The combustion conditions of hydrocarbon flames determine to a large extent the bulk and interfacial properties of the resulting combustion aerosol (soot). We have applied a soft interrogation technique for some of the interfacial functional groups using heterogeneous reactions of six probe gases of differing reactivity, namely \( \text{N}((\text{CH}_3)_3) \), \( \text{NH}_2\text{OH} \), \( \text{CF}_3\text{COOH} \), \( \text{HCl} \), \( \text{NO}_2 \), \( \text{O}_3 \). The experimental method rests upon measuring the rate of uptake of a probe gas under molecular flow conditions in the presence of deposited aerosol particles whose metrology is known (mass, specific surface area). The gas uptake to saturation of the probe molecules was measured in a Knudsen flow reactor and expressed as a density of surface functional groups using the measured BET surface area. The experimental methodology also afforded the measurement of the uptake coefficient of the probe gas to the carbonaceous nanoparticle.

The probe gases taken up by the sample addressed acidic (carboxylic) and basic sites such as pyrones, carbonyl or partially oxidized sites (\( R_1\text{-C(O)-R}_2 \)) and strongly/weakly reducing functional surface groups. The used probes enabled the characterization of the particle surface in terms of its oxidation state (oxidized, partially oxidized, strongly/weakly reducing). The limit of detection was generally well below 1% of a molecular monolayer depending on the BET surface area of the used soot. The soot samples interacted with all probe gases which points to the coexistence of many different functional groups on the same aerosol surface such as acidic, basic, strongly/weakly reducing and oxidizing sites.

Table 1 displays the experimental results on four soot reference materials as well as three multiwalled carbon nanotubes (MWCNT). The salient differences between these carbonaceous materials will be discussed in some detail. For instance, The 5% BTCA-doped Graphitized Thermal Soot (GTS80) showed in fact 17% of a molecular monolayer of carboxylic surface functions, roughly 50 times the amount of the undoped substrate material GTS80 and a factor of 5 more than polyacrylic acid-coated MWCNT. For \( \text{O}_3 \) and \( \text{NO}_2 \) exposure to reference soot a slow steady-state reaction has been measured corresponding to a first-order uptake coefficient of roughly \( 4\times10^{-5} \). It is interesting to note that no significant uptake of \( \text{HCl} \) has been measured in contrast to \( \text{CF}_3\text{COOH} \) which may indicate the presence of basic oxides on the soot. These compounds are derived from \( \alpha \)- or \( \gamma \)-pyrone of which coumarin and chromone are aromatic derivatives. This basicity is based on a special topology between a carbonyl and an ether function and does not necessitate the presence of an amine N.
Table 1: Surface functional group densities for six different gas probes for soot and MWCNT’s. The upper and lower numbers in each box correspond to the number of molecules/cm$^2$ and the fractional surface coverage in monolayers, respectively. The red numbers indicate steady-state uptake (reaction).

<table>
<thead>
<tr>
<th>Samples →</th>
<th>Graphitized Soot</th>
<th>Thermal Soot</th>
<th>Graphitized Soot</th>
<th>GTS80 + 5% BTA</th>
<th>MWCNT 1 Uncoated</th>
<th>MWCNT 2 Polycrystalline Coating</th>
<th>MWCNT 3 PS-PB-PMMA Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probes ↓</td>
<td>GTS6 (6 m$^2$/g)</td>
<td>T900 (6.5 m$^2$/g)</td>
<td>GTS80 (8 m$^2$/g)</td>
<td>(80 m$^2$/g)</td>
<td>(227.4 m$^2$/g)</td>
<td>(54.1 m$^2$/g)</td>
<td>(34 m$^2$/g)</td>
</tr>
<tr>
<td>N(CH$_3$)$_3$</td>
<td>1.1x10$^{-4}$ 0.0030</td>
<td>6.1x10$^{-4}$ 0.1690</td>
<td>1.3x10$^{-4}$ 0.0036</td>
<td>1.2x10$^{-7}$ 0.033</td>
<td>8.0x10$^{-1}$ 0.0022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_2$OH</td>
<td>4.0x10$^{-2}$ 0.005</td>
<td>2.9x10$^{-2}$ 0.037</td>
<td>1.1x10$^{-4}$ 0.139</td>
<td>6.3x10$^{-4}$ 0.797</td>
<td>5.9x10$^{-4}$ 0.747</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>1.3x10$^{-2}$ 0.0015</td>
<td>&lt;7.7x10$^{-1}$ 0.000895</td>
<td>3.6x10$^{-2}$ 0.042</td>
<td>8.1x10$^{-2}$ 0.094</td>
<td>4.1x10$^{-2}$ 0.0048</td>
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</tr>
<tr>
<td>CF$_3$COOH</td>
<td>1.5x10$^{-4}$ 0.0375</td>
<td>7.0x10$^{-4}$ 0.0175</td>
<td>7.7x10$^{-2}$ 0.0193</td>
<td>1.1x10$^{-4}$ 0.0275</td>
<td>1.1x10$^{-7}$ 0.00275</td>
<td>1.7x10$^{-7}$ 0.00425</td>
<td></td>
</tr>
<tr>
<td>NO$_2$</td>
<td>&lt;3.3x10$^{-14}$ 0.00465</td>
<td>1.7x10$^{-14}$ 0.0239</td>
<td>&lt;4.5x10$^{-10}$ 0.0063</td>
<td>1.3x10$^{-10}$ 0.0183</td>
<td>5.3x10$^{-10}$ 0.00746</td>
<td>2.2x10$^{-10}$ 0.00310</td>
<td>5.6x10$^{-10}$ 0.00789</td>
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<tr>
<td>O$_3$</td>
<td>SS-reaction 2.4x10$^{-14}$ 0.324</td>
<td>4x10$^{-14}$ 0.00540</td>
<td>3.0x10$^{-10}$ 0.0405</td>
<td>1.7x10$^{-14}$ 2.30</td>
<td>3.3x10$^{-10}$ 0.446</td>
<td>3.2x10$^{-10}$ 4.324</td>
<td></td>
</tr>
</tbody>
</table>

However, the emphasis of the presentation will be placed on the reducing properties of the reference soot and MWCNT materials as indicated by the reactivity with O$_3$ and NO$_2$. These reducing surface functional groups may be part of a reversible redox-active catalytic system that uses air oxygen for oxidation of biochemical molecules in the presence of the carbonaceous nanomaterial of interest. Examples are the oxidative coupling of dithiothreitol (DTT) and the oxidation of dichlorodihydrofluorescein (DCFH) to dichlorofluorescein (DCF) which is fluorescing with amorphous carbon and soot. The reaction mechanism, reaction (a), (b) and (c) with (d) being the sum, is as follows:

\[
\begin{align*}
O_2 + PM_{\text{red}} &\rightarrow H_2O_2 + PM_{\text{ox}} \\
PM_{\text{ox}} + \text{Red} &\rightarrow PM_{\text{red}} + Ox \\
H_2O_2 + PM &\rightarrow PM_{\text{ox}} + H_2O \\
O_2 + \text{Red} + PM &\rightarrow Ox + PM_{\text{ox}} + H_2O
\end{align*}
\]

Reaction (d) indicates that Red corresponding to an oxidizable thus reducing biomolecule (such as an antioxidant) may be catalytically oxidized by O$_2$ to Ox in the presence of PM (amorphous carbon or soot) that is cycling between its reduced and oxidized form, PM$_{\text{red}}$ and PM$_{\text{ox}}$, respectively. Reaction (c) describes the slow deactivation of the catalyst we have observed in laboratory studies. These results are interesting as they enable the possibility of predicting the condensed phase reactivity of aqueous aerosol suspensions with biologically relevant reducing agents on the basis of simple gas phase titration with NO$_2$ probing for strongly reducing sites. In a wider context, harmful effects of nanoparticles on health have been mostly attributed to the oxidative properties of the aerosols. This work tries to draw attention to the fact that reducing properties of aerosols may be of even greater importance owing to a possible catalytic effect of nanoparticles in biochemical oxidations where the oxidant is air.
oxygen. The enclosed figure shows an example of such a catalytic oxidation of the prototypical antioxidant molecule Dithiothreitol ($\text{C}_4\text{H}_8\text{O}_2\text{S}_2$) to its cyclic (oxidized) form in the presence of molecular oxygen in aqueous solution and a suspension of FW2 amorphous carbon. Reaction (a) is the rate-limiting step controlling the overall kinetics.

In summary, we have searched for evidence of reducing surface functional groups on carbonaceous nanoparticles and have stumbled upon a catalytic reaction involving air oxygen that oxidizes biochemically relevant antioxidant molecules. Indeed, we have found evidence for the importance of reducing surface functional groups such as reaction (a) above that is rate-limiting and therefore shows up in correlation plots. However, these reducing groups do not act by themselves but in concert with oxidation reactions such as reaction (b) above. The concerted action of reactions (a) and (b) very efficiently catalytically oxidize biochemically active molecules such that a small number of catalytically active sites on the surface of carbonaceous nanoparticles max oxidize a large number of antioxidants, given the unlimited supply of the oxidizer air. Reaction (c) limits the turnover (number of catalytic cycles per site) owing to slow deactivation of the active catalytic site with time.

![Aqueous suspension of FW2 am. C. + DTT/O₂](image)

**O₂ consumption measured using a Clark electrode upon repeated injection of DTT serving as a model compound to be oxidized by air oxygen dissolved in the aqueous solution in the presence of catalytic amounts of amorphous carbon FW2. The plot shows that oxidation of DTT starts only after the addition of the aqueous FW2 suspension.**
We may summarize the present findings as follows:

- Surface Composition of Soot and other carbonaceous NP’s is **multifunctional**.
- Use of "chemical" **surface interrogation** techniques delivers different results in comparison with spectroscopic and imaging methods.
- **Correlation** of surface composition in terms of number of surface functional groups with toxicological tests/biomarkers. An even **better correlation** may be obtained when considering the surface reactivity of probe gases instead of the number of active sites reacting with a probe gas.
- In addition to well-documented health effects of oxidized surface groups there are indications that **reduced** surface groups may lead to same. Incidence of NP-catalyzed chain reactions with NP as chain carrier/catalyst. Therefore, the oxidizing and reducing surface groups do not act in isolation, instead they are cycling between oxidized and reduced form an self-sustained efficient catalytic reaction system.
Paul Scherrer Institut

Ari Setyan\textsuperscript{1}, Jean-Jacques Sauvain\textsuperscript{2}, Michael Riediker\textsuperscript{2}, Olga Popovicheva\textsuperscript{3} and Michel J. Rossi\textsuperscript{4}

\textsuperscript{1}ULCO, Dunkerque (F); \textsuperscript{2}IST Lausanne (CH); \textsuperscript{3}Moscow State University; \textsuperscript{4}PSI/LAC Villigen (CH)

Functional Groups on the Surface of Carbonaceous Nanomaterials and Human Health
Various Ways of Characterizing Soot Particles

- Thermal Behavior: Pyrolysis, oxidation, thermogravimetric measurement
- Extraction Behavior: Organic Phase vs. Elemental Carbon (OC/EC) or WSOC/WinSOC, etc.
- Elemental Analysis (C, H, N, O, S,…)
- Surface Spectroscopies (FTIR, XRD, EELS, XPS)
- Imaging (ESEM, HRTEM)
- **Chemical** Composition of the Interface:  ➜ **Surface functional groups independent of chemical speciation.**
Gas Phase Probes for 4 Families of Surface Functions

S-COOH + N(CH₃)₃ ➔ S-COO⁻(CH₃)₃NH⁺ (Salt)

Oxidized surface

S(R)-C=O + NH₂OH ➔ S(R)-C(OH)(NHOH) ➔ S(R)-C=N-OH (Imine, Schiff base) + H₂O

Partially oxidized surface (aldehydes, ketones)

S-B: + HCl/CF₃COOH ➔ S-B:H⁺Cl⁻/CF₃COO⁻ (Salt)

Basic oxides and (N-centered) bases

S-C_red + O₃/NO₂ ➔ S-C_ox + O₂/N(II or III) (HONO or NO)

Reduced adsorption sites, strongly reducing (NO₂) sites (subset), sum = strongly + weakly reducing sites (O₃)
ACIDIC SITES
On carbonaceous particles

BASIC SITES
On carbonaceous particles (excluding N-bases!)

U. Hofmann et al; H.P. Boehm et al. (1970’s)
Surface Interrogation using reactive probe Gases

Knudsen Flow reactor

[Diagram of Knudsen Flow reactor with labels for components such as capillary inlet, plunger reactor, sample holder, orifice plate, cryogenic pump, primary pump, turbo molecular pump, membrane pump, mass spectrometer, lock-in amplifier, and chopper control.]
Two examples of raw data: Bus depot filter (top), hexane flame (bottom)

Typical raw data of a titration experiment using the Knudsen flow reactor. Sample: aerosols collected in the bus depot 2 (23.05.2006, daytime) on silanized quartz fiber filter. Probe gas: HCl. m/z: 36. $S_0$: mass spectrometer signal at steady state. SR: mass spectrometer signal immediately after the beginning of the reaction.

$N_r(uptake) \rightarrow N_r/S \ (\# \ cm^{-2})$

$N_r(uptake) \rightarrow N_r/M \ (\# \ mg^{-1})$

1ML coverage $\rightarrow N_r/ML \ (\# \ cm^{-2})$

Raw data of $O_3$ uptake on 1.14 mg of soot from a rich hexane flame at a flow rate of $6.7 \times 10^{15}$ molecule s$^{-1}$ monitored at m/e 48 in the 1 mm diameter aperture Knudsen flow reactor ($k_{esc} = 0.0509$ s$^{-1}$) leading to the initial uptake coefficient $\gamma_0 = 1.6 \times 10^{-3}$. 
## UPTAKES of Probe Gases ($N_i^M$)

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<tr>
<th>$N_i^M$/mg</th>
<th>Surface BET [m²/g]</th>
<th>N(CH₃)₃</th>
<th>NH₂OH</th>
<th>CF₃COOH</th>
<th>HCl</th>
<th>O₃</th>
<th>NO₂</th>
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<td>20³</td>
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<td>7.3 · 10¹⁷</td>
<td>2.0 · 10¹⁵</td>
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<td></td>
<td></td>
<td>2.9 · 10¹²</td>
<td>6.0 · 10¹³</td>
<td>9.2 · 10¹²</td>
<td></td>
<td>3.7 · 10¹⁵</td>
<td>9.8 · 10¹²</td>
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<td></td>
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<td>1.8 · 10¹³</td>
<td>3.5 · 10¹²</td>
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<td></td>
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<td>9.6 · 10¹³</td>
<td>9.9 · 10¹²</td>
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<td>9.6 · 10¹³</td>
<td>8.9 · 10¹²</td>
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<td>3.2 · 10¹⁵</td>
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<td>1.3 · 10¹⁶</td>
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<td><strong>Hexane soot from rich flame</strong></td>
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<td>1.8 · 10¹⁵</td>
<td>9.0 · 10¹⁵</td>
<td>9.5 · 10¹⁷</td>
<td>2.6 · 10¹⁶</td>
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<td></td>
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<td>3.8 · 10¹²</td>
<td>4.4 · 10¹⁴</td>
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<td>2.0 · 10¹⁵</td>
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<td></td>
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<td><strong>Hexane soot from lean flame</strong></td>
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<td>3.1 · 10¹⁵</td>
<td>2.0 · 10¹⁸</td>
<td>1.9 · 10¹⁶</td>
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<tr>
<td></td>
<td></td>
<td>3.8 · 10¹²</td>
<td>4.5 · 10¹⁴</td>
<td>4.3 · 10¹²</td>
<td>4.2 · 10¹²</td>
<td>2.7 · 10¹⁵</td>
<td>2.6 · 10¹³</td>
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<tr>
<td></td>
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<td>1.1</td>
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<td>0.5</td>
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<td>GTS80 + 5% BTA (80 m²/g)</td>
<td>MWCNT 1 Uncoated (227.4 m²/g)</td>
<td>MWCNT 2 Polymer Coating (54.1 m²/g)</td>
<td>MWCNT 3 PS-PB-PMMA Coating (34 m²/g)</td>
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<tr>
<td>---------</td>
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<tr>
<td>N(CH₃)₃</td>
<td>1.1x10¹²</td>
<td>0.0030</td>
<td>6.1x10¹³</td>
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<td>CF₃COOH</td>
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<td>&lt; 4.5x10¹²</td>
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<tr>
<td>O₃</td>
<td>SS-reaction</td>
<td>2.4x10¹³</td>
<td>4x10¹²</td>
<td>3.0x10¹³</td>
<td>1.7x10¹⁵</td>
<td>3.3x10¹⁴</td>
<td>3.2x10¹⁵</td>
</tr>
</tbody>
</table>
Hypothesis: Role of reduced surface sites

- Atmosphere is **oxidizing**: Trend to long-term oxidation of organics ➔ Atmospheric Aerosol surface believed to be oxidized ➔ Health Effects of Aerosols due to oxidized surface functional groups or molecules.
- Few reports on Correlation of health markers with **reducing capacity** of carbonaceous NP‘s:
  - Experimental results of Setyan, 2009 (PhD thesis, UNI Lausanne)
    - Correlation of 8OHdg (urinary biomarker) with no. of reducing surface sites/cm² on carbonaceous NP‘s sampled in bus depot.
    - Even better correlation with uptake kinetics (uptake coefficients) of probe gas with NP surface: O₃(+), N(CH₃)₃(-), NH₂OH(+), CF₃COOH(+), HCl(+).
- **Hypothesis**: Reducing Capacity of NP-interface may lead to negative health outcomes. **Reactivity (γ)** more important than abundance of sites.
Reactive Site density and uptake coefficient of amC for O₃

Correlation of no. of sites Nᵢ(O₃) reacting with O₃ (= reducing sites) vs. relative 8OHdg change in non-smokers

Correlation of uptake coefficient γ (= interfacial reactivity of probe gas) vs. relative 8OHdg change in non-smokers

<table>
<thead>
<tr>
<th>Number of sites</th>
<th>γ value</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
</tr>
</tbody>
</table>
Three typical probe reactions for oxidized surface sites

**Mild reducing agents = „Red“**

2e-transfer systems

**DTT (Dithiothreitol)**

![DTT structure](image)

Only the monoanion of DTT is oxidized

**L-Ascorbic Acid or Vitamin C**

![L-Ascorbic Acid structure](image)

Oxidized form is fluorescent

**Dihydrofluorescein (diacetate or dichlorosubst.)**

![Dihydrofluorescein structure](image)

Oxidized form is fluorescent

**2,7-Dichlorofluorescein**

![2,7-Dichlorofluorescein structure](image)

Is oxidized form (lactol)
O₂ consumption kinetics in presence of „Red“, am. C NP’s

0.100 mM DTT, 28 mg/L FW2 in suspension

L-Ascorbic acid (Vitamin C), FW2, Printex 60

Relationship between O₂ consumption and strongly reducing (NO₂) and total reducing sites on FW2: ΔO₂ consumption is 2.5 mg/L or 4.7x10¹⁹ #/L for 1.2x10¹⁸ #/L strongly, 1.2x10¹⁹ total reducing sites. ΔO₂ is roughly equimolar with 6x10¹⁹ #DTT/L leading to bimolecular (experimentally confirmed) kinetics. There is a shortfall of strongly reducing (NO₂ probe) and total (O₃ probe) reducing sites on FW2 by a factor of 40 and 4, respectively.

The oxidation of DTT is therefore catalytic in FW2 soot nanoparticles.

Oxidation of DTT by O₂ w/o catalyst is slow: DTT(Red)+O₂→Ox+H₂O₂
Yield Ratios and Rate Law: \( \text{RATE}_\text{DTT} = k[O_2] [\text{DTT}] [\text{CB}] \)

Stoichiometric line (1:1)

Between \( O_2 \) and DTT consumed in the presence of the amC catalyst

Every point above the red line represents “excess” \( O_2 \) consumed in oxidation of “Red” (reducing agent) in the presence of amC:

\[ O_2 + 2\text{Red} \rightarrow 2\text{Ox} + 2\text{H}_2\text{O} \]
Aqueous suspension of FW2 am. C. + DTT/O₂

DTT-INJECTION

INJECTION of aqueous FW2-SUSPENSION
Positive Correlation of DCFH reactivity with # of strongly reducing surface sites

Correlation: DCFH reactivity vs. # strongly reducing sites

\[ y = 5.71 \times 10^{13} x \]

\[ R^2 = 0.910 \]

NO\(_2\) titration reveals strongly-reducing sites

No correlation with oxidized and partially oxidized sites (N(CH\(_3\))\(_3\), NH\(_2\)OH-titration)

Correlation of DCFH reactivity with # of all reducing sites (O\(_3\)) is less good than with strongly-reducing sites (NO\(_2\)), \( R^2 = 0.720 \)

This is not what we expected: DTT and/or DCFH reactivity is expected to correlate with # of oxidized or partially oxidized adsorption sites. How can we understand?

Look at quantitative aspects of kinetics, surface sites and stoichiometry.
Reaction Stoichiometry for oxidation of reducing agents

Detailed Mechanism satisfying the measured stoichiometry for O₂ consumption in acellular toxicity tests:
(all reaction equations correspond to either two-hydrogen or two-electron transfer processes):

\[
\begin{align*}
PM_{\text{red}} + O_2 &\rightarrow PM_{\text{ox}} + H_2O_2 \\
PM_{\text{ox}} + \text{Red} &\rightarrow PM_{\text{red}} + \text{Ox} \\
aH_2O_2 + a\text{Red} &\rightarrow a\text{Ox} + 2aH_2O \\
(1-a)H_2O_2 + (1-a)PM &\rightarrow (1-a)PM_{\text{ox}} + 2(1-a)H_2O \\
O_2 + (1+a)\text{Red} + (1-a)PM &\rightarrow (1+a)\text{Ox} + (1-a)PM_{\text{ox}} + 2H_2O
\end{align*}
\]

With \( a = 1 \) (simple mechanism) the stoichiometry becomes:
\[
O_2 + 2\text{Red} \rightarrow 2\text{Ox} + 2H_2O
\]

RATE LAW: \[ \text{DTT} = k[O_2][\text{DTT}][\text{CB}] \]

Branching Ratio

\[ 0.0 \geq a \geq 1.0 \]
CONCLUSIONS – 4 Take-Home Lessons

• Surface Composition of Soot and other carbonaceous NP’s is MULTIFUNCTIONAL

• Use of „chemical“ surface interrogation techniques delivers different results respectometric methods

• Correlation of surface composition in terms of surface functional groups with toxicological tests/biomarkers

• In addition to well-documented health effects of oxidized surface groups there are indications that REDUCED surface groups may do the same. Incidence of NP-based chain reactions with NP as chain carrier/catalyst
CONCLUSIONS

• Surface composition of the NP surface remains unaffected, instead air $O_2$ is effectively used to oxidize « Red ».
• Rate of « Red » oxidation correlates best with no. of surface sites reacting with NO$_2$, that is with strongly reducing sites.
• However, we set out to probe the oxidative capacity of the NP surface and therefore expected to titrate the PM$_{ox}$ sites on the NP surface.
• The rate-limiting step in the catalytic reaction of « Red » oxidation by air $O_2$ in the presence of carbonaceous NP’s is the oxidation of reduced surface groups (= oxidation of PM$_{red}$ by $O_2$).
• Chain length of catalytic oxidation ranges from a few tens to a few hundreds depending on « Red ». Together with the branching ratio « a » these two parameters define the catalytic oxidation of « Red ».
Three **Constraints** for observing a titration reaction:

- Reactions must be fast (time scale of $1/k_{esc} \sim 10$ s)
- Reactions are occurring at low pressure: $\sim 10^{-3}$ mbar
- Reactions must occur at ambient temperature
Comparison of GTS#3 and GTS#4

• Factor x50 more acidic (carboxylic) groups on soot #4 compared to soot #3 (TMA probe). Compare polyacrylic acid-coated MWCNT's (Tabet et al., P&FT 2011) which has x6 times less acidic sites compared to soot #4.
• Surprising abundance of partially oxidized sites (NH₂OH probe, aldehyde, ketone) increasing by x7.5 in going from soot #3 to soot #4. Are some of the deposited aromatic tricarboxylic acid molecules reduced to ketones/aldehydes by the reducing PM interface?
• Abundance of basic sites for both soot types. Propensity for TFA over HCl adsorption. This would indicate α- or γ-Pyrone-type (basic) oxides.
• Abundance of reducing sites of soot #4. Apparent coexistence between acidic and therefore highly oxidized (TMA probe) together with reducing (NO₂, O₃ probe) sites on the same interface.
• Sensitivity of the method is 2.5 x 10¹⁴ molecule mg⁻¹ or 3 x 10¹¹ molec cm⁻² or 4 x 10⁻⁴ of a molecular monolayer for soot #4 (GTS80 with BET = 80 m²/g).
• Both O₃ and NO₂ show steady-state uptake coefficients on the order of 3 x 10⁻⁵ for soot #3 and #4.
• Correlation between strongly-reducing (NO₂ probe) and all reducing (O₃ probe) sites.
Clark Electrode for the measurement of the $O_2$ consumption rate

**Cathode (reduction of $O_2$ at “A“):**

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

**Anode (oxidation of Ag$^0$ at “B“):**

$$4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-$$

$$4Ag + O_2 + 4Cl^- + 2H_2O \rightarrow 4AgCl + 4OH^-$$
CONCLUSIONS

- Catalytic activity of carbonaceous NP’s: dissolved $O_2$ oxidizes reducing agent „Red“ instead of NP surface
- „Red“ oxidation correlates with strongly reducing (PM$_{\text{red}}$), not oxidizing (PM$_{\text{ox}}$) NP surface sites
- NP is redox cycled (quinone-hydroquinone pair, no metal): Chain lengths of 40-800 $O_2$ per reducing site PM$_{\text{red}}$
- NP loss due to competition between irreversible oxidation of PM and oxidation of „Red“ for $H_2O_2$. This leads to stoichiometry $[\Delta DTT]/[\Delta O_2] \leq 2.0$ ranging from 1.2 to 1.6 depending on type of amorphous carbon
PM leads to oxidative stress via production of ROS

External influence:
- UV Radiation
- Cigarette smoke
- Drugs
- Alcohol
- Stress
- PM

Metabolism of $O_2$ leads to ROS

ROS = Reactive Oxygen Species (OH\textsuperscript{•}, $O_2$\textsuperscript{•}, singlet oxygen; $H_2O_2$, $HO_2$,...)

Damage (DNA, lipid membrane,..)

Antioxidants = Defense