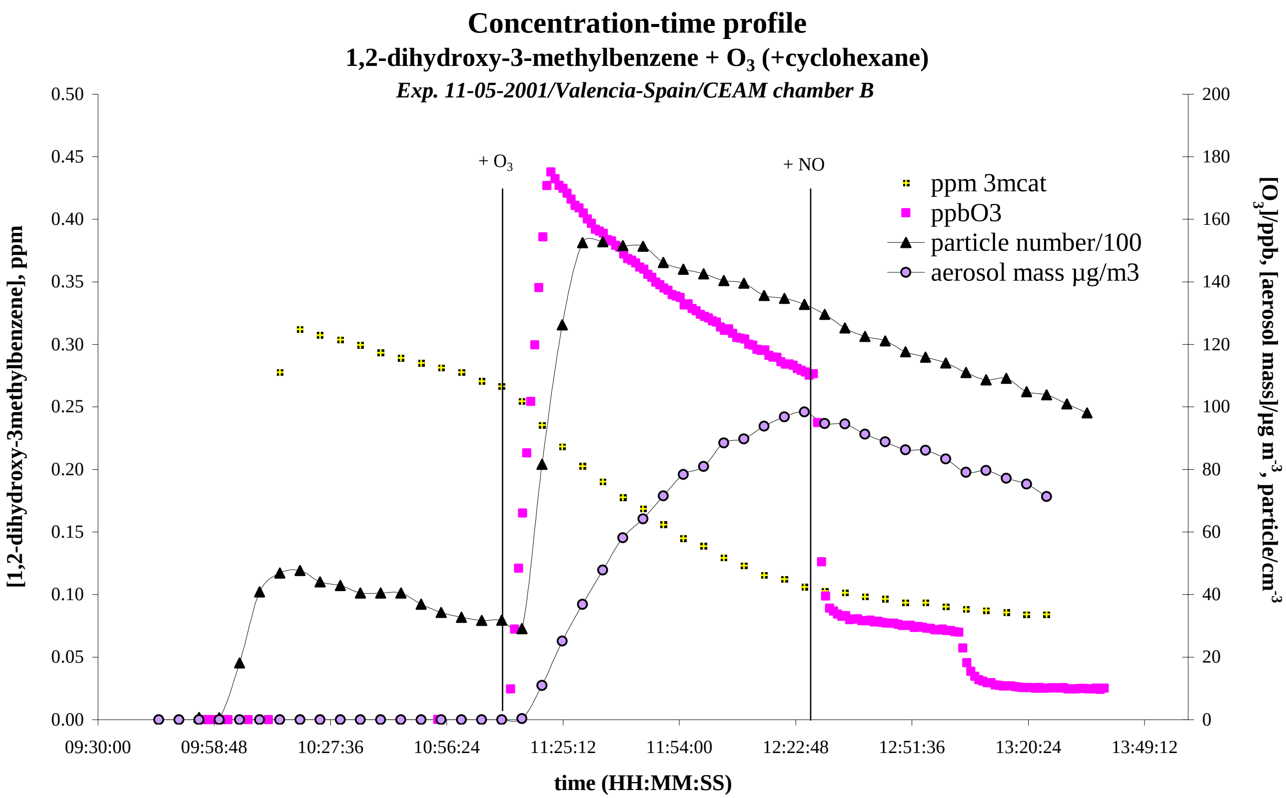
Aromatic Hydrocarbon	Aromatic Hydrocarbon [ppm]	NO [ppm]	NO_2 [ppm]	Aerosol Yield [%]
phenol	2.17	0.37	0	1.08
	2.30	0.79	0	0.75
	2.43	2.83	0.87	0.2
	2.15	4.31	0.96	0
o-cresol	1.16	0.7	0.16	2.17
	1.17	1.4	0.3	1.09
	1.16	2.7	0.5	0.66
m-cresol	0.92	0	0	4.96
	0.98	1.44	0.49	2.49
	0.97	2.79	0.62	0.74
p-cresol	0.63	0	0	6.08
	0.54	0.62	0.87	2.0
	0.61	1.25	1.1	0.85

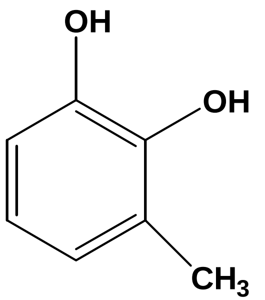
Aromatic HCs: Products OH + Phenols



Aromatic HCs: Aerosol Formation (SOA)

Particle formation from O_3 + 1,2-dihydroxy-3-methylbenzene



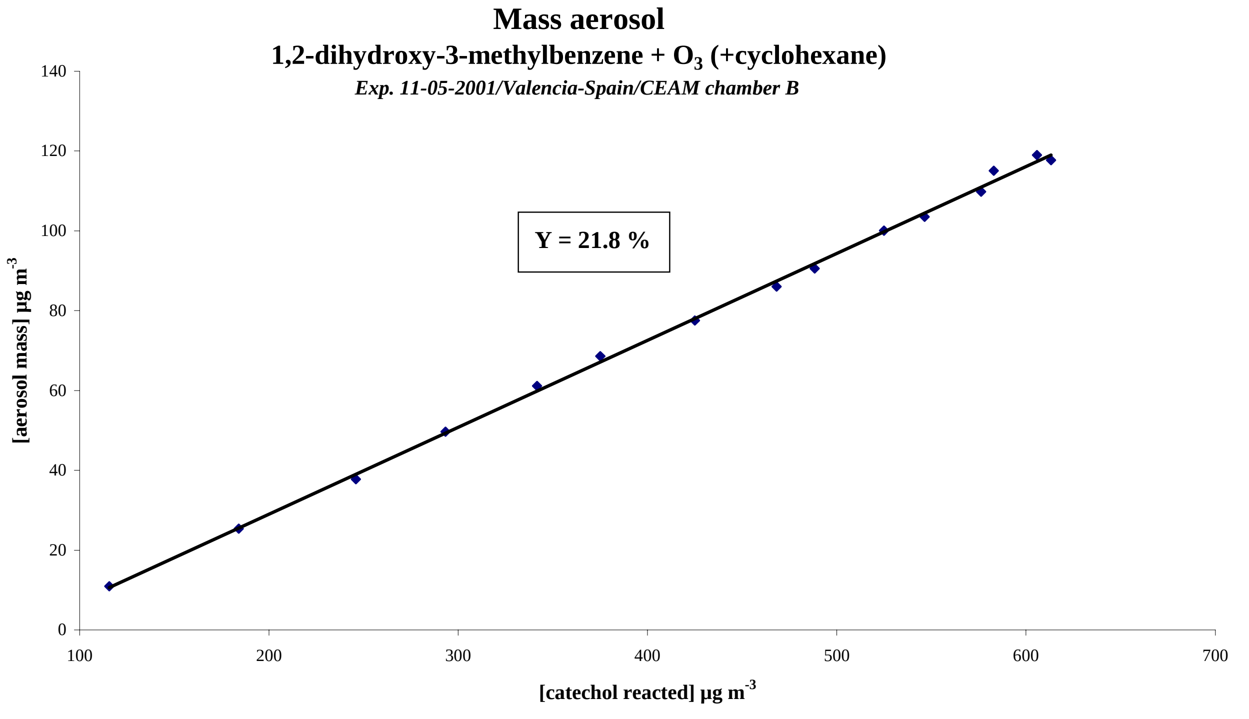


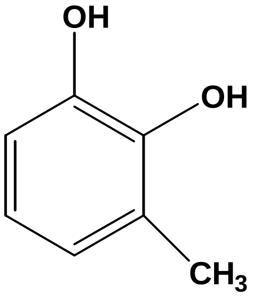
R.I. Olariu, A. Tomas, I. Barnes, K. H. Becker

Bergische Universität Wuppertal

Aromatic HCs: Aerosol Formation (SOA)

Particle formation from O_3 + 1,2-dihydroxy-3-methylbenzene





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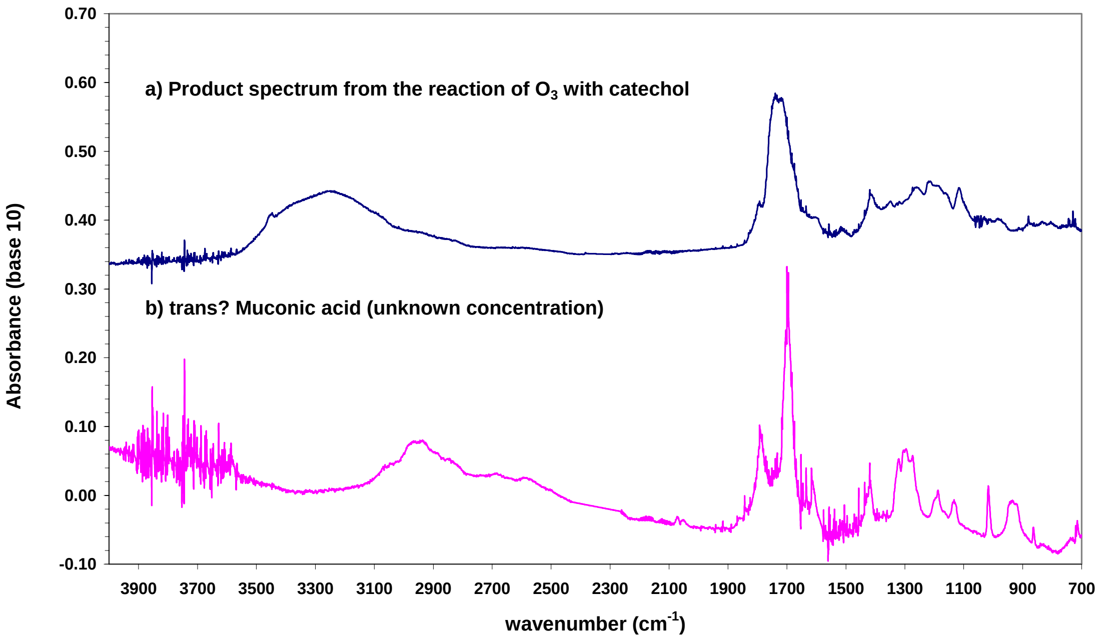
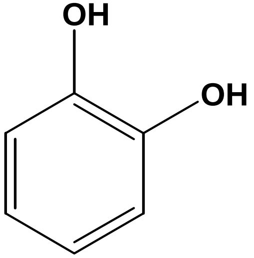
IR Product spectrum from O_3 + 1,2-dihydroxybenzene

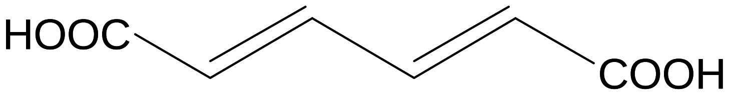


O_3 +

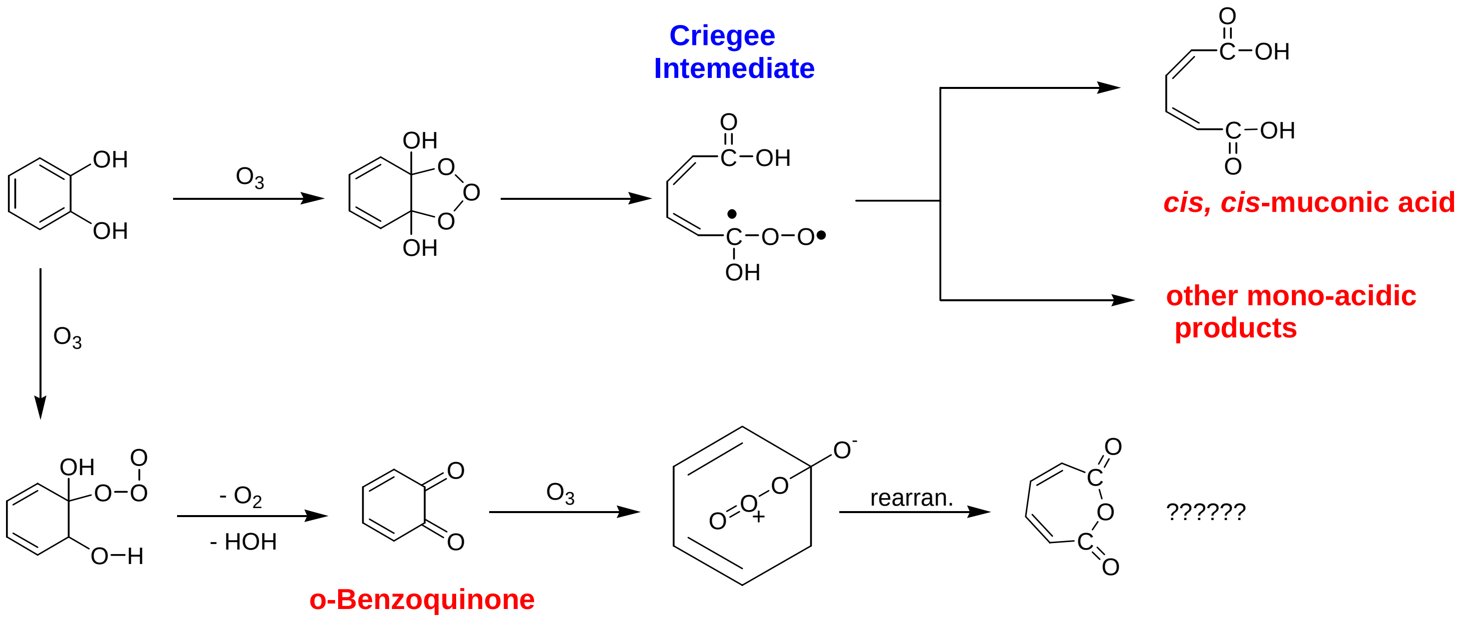


Muconic acid is known to be product from GC-MS studies

(Wuppertal / Dortmund – OSOA/EXACT projects)



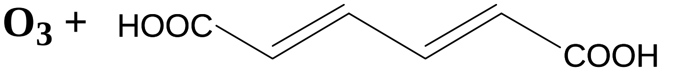
Aromatic HCs: Aerosol formation

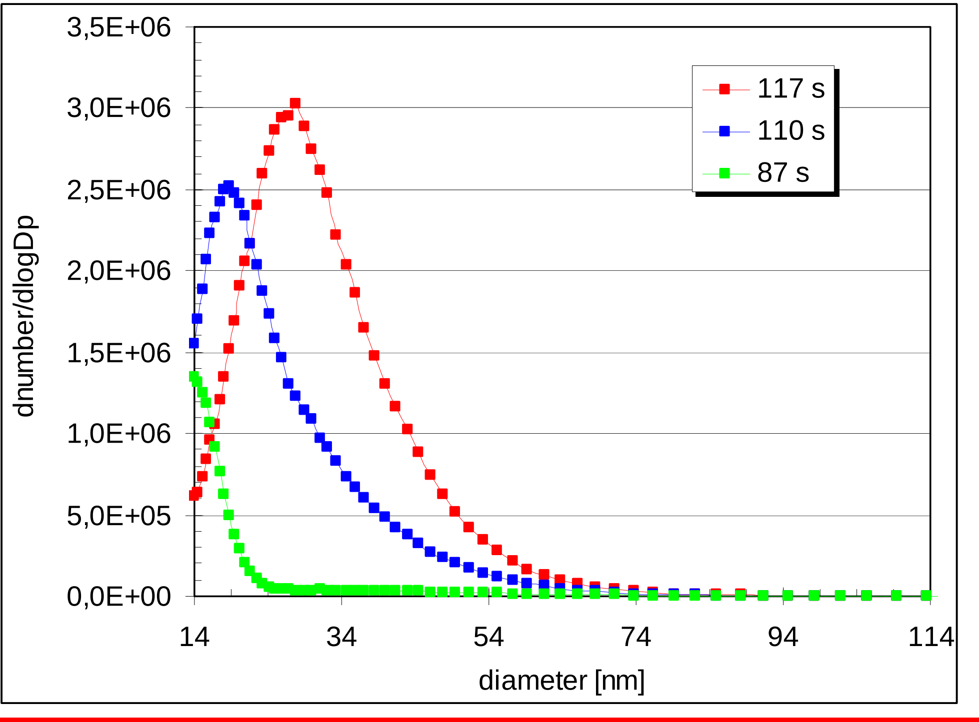


Possible Mechanism for the reaction of ozone with catechol in the Gas Phase

Aromatic HCs: Aerosol Formation (SOA)

Particle formation from O_3 + muconic acid in a flow system





R. Bröske, R.I. Olariu, A. Tomas, I. Barnes, K. H. Becker

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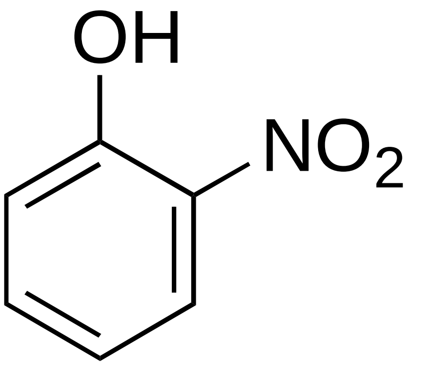
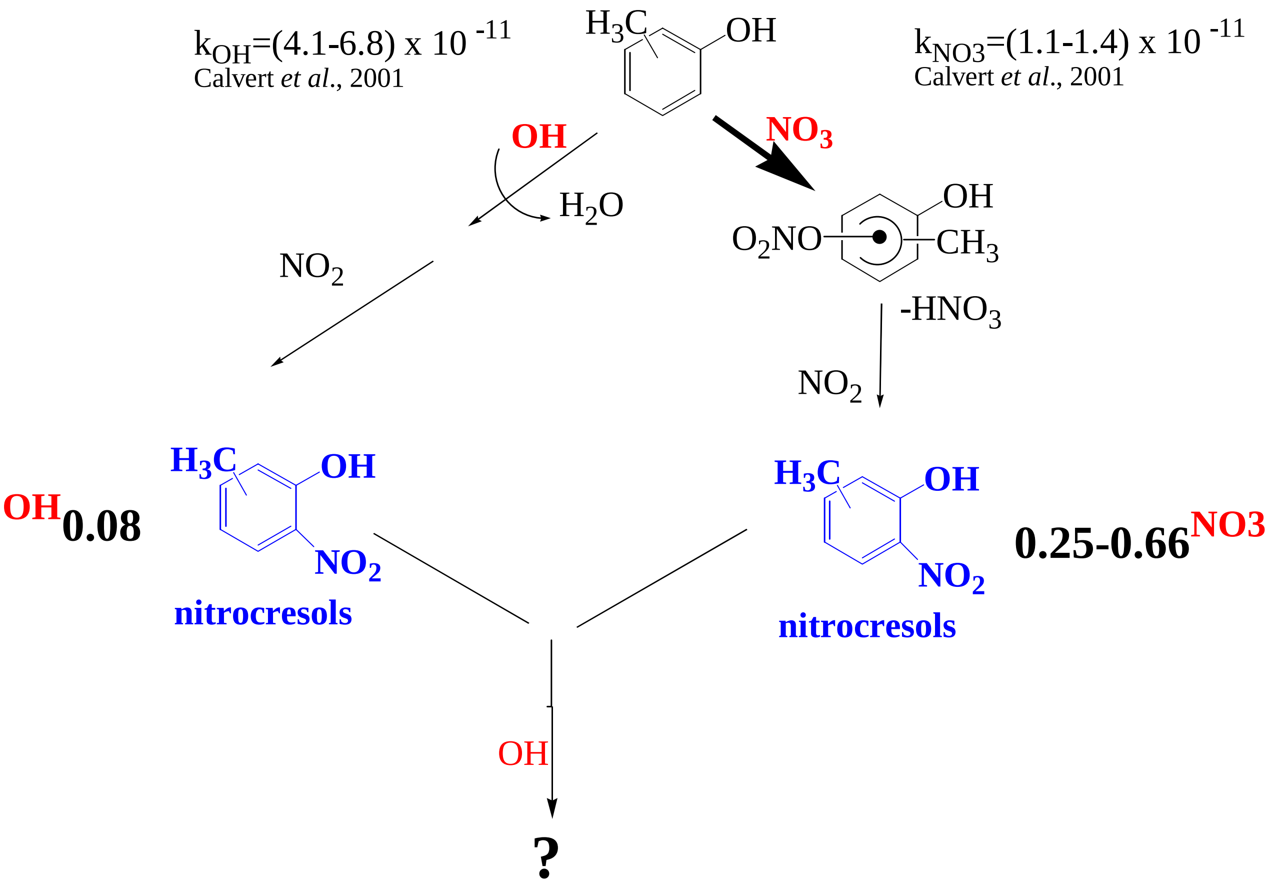


2-nitro-hydroxybenzene

Aromatic HCs: Formation of nitrophenols

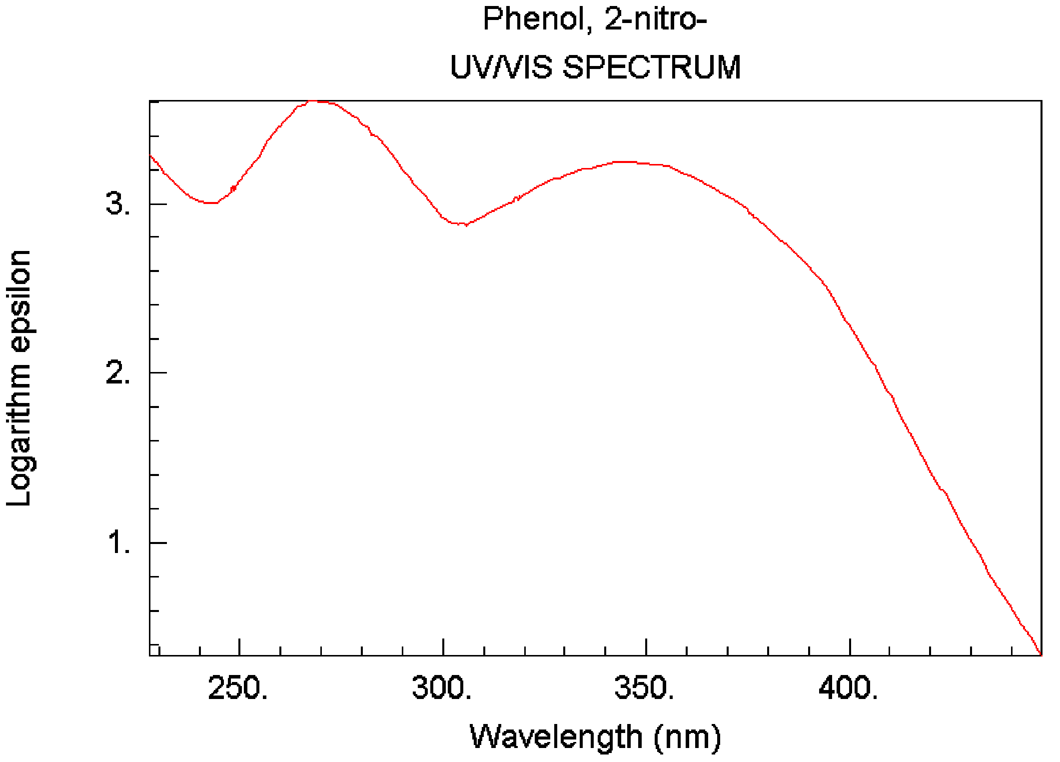


Aromatic HCs: OH kinetics and photolysis of nitrophenols

Compound	k_{OH} (expt) (10^{-12} cm^3s^{-1})	k (literature)[a] (10^{-12} cm^3s^{-1})	τ (h)	photolysis rate (s^{-1})	OH concentration (molecule cm^{-3})
3-methyl-2-nitrophenol	3.69 ± 0.16	11.2	47	1.67×10^{-4}	3.10×10^{5}
4-methyl-2-nitrophenol	3.46 ± 0.18	5.38	50	8.86×10^{-5}	1.96×10^{5}
5-methyl-2-nitrophenol	7.34 ±0 .52	11.2	24	1.07×10^{-4}	2.88×10^{5}
6-methyl-2-nitrophenol	2.70 ± 0 .17	-	64	7.81×10^{-5}	1.97×10^{5}

[a] computer estimation study [Meylan et all., 1993]

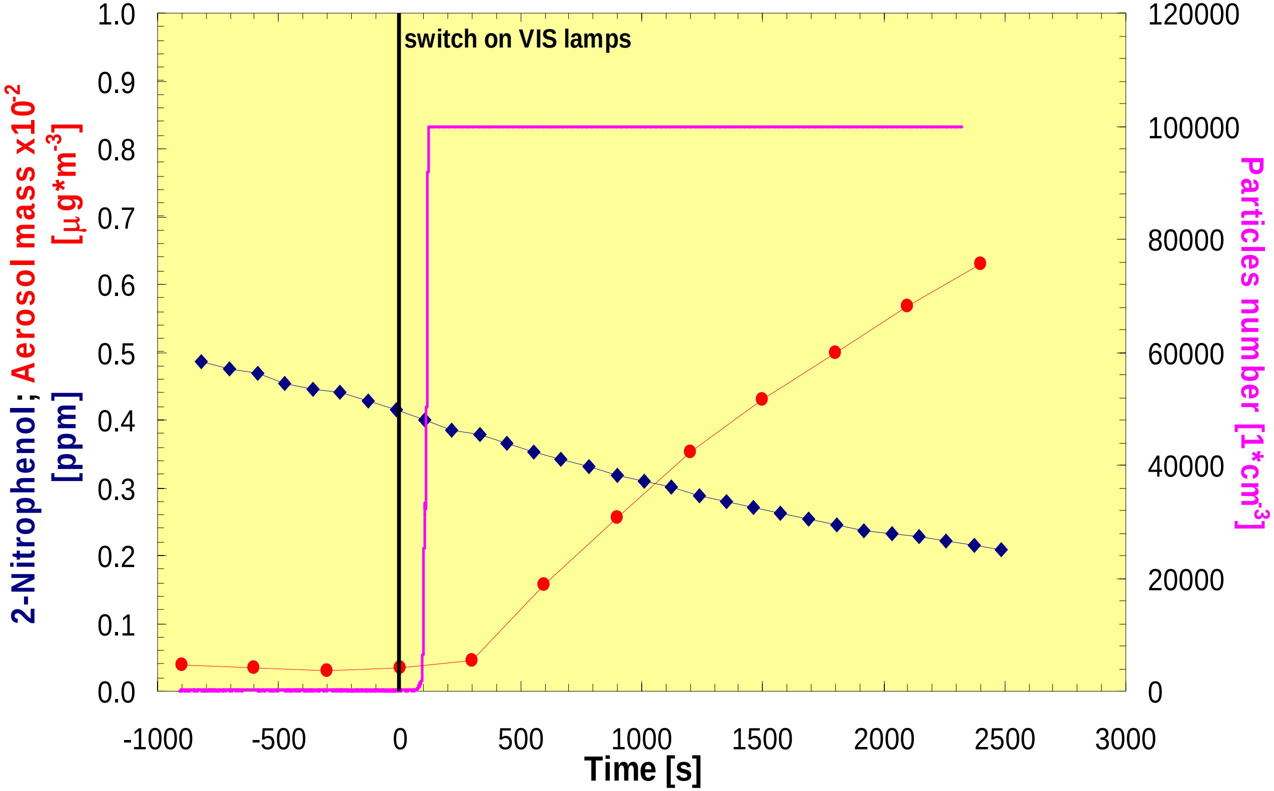
Aromatic HCs: UV spectrum 2-nitrophenol



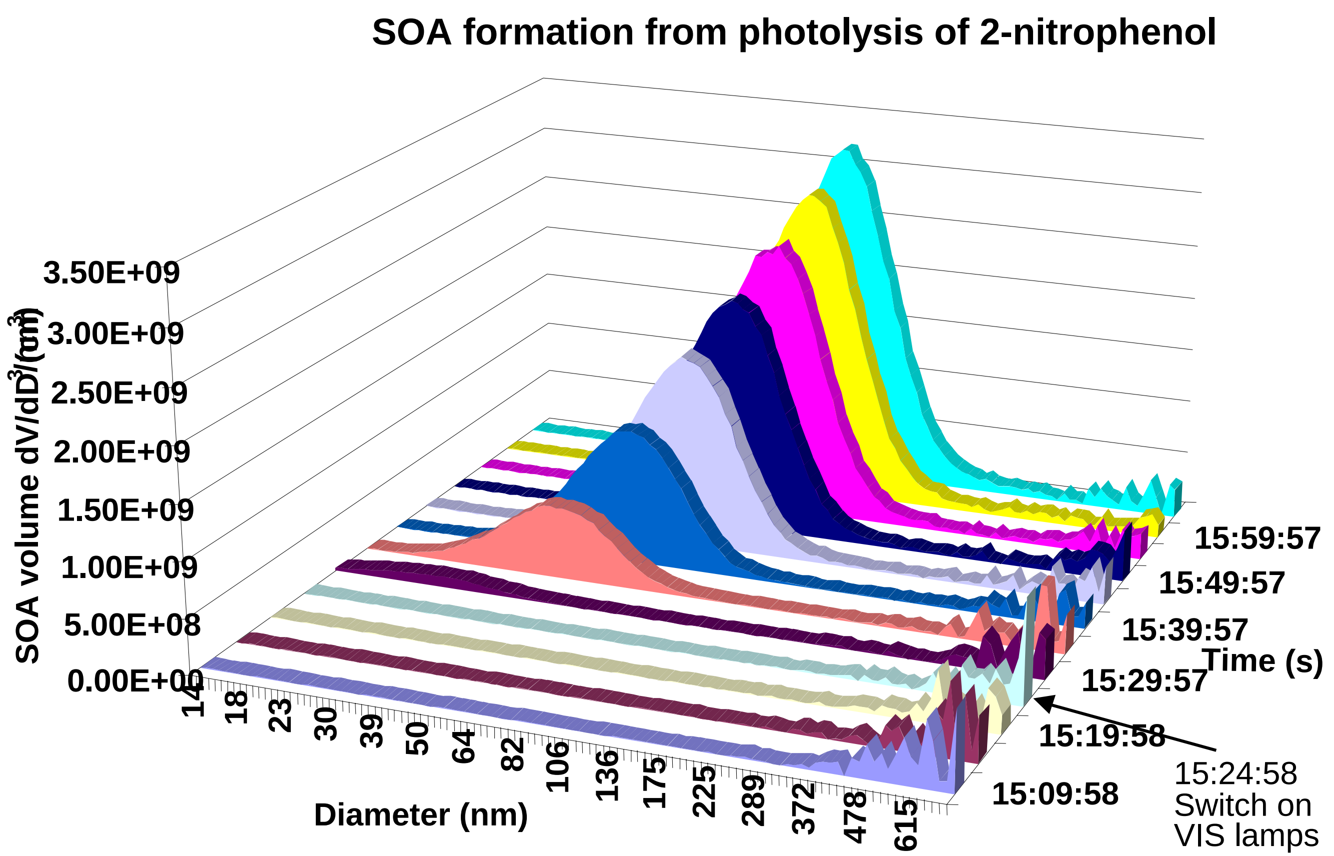
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Aromatic HCs: nitrophenols and SOA formation

Concentration-time profiles of 2-nitrophenol and the aerosol formed from an experiment in the Wuppertal guartz glass reactor

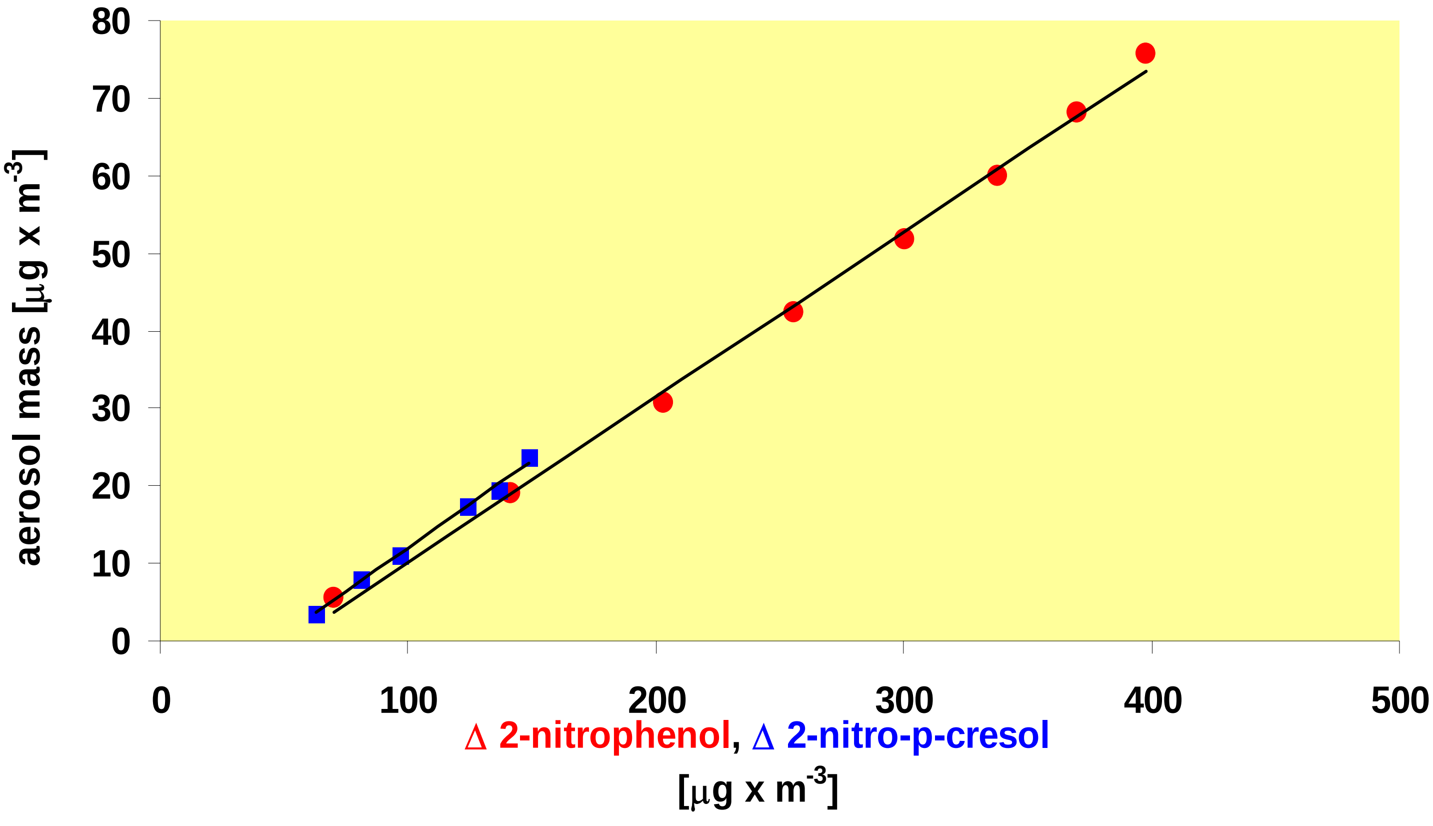


Aromatic HCs: 2-nitrophenol photolysis – SOA formation

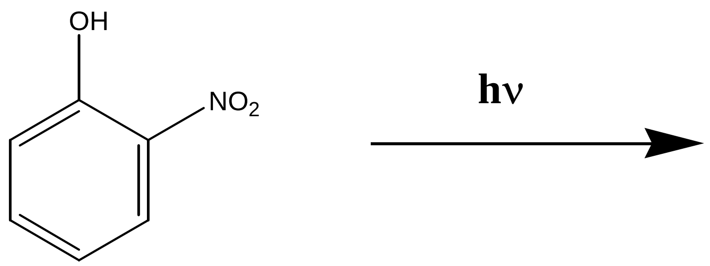


Aromatic HCs: nitrophenols and SOA formation

Particles mass yield as a function of 2-nitrophenol and 2-nitro-p-cresol reacted



Aromatic HCs: Aerosol from nitrophenol photolysis

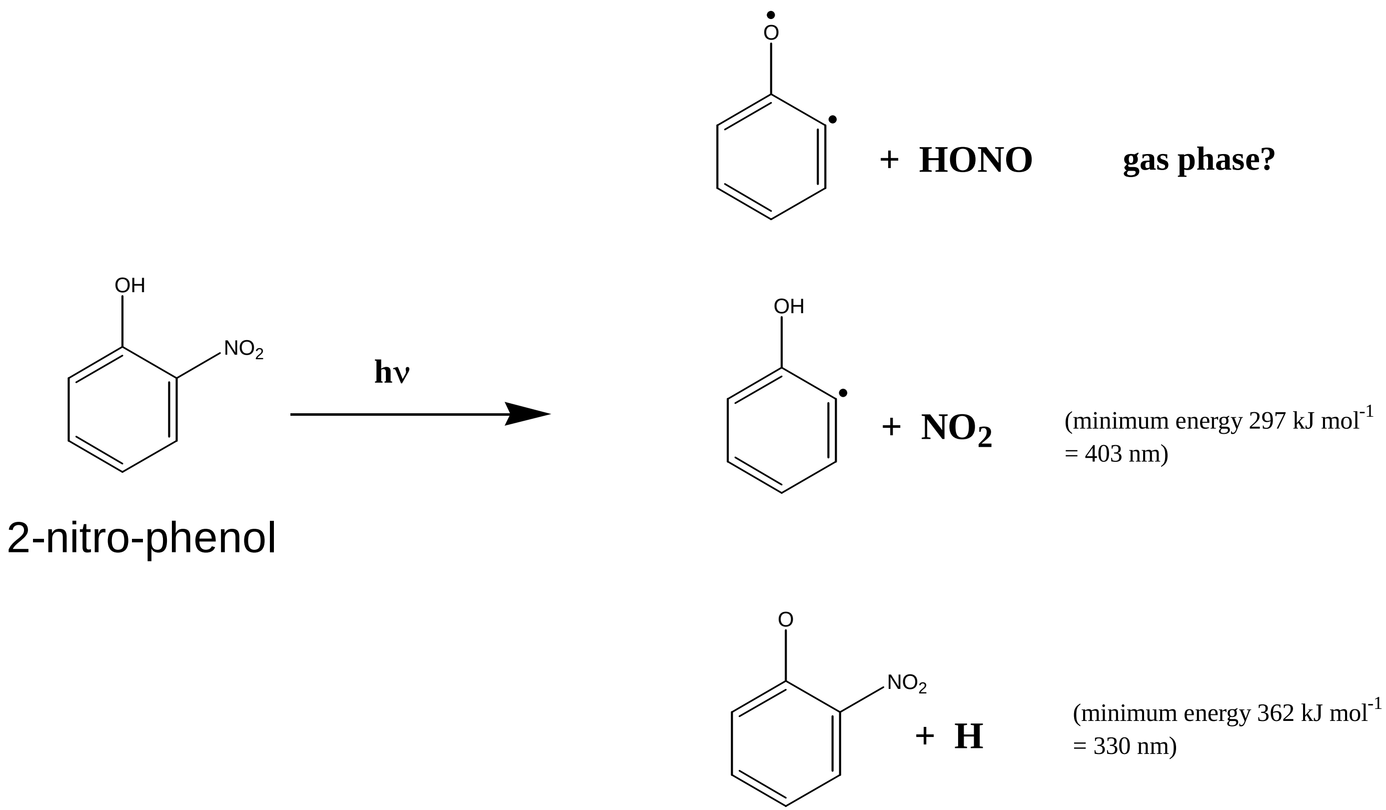


aerosol formation

HONO formation

2-nitro-hydroxybenzene

Mechanism ?



other products?

Aromatic HCs: SOA requirements

Over the past decade significant progress has been made in our understanding of the gas-phase oxidation mechanisms of aromatic hydrocarbons. However, our knowledge is far from being complete and many gaps exist and we need:

– a better grasp of the secondary photooxidation processes in the gas phase leading to low volatility compounds and thus to SOA formation,

– a better understanding the impact of NOx levels on the final products of the SOA formation chemistry

– knowledge on the heterogeneous reactions between particle associated substances and gaseous compounds able to modify the composition and the mass of aerosol,

– a better understanding of the aerosol chemistry responsible for the recently reported polymer formation which increases the aerosol mass,

– quantitative knowledge on the molecular composition of the major components of the aerosol produced from the above mentioned processes.

A full appreciation of all the processes involved will probably have to await the evolution of new more powerful analytical probing techniques that are starting to emerge.

Further experimental work is also needed in order to transpose laboratory results often obtained under high concentrations of organic precursors and oxidants to atmospheric conditions.

Atmos. Chem. Phys. Discuss., 4, 5855–6024, 2004
www.atmos-chem-phys.org/acpd/4/5855/
SRef-ID: 1680-7375/acpd/2004-4-5855

Organic aerosol and global climate modelling: a review

M. Kanakidou, J. H. Seinfeld, S. N. Pandis, I. Barnes, F. J. Dentener,
M. C. Facchini, R. van Dingenen, B. Ervens, A. Nenes, C. J. Nielsen,
E. Swietlicki1, J. P. Putaud, Y. Balkanski1, S. Fuzzi, J. Horth,
G. K. Moortgat, R. Winterhalter, C. E. L. Myhre, K. Tsigaridis, E. Vignati,
E. G. Stephanou, and J. Wilson

Aromatic HCs: recent papers

Secondary Organic Aerosol Formation from Aromatic Precursors.
1. Mechanisms for Individual Hydrocarbons
W. Dechapanya, A. Eusebi, Y. Kimura, D. T. Allen
Environ. Sci. Technol. 37 (2003) 3662-3670

Secondary Organic Aerosol Formation from Aromatic Precursors.
2. Mechanisms for Lumped Aromatic Hydrocarbons
W. Dechapanya, A. Eusebi, Y. Kimura, D. T. Allen
Environ. Sci. Technol. 37 (2003) 3671-3679

The authors conclude that:
Mechanisms describing SOA formation from aromaic species must incorporate the reactions of reactive intermediates

Simulating Secondary Organic Aerosol Activation by Condensation of Multiple Organics on Seed Particles

J. D. Fillo, C. A. Koehler, T. P. Nguyen, D. O. DeHaan, B. A. Gilbert, K. P. Flinn

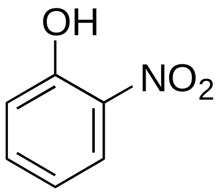
Environ. Sci. Technol. 37 (2003) 4672-4677

It is evident that a more complete molecular identification of aromatic photooxidation aerosol awaits analytical techniques not yet brought to bear on this problem.

D.R. Cocker, B. T. Mader, M. Kalberer, R. C. Flagan and J. H. Seinfeld

Atmospheric Environment 35 (2001) 6073-6085

Aromatic HCs: Aerosol formation

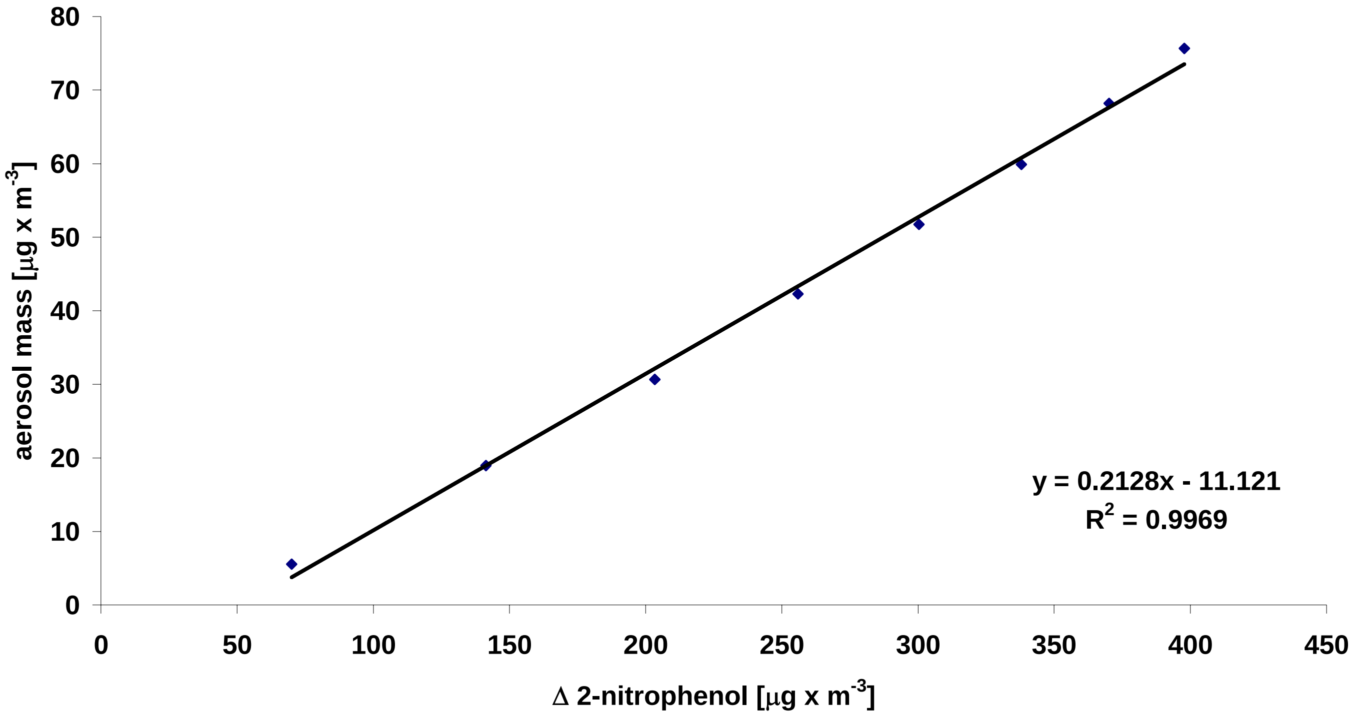


2-nitro-hydroxybenzene

- UV spectrum 200 - 360 nm
- aerosol formation upon irradiation with sun lamps
- possible formation of OH radicals (isoprene as tracer)
- how fast is the photolysis?
- underestimation of nitrophenol yields in the oxidation of aromatic hydrocarbons?
- still early days we need more test experiments

Aromatic HCs: aerosol yield 2-nitrophenol photolysis

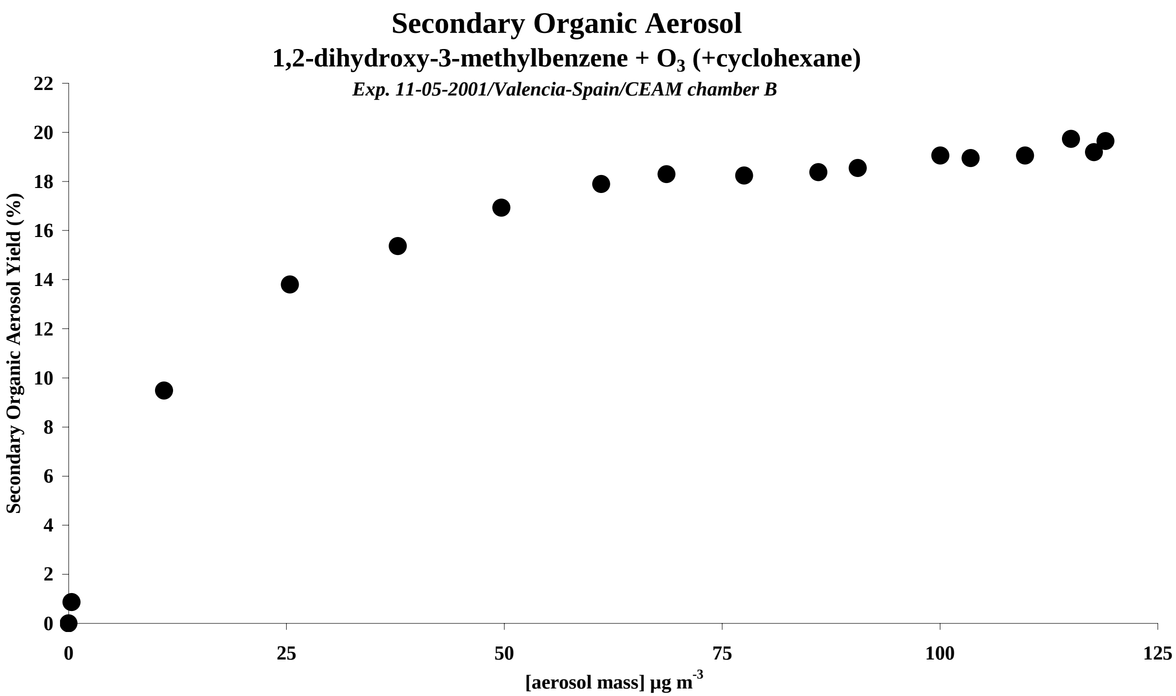
Particle mass yield as a function of 2-nitrophenol reacted

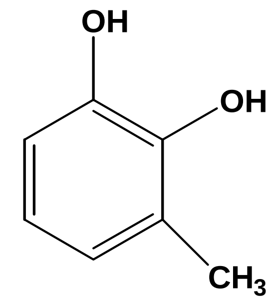


-no background aerosol reactor in after 30 minutes irradiation with VIS lamps
-the nitrophenol wall loss rate was 1.84 x 10^{-4} s^{-1}
-initial concentration of 2-nitrophenol was approx 400 ppbV
-aerosol formation observed after 64 s irradiation, and 12 ppbV consumption of 2-nitrophenol
- the nitrophenol photolysis rate after wall loss correction was 9.28 x 10^{-5} s^{-1}
- no reaction with OH (possible formation in system); scavenger experiments with isoprene
- application of a partitioning model (Odum *et al*. 1996); fit works assuming 1 compound partitioning between gas and particulate phase
- product detection from the photolysis of 2-nitrophenol was not possible

Aromatic HCs: Aerosol Formation (SOA)

Particle formation from O_3 + 1,2-dihydroxy-3-methylbenzene





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