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Large Enhancement in the Heterogeneous Oxidation Rate of Organic Aerosols by Hydroxyl Radicals in the Presence of Nitric Oxide

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Supporting Information

ABSTRACT: In the troposphere, the heterogeneous lifetime of an organic molecule in an aerosol exposed to hydroxyl radicals (OH) is thought to be weeks, which is orders of magnitude slower than the analogous gas phase reactions (hours). Here, we report an unexpectedly large acceleration in the effective heterogeneous OH reaction rate in the presence of NO. This 10−50 fold acceleration originates from free radical chain reactions, propagated by alkoxy radicals that form inside the aerosol by the reaction of NO with peroxy radicals, which do not appear to produce chain terminating products (e.g., alkyl nitrates), unlike gas phase mechanisms. A kinetic model, constrained by experiments, suggests that in polluted regions heterogeneous oxidation plays a much more prominent role in the daily chemical evolution of organic aerosol than previously believed.

Organic material comprises a significant fraction of submicron tropospheric aerosol (20−90%).1,2 Organic aerosol (OA), once formed or emitted into the atmosphere, is transformed by photochemical reactions, heterogeneous oxidation, aqueous phase chemistry, and the condensation of low-volatility organic species from the gas phase. These chemical transformations alter key microphysical OA properties (e.g., particle size, optical properties, volatility, toxicity, hygroscopicity) that in turn have large scale impacts on cloud droplet formation, human health, and radiative forcing.3 For chemical transport models to accurately predict the impact that OA has on air quality and climate relies on accurate descriptions of multiphase chemistry and their associated kinetic time scales.4 Secondary organic aerosol (SOA) formation is fast and occurs within hours by reactions of O3 and OH with gas phase anthropogenic and biogenic SOA precursors. Heterogeneous aerosol oxidation is generally considered to be at least ~10 times slower (i.e., weeks), occurring on a similar time scale as dry and wet deposition. Here, new experimental evidence is reported for radical chain reactions initiated by a heterogeneous reaction in the presence of two common anthropogenic pollutants. This free radical chain reaction leads to large effective reaction rates and much shorter kinetic lifetimes (hours) than previously thought possible for heterogeneous oxidation.

Scheme 1 shows a canonical reaction mechanism used to explain the heterogeneous OH oxidation of hydrocarbons (RH) in the presence of O3. OH reacts with RH by H atom abstraction forming an alkyl radical (R) and H2O. The heterogeneous rate of the reaction is quantified by a reactive uptake coefficient (γ), which is determined by measuring the loss of either gas-phase OH or particle phase RH. Kinetic measurements of OH loss by definition yield γOH ≤ 1. This is not necessarily the case when the reaction is measured by the decay of RH because, in addition to OH, other free radical intermediates (i.e., RO, Scheme 1) can consume the hydrocarbon leading to effective uptake coefficients (γeff) larger than 1. γeff > 1 simply means that the reactive decay of the hydrocarbon includes secondary chemistry.

Once formed, the alkyl radical (R) quickly reacts in the atmosphere with O3 to produce a peroxy radical (RO2). Peroxy radicals are relatively slow to react and can diffuse over much larger distances within the aerosol than either OH or R. In the absence of NOx, RO2 reacts primarily with another RO2 to form either a carbonyl−alcohol pair or two alkoxy radicals (RO). RO, if formed, is significantly more reactive than RO2 and, for instance, can abstract a H atom (chain propagation) from a neighboring molecule to form another R and subsequently another RO2.5 This and many other laboratories report that 0.1 ≤ γeff ≤ 1, suggesting that in the atmosphere, heterogeneous oxidation is slow and only important for oxidative aging at longer time scales (weeks to months).6 This also indicates that in the particle phase the branching ratio to form RO from the RO2 + RO2 reaction is small, producing instead mainly stable chain termination reaction products.

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In polluted atmospheres, NO\textsubscript{x} (NO + NO\textsubscript{2}) is emitted from fossil fuel combustion with atmospheric mixing ratios as high as 200 ppb.\textsuperscript{7−10} RO\textsubscript{2} radicals have been shown to readily oxidize nitric oxide (NO) both in the gas and aqueous-phase resulting in the formation of RO (and NO\textsubscript{2}) and organic nitrates (RONO\textsubscript{2}),\textsuperscript{11−13} To examine how NO controls $\gamma\textsubscript{eff}$, heterogeneous OH reactions were measured on three organic aerosol proxies: squalane (Sq, C\textsubscript{30}H\textsubscript{62}, liquid), bis(2-ethylhexyl) sebacate (BES, C\textsubscript{26}H\textsubscript{50}O\textsubscript{4}, liquid), and triaccontane (Tri, C\textsubscript{30}H\textsubscript{62}, solid). Kinetic measurements (described in the Supporting Information section 1 and 2), used to determine $\gamma\textsubscript{eff}$, are conducted over a large range of concentrations: $\sim 6 \times 10^6 \leq [OH] \leq \sim 1 \times 10^{10}$ molecules cm\textsuperscript{-3}, 40 ppb $\leq [NO] \leq 2$ ppm (residence time of 37 s to hours).\textsuperscript{14,15}

Figure 1a-c shows $\gamma\textsubscript{eff}$ as a function of [NO\textsubscript{x}] for the three proxy organic aerosols at two average [OH]\textsubscript{avg}: $1 \times 10^8$ and $1 \times 10^{10}$ molecules cm\textsuperscript{-3}. For all of the aerosols, $\gamma\textsubscript{eff}$ exhibits a clear increase as a function of [NO\textsubscript{x}]. At [OH] = $1 \times 10^8$ molecules cm\textsuperscript{-3} and NO\textsubscript{x} = 250 ppb, the $\gamma\textsubscript{eff}$ is 0.45, 0.88, and 0.19 for Sq, BES, and Tri, respectively, whereas at NO\textsubscript{x} = 2 ppm, the $\gamma\textsubscript{eff}$ is increased to 1.1, 1.7, and 0.3 for Sq, BES, and Tri, respectively. At [OH] = $1 \times 10^8$ molecules cm\textsuperscript{-3}, the increase in $\gamma\textsubscript{eff}$ is much more pronounced. For example, at [NO\textsubscript{x}] = $\sim 50$ ppb the $\gamma\textsubscript{eff}$ is 0.77, 1.7, 0.37 for Sq, BES, and Tri, respectively, and at NO\textsubscript{x} = 150 ppb the $\gamma\textsubscript{eff}$ is 1.6, 3.9, and 0.6 for Sq, BES, and Tri, respectively. Values of $\gamma\textsubscript{eff} > 1$ indicate that Sq and BES are consumed faster than the collision rate of OH with the aerosol particles, providing clear evidence of radical chain propagation chemistry within the particle. At all [OH], solid Tri particles exhibit a similar trend as the liquid particles, although overall increase in $\gamma\textsubscript{eff}$ is much slower due to diffusive limitations.\textsuperscript{16,17}

Although NO\textsubscript{2} is formed in the reactors, we conducted experiments with NO\textsubscript{2} only and found no discernible enhancement in the rate relative to the OH-only case (see Supporting Information section 3), suggesting that NO, rather than NO\textsubscript{2}, is accelerating the reaction.

In addition to [NO], absolute [OH] plays a significant role in determining the overall rate of the heterogeneous reaction.
Table 1. Reaction Scheme and Rate Constants for Stochastic Simulations

<table>
<thead>
<tr>
<th>number</th>
<th>reaction</th>
<th>$k$</th>
<th>comment/ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>RH(n) + OH → R(n) + H₂O (n = 0−4)</td>
<td>$6.23 \times 10^9$</td>
<td>(a)</td>
</tr>
<tr>
<td>R2</td>
<td>R(n) + O₂ → ROO(n) (n = 0−4)</td>
<td>$4.00 \times 10^{-15}$</td>
<td>5</td>
</tr>
<tr>
<td>R3</td>
<td>ROO(n) + ROO(m) → RH(n + 1) + RH(m + 1) (n,m = 0−4)</td>
<td>$1.00 \times 10^{-16}$</td>
<td>5</td>
</tr>
<tr>
<td>R4</td>
<td>2 ROO(n) → 2 RO(n)</td>
<td>$1.66 \times 10^{-15}$</td>
<td>5</td>
</tr>
<tr>
<td>R5</td>
<td>RH + RO(n) → R(n + 1) + R(n)</td>
<td>$6.5 \times 10^{-12}$</td>
<td>(d)</td>
</tr>
<tr>
<td>R6</td>
<td>ROO(n) + NO → RO(n) + NO₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This dependence is shown explicitly in Figure 1d–f at [NO] = 84 ± 22 ppb. As [OH] decreases from $10^{10}$ to $10^{12}$ molecule cm$^{-3}$, there is a steep increase in $\gamma_{eff}$ (note the logarithmic scales). For Sq at [OH] = $3 \times 10^{10}$ molecules cm$^{-3}$, $\gamma_{eff}$ = 2.7, which is ~10X faster than observed at $10^{12}$ molecules cm$^{-3}$. For BES, $\gamma_{eff}$ = 23 at [OH] = $3 \times 10^{5}$ molecules cm$^{-3}$, which is 26 times faster than observed at [OH] = $10^{10}$ molecules cm$^{-3}$. For Tri, $\gamma_{eff}$ increases from 0.19 at [OH] = $1 \times 10^{11}$ molecules cm$^{-3}$ to near 1 at [OH] = $8 \times 10^{5}$ molecules cm$^{-3}$. Also shown in Figure 1d–f are values for $\gamma_{eff}$ measured in the absence of NO, which exhibit no strong dependence on [OH] and for all conditions remain less than 1. Several experiments were conducted to determine if O$_3$ (the OH precursor) or photochemistry were contributing to the large $\gamma_{eff}$ observed in Figure 2 (Supporting Information section 4). Instead of O$_3$, H$_2$O$_2$ was used as the OH precursor and there was no discernible difference in the $\gamma_{eff}$ at the same [OH] and [NO$_2$]. Measurements were also conducted using 355 nm lamps instead of 254 nm lamps to determine if photochemistry played a possible role, and again, there was no difference in the $\gamma_{eff}$ or in product formation.

A kinetic model (Supporting Information section 5) of R1–R6 (Scheme 1) is formulated to elucidate the underlying reaction mechanism for the large enhancement in $\gamma_{eff}$ with NO. Rate coefficients are from previous literature and are shown in Table 1.\(^5,18\) The branching ratios, for the RO$_2$ self-reaction (R3) and (R4) to form either a carbonyl-alcohol pair (90%) or two RO (10%) are based upon a previous study.\(^19\) Monodisperse aerosol size measurements, in which the surface-to-volume ratio of the particles was varied (Supporting Information section 6) indicate that the RO$_2$ + NO reaction occurs within the bulk of the aerosol and not at its surface. Thus, in the model, the [NO] in the particle phase is fixed by a unitless Henry’s law constant of 8.2 ± 2.8 consistent with previous measurements.\(^20,21\) Finally, after extensive efforts (documented in the Supporting Information section 7) failed to either detect any RONO$_2$ species or that they were formed but photolyzed in our reactor, we assume, unlike the gas phase, that the RO$_2$ + NO branching ratio to form RO is unity.

The only adjustable model parameter is the RO$_2$ + NO rate constant (R6). Previous literature constrains this to be on the order of $10^{-12}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$.\(^11,12\) With this constraint, the model RO$_2$ + NO rate constant was varied to replicate the global data set (i.e., $\gamma_{eff}$ vs [OH] and [NO]) as shown in Figure 1). Modeled and observed $\gamma_{eff}$ match well for Sq and BES, using a RO$_2$ + NO rate constant of $6.5 ± 3.2 \times 10^{-12}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$; consistent with previous literature ($2-5 \times 10^{-12}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$).\(^11,12\) Tri particles were not modeled here because to accurately describe heterogeneous reactions in solid particles requires a spatially resolved reaction-diffusion model.

The model reveals that the relationship between $\gamma_{eff}$ [OH] and [NO] is controlled by the competition between free radical chain propagation (RO$_2$ + NO) and termination (RO$_2$ + RO$_2$). The competition is clearly illustrated in Figure 1, which shows $\gamma_{eff}$ vs [OH] at 84 ± 22 ppb NO for each of the proxies. At high OH ($10^−10^{20}$ molecules cm$^{-3}$), the concentration of RO$_2$ is also relatively high, so that the loss of RO$_2$ is dominated by reactions with other RO$_2$ to form stable chain terminating products. This also explains why a much higher [NO] is required at [OH] = $10^{10}$ molecules cm$^{-3}$ than [OH] = $10^8$ molecules cm$^{-3}$ to achieve the same $\gamma_{eff}$ (e.g., [NO] = 2 ppm vs 100 ppb). At much lower [OH] approaching atmospheric levels ($10^5−10^7$ molecules cm$^{-3}$), RO$_2$ reacts primarily with NO to form RO, which chain propagate by H abstraction from a neighboring molecules to form R. This R reacts rapidly with O$_2$ to form another RO$_2$, which again reacts with NO to generate another RO (and so on), thereby propagating a radical chain reaction and increasing $\gamma_{eff}$. The kinetic model, constrained by measurements, predicts a drastic acceleration in chain propagation chemistry in polluted atmospheric conditions. In megacities,\(^7−10\) for example, we predict that $\gamma_{eff}$ (i.e., BES) at the lowest [OH] ($8 \times 10^5$ molecules cm$^{-3}$, [NO] = 85 ppb) is 5-2 and 0.8 in the presence of NO and without added NO, respectively.

A simple time scale analysis of these results suggests significant new implications for the short time evolution of OA by heterogeneous oxidation (with NO) in polluted regions. The heterogeneous lifetime of an alkane (i.e., squalane) in a 150 nm diameter particle with a $\gamma_{eff}$ of 0.3 in a remote region (i.e., low NO$_2$) is four days, assuming a global mean [OH] of $2 \times 10^5$ molecules cm$^{-3}$. Under these same conditions, the lifetime of a gas-phase alkane (e.g., dodecane, C$_{12}$H$_{26}$) whose bimolecular rate constant is $k = 1.32 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is 11 h. This large difference in gas vs heterogeneous lifetime (without NO added) is because particle phase molecules remain “hidden” inside the interior of the aerosol during most of their atmospheric lifetime and, therefore, unavailable for a surface reaction with OH. As shown here, the presence of free radical chain reactions initiated by OH at the surface, travel throughout the interior of the particle and accelerate oxidation rates by 10 to 50 times the OH collision frequency. Thus, we predict that in polluted environments,
such as megacities, where NO concentrations are \( \sim 84 \) ppb and \( \gamma_{\text{eff}} = 9 \) (e.g., squalane) the heterogeneous lifetime is as short as \( \sim 3 \) h. Even at much lower [NO] (20 ppb, refer to Supporting Information section 8 for atmospheric conditions) but still significantly higher than pristine environments, \( \gamma_{\text{eff}} \) is predicted to be 3, yielding a heterogeneous oxidative lifetime of 10 h; comparable to the gas phase lifetime of dodecane. Therefore, in highly polluted regions, such as polluted urban centers, this chemistry could significantly accelerate the oxidative aging of OA.

Although these experiments use simple single component OA proxies that clearly do not reflect the immense complexity of real ambient aerosols, the free-radical chain propagation mechanism is general and expected to be relevant for the class of chemically reduced compounds (e.g., diesel emissions) commonly measured in primary urban OA.\(^{23}\) Furthermore, the chain propagation pathway is based upon a well-established mechanism in the gas phase, but unlike the gas phase, the RO₂ + NO reaction in the organic aerosol phase appears to produce little if any chain termination products (RONO₂). In the condensed phase for large hydrocarbons, we would expect that the RO₂ self-reactions (R3) and (R4) to form either a (Supporting Information section 5) for chemical kinetics and hinsberg.net/kinetiscope/), which uses stochastic algorithms (Supporting Information section 1). A description of the kinetic analysis (VUV) photoionization aerosol mass spectrometer (Supporting Information section 1). 5

**EXPERIMENTAL METHOD**

Organic aerosol oxidation in the presence of NO was investigated by measuring the OH oxidation kinetics of three organic compounds: squalane (\( C_{90}H_{172} \) liquid), bis(2-ethyl-hexyl) sebacate (\( C_{38}H_{60}O_{11} \) liquid), or triacantane (\( C_{46}H_{92} \) solid). Kinetic measurements were made in either a flow-tube reactor or a continuous-flow stir tank reactor (CFSTR), both are described in detail elsewhere.\(^{14,15}\) using a vacuum ultraviolet (VUV) photoionization aerosol mass spectrometer (Supporting Information section 1). A description of the kinetic analysis conducted is provided in Supporting Information section 2.

Modeling was conducted using Kineticscope (http://www.hinsberg.net/kinetiscope/), which uses stochastic algorithms (Supporting Information section S) for chemical kinetics and was recently used for aerosol chemistry.\(^{14,15}\) The kinetic model of R1−R6 (Figure 1) was formulated to elucidate the underlying reaction mechanism. Rate coefficients are from previous literature and are shown in Table 1.\(^{1,17}\) The branching ratios for the RO₂ self-reactions (R3) and (R4) to form either a carbonyl–alcohol pair or two RO* are fixed at 10:90, respectively, and based upon a previous study.\(^{19}\)

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b02121.

Detailed description of experiment and model. (PDF)

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Notes

The authors declare no competing financial interest.

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