Nucleation-Particle Formation in Diesel Vehicle Exhaust: Role of Acid-Base interactions

F. Arnold(1,2), L. Pirjola (3,4), T. Rönkkö (5), U. Reichl (1), H. Schlager (2), T. Lähde (3,4), J. Heikkilä (5), and J. Keskinen (5)

(1) Max Planck Institute for Nuclear Physics (MPIK), Heidelberg, Germany
(2) Deutsches Zentrum für Luft und Raumfahrt (DLR), Oberpfaffenhofen, Germany
(3) Department of Technology, Metropolia University of Applied Sciences, Helsinki, Finland
(4) Department of Physics, University of Helsinki, Helsinki, Finland
(5) Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, Finland

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Diesel-Nucleation-Particles (NUPs)

- NUPs reach large number-concentrations
- NUPs have diameters of about 10 nm
- NUPs have large total surface-area-concentrations
- NUPs have just the perfect size for most efficient intrusion of the lowest and most vulnerable region of human lung (alveolae-region)
- Important aspects of NUP formation are not well understood. In particular, nucleating gases and condensing gases are not well known.
- NUPs are not regulated by legislation! Regulation only for particles with D > 20 nm (Europe)
Diesel-Nucleation-Particles (NUPs)

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- NUPs have mean \textit{diameters of about 10 nm}
- NUPs have large \textit{total surface-area-concentrations}
- NUPs have perfect size for most efficient intrusion of the lowest and most vulnerable region of human lung (alveolae)
- Important aspects of NUP formation are \textit{not well understood}
  In particular, \textit{nucleating gases and gases involved in early growth of nascent NUOs} are not well known
- NUPs are \textit{not regulated by legislation!}
  Regulation only for particles with $D > 20$ nm (Europe) and $D > 23$ nm (USA)
Investigations of Nucleation-Particle (NUP) Formation in Modern Diesel Vehicle Exhaust

**Lab Experiments**
- Test bed (with Heavy Duty Diesel Vehicle Engine)
- different Fuels
- different Fuel sulfur content (FSC)
- different engine loads (EL)
- different exhaust aftertreatment systems (ATS: DOC; DPF)

**Model Simulations**
- different nucleation mechanisms
- different organics
- different FSC
Time series of gas-phase sulfuric acid in heavy duty vehicle engine test-run

FSC = 36 ppm ; EL = 25, 50, 75, 100 % ; ATS (DOC + POC)
Time series of gas-phase acids in heavy duty vehicle engine test-run

FSC = 36 ppm ; EL = 25, 50, 75, 100 % ; ATS ( DOC + POC)

Engine Load

H2SO4
Total of all strong acids HX  except H2SO4
Acid  164
Acid  142
Background

without ATS

with ATS

$H_X$ (sum mole fraction)

$H_2SO_4$ [mole fraction]
H2SO4/H2O - Nucleation-Particle Formation in Modern Diesel Vehicle Exhaust (simplified scheme without soot)

Burnt Gas:
- H2O
- SO2
- NOx
- HC
- SOOT

Exhaust After-Treatment-System
- OXICAT
- SCR
- DPF

Nucl → Cond
H2SO4 + H2O → Coagulation-Growth
H2SO4/H2O - Nucleation-Particle Formation in Modern Diesel Vehicle Exhaust (simplified scheme without soot)

Burnt Gas:
- H2O
- SO2
- NOx
- HC
- SOOT

Exhaust After-Treatment-System
- DPF
- OXICAT

Condensation:
SO3 + H2O → H2SO4
H2SO4 identified and rate coefficient measured originally by Reiner and Arnold

Coagulation-Growth

Nucl → Cond → H2SO4 + H2O
BHN-modelled and measured NUP size-distributions:
FSC = 36 ppm ; ATS (DOC (ECO) + POC (ECO))

[Graph showing size distributions with labels for measured and modelled data]
09:30 LT

ION-RECTION SCHEME for HX DETECTION:

\[
\text{NO}_3^-\text{HNO}_3 + \text{HX} \rightarrow \text{X-HNO}_3 + \text{HNO}_3
\]

(HX is acid having GA larger than GA (HNO3)
**ION-RECTION SCHEME for HX DETECTION:**  
$tr = 0.1 \text{ s } , \ tc = 0.1 \text{ s } , \ tr/tc = 1$

$\text{NO}_3\text{-HNO}_3 + \text{HX} \rightarrow \text{X-HNO}_3 + \text{HNO}_3$ \hspace{1cm} (HX is acid having GA larger than GA (HNO3))

$\text{X-HNO}_3 + \text{HX} \rightarrow \text{X-HX} + \text{HNO}_3$

**Table:**

- 125 : NO$_3$-HNO$_3$ (reagent ion)
- 160 : HSO$_4$-HNO$_3$
- 162 : isotopomer
- 195 : HSO$_4$-H$_2$SO$_4$
- 197 : isotopomer

**Graph:**

- Engine load
- H$_2$SO$_4$
- Sum of all acids exclusive of H$_2$SO$_4$
- Acid with m/z = 204 amu
- Acid with m/z = 226 amu

**Legend:**

- Engine load at 1800 ppm [%]
- Local time: 28/11/2007 11:10
IONS-RECTION SCHEME for HX DETECTION:

\[ \text{NO}_3^- \text{HNO}_3 + HX \rightarrow X \text{-HNO}_3 + \text{HNO}_3 \]  (HX is acid having GA larger than GA (HNO_3))

\[ X \text{-HNO}_3 + HX \rightarrow X \text{-HX} + \text{HNO}_3 \]
Ion Identification via

- Mass number
- Isotopic signatures
- CID (Collision-Induced-Dissociation). Energetic collisions (with He-Atoms) of mass selected ions stored in a Quadrupole Ion Trap, leading to first-generation fragment ions.
CID-Investigations (negative ions)

- Parent-Ion HSO4-H2SO4 (mass number: 195)
- Fragment ions: HSO4- (97) ; HSO4SO3- (177)
Collision-Induced-Dissociation (CID) of mass selected ion 195 (at two collision-energies)

- 97 : HSO4-
- 98 : - H2SO4
- 18 : - H2O
- 177 : HSO4-SO3
- 195 : HSO4-H2SO4
**FLOW REACTOR EXPERIMENT: Ion-Nucleation**

T=295 K , RH= 4.7 % , RA< 2.0 %  →  no HONU ! , tres = 0.9 s / tr/tc = 10 , 20 , 40
A. Sorokin, D. Wiedner, and F. Arnold (2006)

**HSO₄⁻(H₂SO₄)ₐ(H₂O)ₜ**

**Acid Mole Fraction**

**Number of H₂SO₄ molecules in cluster ion**

**T=295 K**

**RH=4.5 %**
Time series of gas-phase H2SO4 (mole fract. in raw exhaust): FSC = 36 ppm; ATS (DOC (ECO) + POC (ECO))

Engine Load
H2SO4
Total of all strong acids HX except H2SO4
Acid 164
Acid 142
CID-Investigations (negative ions)

- Parent-Ion (mass number: 226) for 2 collision energies:
- Fragment ions: HSO4- (97) ; HSO4SO3- (177)
CID (MS-2) of PARENT-ION 226- (at two collision-energies)

- 63

- 44
CID (MS-2) of PARENT-ION 226- (at two collision-energies)

163 : 119COOH-

- 63 : HNO3

226 : 163-HNO3

- 44 : CO2

119 : 163
CID-Investigations (negative ions)

• Parent-Ion (mass number: 204-) for 2 collision energies:
• Fragment ions: 163- ; 141-
• Neutral fragment 63 (probably HNO3)
• Neutral fragment 44 (probably CO2; if so, indication that ion 163- is de-protonated carboxylic acid)
CID (MS-2) of PARENT-ION 204- (at two collision-energies)

204 : 141-HNO3

- 63 : HNO3

141

204
CID-Investigations (negative ions)

- Mass selected First-Generation Fragment-Ion (mass number: 141) for 2 collision energies:
- Second-generation fragment ion 97
- Neutral fragment: 44 (probably CO2; if so, indication that ion 141- is de-protonated carboxylic acid)
CID (MS-3) of FRAGMENT-ION 141- (at two collision-energies)

- 44 : CO2

97

141
Nucleation-Particle Formation in Diesel Vehicle Exhaust (simplified scheme without soot)

Burnt Gas:
- H2O
- SO2
- NOx
- HC
- SOOT

Exhaust After-Treatment-System
- OXICAT
- DPF

Nucl

Cond

H2SO4 + H2O

Coagulation-Growth

Org. Acids

Cond
BHN-modelled and measured NUP size-distributions:
FSC = 36 ppm ; ATS = DOC (ECO) + POC (ECO)
Nucleation-Particle Formation in Diesel Vehicle Exhaust (simplified scheme without soot)

Burnt Gas: H2O, SO2, NOx, HC, SOOT

Exhaust After-Treatment-System

DPF

OXICAT

H2SO4 + H2O

Nucl

Cond

Nucl

Cond

Org. Acids

Coagulation-Growth
Particle Number Size Distribution: FSC = 36 ppm; EL = 100%; ATS (DOC + OpenFilter)
Nucleation-Particle Formation in Diesel Vehicle Exhaust (simplified scheme without soot)

Burnt Gas:
- H2O
- SO2
- NOx
- HC
- SOOT

Exhaust After-Treatment-System
- OXICAT
- SCR
- DPF

Nucl: H2SO4 + H2O

NH3

HNO3

Org. Acids

Cond

Coagulation-Growth
For more Information see: references (following 2 slides)
First Online Measurements of Sulfuric Acid Gas in Modern Heavy-Duty Diesel Engine Exhaust: Implications for Nanoparticle Formation

F. Arnold,* I. Pirjola,§ T. Rönkkö,∥ U. Reichl,* H. Schlager,† T. Lähde,§ J. Hakkinen,† and J. Keskinen†

1Max Planck Institute for Nuclear Physics (MPIK), P.O. Box 103980, D-69029 Heidelberg, Germany
2Deutsches Zentrum für Luft und Raumfahrt (DLR), Oberpfaffenhofen, Germany
3Department of Technology, Metropolia University of Applied Sciences, P.O. Box 4021, FIN-00180 Helsinki, Finland
4Department of Physics, University of Helsinki, P.O. Box 64, FIN-00014 Helsinki, Finland
5Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, P.O. Box 692, FIN-33101 Tampere, Finland

ABSTRACT: To mitigate the diesel particle pollution problem, diesel vehicles are fitted with modern exhaust after-treatment systems (ATS), which efficiently remove engine-generated primary particles (soot and ash) and gaseous hydrocarbons. Unfortunately, ATS can promote formation of low-vapor pressure gases, which may undergo condensation and condensation leading to formation of nucleation particles (NUP). The chemical nature and formation mechanism of these particles are only poorly explored. Using a novel mass spectrometric method, online measurements of low-vapor-pressure gaseous SO2 and NOx were performed for exhaust of a modern heavy-duty diesel engine operated with modern ATS and combusting low and ultralow sulfur fuels and also biofuel. It was observed that the gaseous sulfuric acid (GSA) concentration varied strongly, although engine operation was stable. However, the exhaust GSA was observed to be affected by fuel sulfur level, exhaust after-treatment, and driving conditions. Significant GSA concentrations were measured also when biofuel was used, indicating that GSA can be originated also from lubricant oil sulfur. Furthermore, accompanying NUP measurements and NUP model simulations were performed. We found that the exhaust GSA promotes NUP formation, but also organic (acidic) precursor gases can have a role. The model results indicate that to that the measured GSA concentration alone is not high enough to grow the particles to the detected sizes.

INTRODUCTION

Exhaust aerosol particles emitted by traffic, especially by diesel vehicles, represent major air pollutants in cities and near motorways.1–3 In order to minimize these emissions, modern diesel vehicles are fitted with exhaust after-treatment systems (ATS) which decreases efficiently the solid soot particle and gaseous emissions. Typically, the ATS with quasi-continuous regeneration involve a combination of a diesel particle filter (DPF)4 and a diesel oxidation catalyst (DOC).5 The most efficient DPFs are so-called wall-flow DPFs, which trap more than 95% of the soot particles. However, wall-flow DPFs are subject to relatively rapid clogging by soot; thus, they require active regeneration, e.g., fuel additives. Nearly continuous soot regeneration is often achieved by NOx-induced soot burn-up. The NOx, which acts as an oxidant already at typical heavy-duty diesel exhaust temperatures, is generated by catalytic conversion of engine-generated NO using a DOC upstream of the DPF. Unfortunately, the oxidative exhaust after-treatment may also generate undesired oxidation products. A striking example is SO2, which is formed by oxidation of engine-generated SOx and reacts with water vapor, leading to gaseous sulfuric acid (GSA).6,7 GSA has a very low saturation vapor pressure, and therefore, it may condense and even nucleate in the cooling dilution process of the exhaust. Thus, the existence of GSA can lead to formation and growth of sulfuric acid–water particles, a particular form of nucleation particles (NUP). Due to the small sizes the NUP can intrude the lowest compartment of the human lung.8,9 Other possible oxidation products are partially oxidized hydrocarbons. These may include also condensable gases, particularly organic dicarboxylic acid, some of which possess very low vapor pressures and therefore would be potential condensing and eventually even nucleating gases. In fact, organic dicarboxylic acid have been observed in car exhaust.10,11 Additionally, oxidation products may include also carboxylic compounds like oxygenated polycyclic organic compounds, particularly ones bearing a NOx group (Nitro-PAHs), whose formation may be promoted by NOx, and some of which may...
Model studies of volatile diesel exhaust particle formation: are organic vapours involved in nucleation and growth?

L. Pirjola¹,², M. Karl³, T. Rönkkö⁴, and F. Arnold⁵,⁶

¹Department of Technology, Metropolia University of Applied Sciences, P.O. Box 4021, 00180 Helsinki, Finland
²Department of Physics, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland
³Norwegian Institute for Air Research, P.O. Box 100, 2027 Kjeller, Norway
⁴Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, P.O. Box 692, 33101 Tampere, Finland
⁵Max-Planck-Institut für Kernphysik, Heidelberg, Germany
⁶Deutsches Zentrum für Luft und Raumfahrt (DLR), Oberpfaffenhofen, Germany

Correspondence to: L. Pirjola (liisa.pirjola@metropolia.fi, liisa.pirjola@helsinki.fi)

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Conclusions

- Numerous acidic gases HX with gas-phase acidities $GA(HX) > GA(HNO3)$ detected in modern Diesel-exhaust.
- H2SO4 has an important role in NUP formation, but does not seem to be the only relevant nucleating gas.
- NUP growth promoted by condensing gases (including also carboxylic diacids?)
- As NUP grow, the Kelvin-Effect decreases and more gaseous species may condense on grown NUPs.
- We look forward to greatly improved measurements. We have recently increased (by factor up to 120!) the sensitivity of our trace gas and gas-phase ion detection instrument.
Thank You

for your interest