Supporting information for:

NO\textsubscript{2} suppression of autoxidation - inhibition of gas-phase highly-oxidized dimer product formation

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Methods

Cyclohexene (c-C\textsubscript{6}H\textsubscript{10}) oxidation was investigated in 2.4 and 7.6 cm inner diameter and 100 to 200 cm length flow tubes under ambient atmospheric conditions (\(T = 293 \pm 3\) K, \(p = 1\) Atm). Gas flow rate inside the flow tube was determined by the sampling need of the chemical ionization inlet, which was at around 10 liters per minute (lpm) and resulted in laminar flow conditions and residence times between 2 and 20 seconds. The carrier gases used were nitrogen (Aga, N\textsubscript{2}, purity 5.0) and synthetic air (Aga, N\textsubscript{2} and O\textsubscript{2}, purity 5.0). Nitrogen dioxide and nitrogen oxide used were 50 parts per million (ppm) mixtures with N\textsubscript{2} as the pressure gas (Aga, NO/NO\textsubscript{2}, 50 ppm in N\textsubscript{2}). Ozone was produced by a commercial ozone generator (UVP products SOG-3) from the synthetic air (or filtered and pressurized air) and its concentration was monitored by an ozone analyzer (Thermo Scientific model 49). Cyclohexene was obtained from Sigma-Aldrich (\(\geq 99\%\) purity), and its concentration in the experiment was determined by the pure compound vapor pressure and dilution factors in the gas flow system. Detection of the oxidized intermediates and products was accomplished by means of chemical ionization mass spectrometry (CIMS) applying nitrate (NO\textsubscript{3}\textsuperscript{-}) reagent ions to cluster with the target compounds. This technique was originally devised to selectively detect atmospheric sulfuric acid and has recently been devoted for studying highly-oxidized multifunctional organic compounds (HOM) resulting from hydrocarbon autoxidation. The mass spectrometer utilized was an atmospheric pressure interface time-of-flight instrument manufactured by TofWerk (APi-ToF, Tofwerk Ltd, Thun, Switzerland). Schematic of the experimental setup is given in Figure S1.
Figure S1 Schematic of the experimental setup.

The experiments were conducted under various concentrations of cyclohexene \([c-C_6H_{10}] = (3-235) \times 10^{13} \text{ cm}^{-3}\) [=3 to 96 ppm], ozone \([O_3] = (1.23-14.8) \times 10^{11} \text{ cm}^{-3}\) [=5 to 60 ppb], NO\(_x\) \([NO_2] = (1.27-63.4) \times 10^{12} \text{ cm}^{-3}\) [=51 to 2577 ppb]; \([NO] = (1.27-10.1) \times 10^{12} \text{ cm}^{-3}\) [=51 to 412 ppb]), and reaction time \((t = 2.2-22.4 \text{ s})\), constituting a wide range of experimental conditions with different oxidative capacity and potential for product formation.

**Charging probabilities and transmission, and their influence on measured concentrations**

NO\(_3^-\) ionization has been frequently applied in quantifying HOM product signals, with a calibration procedure utilizing SO\(_2\) + OH (+H\(_2\)O) derived H\(_2\)SO\(_4\) to determine the lower limit concentrations of the products observed. This analysis relies on the assumption that HOM products experience the same collision limit charging in the chemical ionization inlet as does sulfuric acid. In addition, Ehn et al.\(^1\) have further rationalized the measured concentrations by using further empirical constraints and arrived into good agreement with the single-calibration-factor procedure. On the other hand, the detection efficiency of NO\(_3^-\) charging is known to depend on the available H-bond donating functional groups and on the number of O-atoms in the structure, both increasing the detection sensitivity and thus leading to a positive bias relative to the less oxidized compounds\(^2,3\). The sensitivity is further
dependent on the detailed settings of the atmospheric pressure interface (APi) altering the ion transmission in the mass range of interest\(^4\). In considering these issues it becomes clear how difficult it is to adequately account for the compound specific detection sensitivity, and thus this was not attempted here, and instead all the concentrations are given as measured ion signals in ion counts per second (cps), and where relevant (i.e., to be able to compare signals), they are normalized to the total reagent ion current which was c.a. 10 000 to 20 000 cps.

**Oxidation pathways**

The product peaks detected in cyclohexene ozonolysis experiments without addition of NO\(_x\) have been collected to Table S1.

**Table S1** The most prominent mass peaks measured without NO\(_x\) addition to the gas mixture.

| Without NO\(_x\) | \(^a\) C\(_6\)H\(_4\)O\(_4\) | \(^c\) C\(_4\)H\(_6\)O\(_4\) | \(^c\) C\(_6\)H\(_9\)O\(_4\) | C\(_4\)H\(_6\)O\(_3\) | C\(_4\)H\(_3\)O\(_4\) | C\(_6\)H\(_10\)O\(_4\) | C\(_3\)H\(_8\)O\(_5\) |
|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| \(^b\) 117.0193 | 131.0350         | 145.0506         | 180.0150         | 192.0514         | 194.0306         | 208.0463         | 210.0250         |
| C\(_6\)H\(_10\)O\(_5\) | C\(_4\)H\(_6\)O\(_5\) | C\(_4\)H\(_9\)O\(_5\) | C\(_4\)H\(_6\)O\(_6\) | C\(_4\)H\(_9\)O\(_6\) | C\(_4\)H\(_6\)O\(_6\) | C\(_4\)H\(_9\)O\(_6\) | C\(_4\)H\(_6\)O\(_6\) |
| 212.0412 | 222.0255 | 224.0412 | 227.0283 | 228.0283 | 238.0205 | 239.0283 | 240.0361 |
| C\(_4\)H\(_11\)O\(_6\) | C\(_4\)H\(_6\)O\(_7\) | C\(_4\)H\(_9\)O\(_7\) | C\(_4\)H\(_11\)O\(_7\) | C\(_4\)H\(_6\)O\(_8\) | C\(_4\)H\(_9\)O\(_8\) | C\(_4\)H\(_6\)O\(_9\) | C\(_4\)H\(_9\)O\(_9\) |
| 241.0439 | 254.0154 | 255.0232 | 256.0310 | 257.0388 | 270.0103 | 271.0181 | 272.0259 |
| C\(_6\)H\(_4\)O\(_8\) | C\(_4\)H\(_6\)O\(_8\) | C\(_4\)H\(_9\)O\(_8\) | C\(_4\)H\(_10\)O\(_8\) | C\(_4\)H\(_10\)O\(_9\) | C\(_4\)H\(_10\)O\(_10\) | C\(_6\)H\(_10\)O\(_10\) | C\(_6\)H\(_10\)O\(_10\) |
| 286.0052 | 287.0052 | 288.0052 | 300.9923 | 300.9923 | 302.0001 | 303.0079 | 303.0079 |
| C\(_6\)H\(_10\)O\(_10\) | C\(_6\)H\(_11\)O\(_10\) | C\(_6\)H\(_13\)O\(_7\) | C\(_6\)H\(_12\)O\(_7\) | C\(_6\)H\(_12\)O\(_8\) | C\(_6\)H\(_12\)O\(_9\) | C\(_6\)H\(_14\)O\(_9\) | C\(_6\)H\(_14\)O\(_9\) |
| 304.0158 | 305.0236 | 324.0936 | 326.1093 | 338.1093 | 352.0885 | 356.0834 | 358.0991 |
| C\(_12\)H\(_10\)O\(_9\) | C\(_12\)H\(_20\)O\(_9\) | C\(_11\)H\(_15\)O\(_10\) | C\(_12\)H\(_18\)O\(_10\) | C\(_12\)H\(_18\)O\(_10\) | C\(_12\)H\(_20\)O\(_10\) | C\(_12\)H\(_18\)O\(_11\) | C\(_12\)H\(_18\)O\(_11\) |
| 368.0834 | 370.0991 | 372.0784 | 382.0784 | 384.0784 | 386.0940 | 388.0733 | 400.0733 |
| C\(_11\)H\(_10\)O\(_12\) | C\(_12\)H\(_10\)O\(_12\) | C\(_12\)H\(_10\)O\(_13\) | C\(_12\)H\(_18\)O\(_13\) | C\(_13\)H\(_16\)O\(_14\) | C\(_12\)H\(_16\)O\(_14\) | C\(_12\)H\(_16\)O\(_14\) | C\(_12\)H\(_16\)O\(_15\) |
| 404.0682 | 416.0676 | 430.0475 | 432.0631 | 434.0424 | 446.0424 | 448.0580 | 464.0529 |

\(^a\)Observed product composition, and \(^b\) its exact mass in the spectrum (including the mass of NO\(_3\) of 61.9884 Th). \(^c\) Detected as deprotonated product ion; does not include NO\(_3\) mass. All masses are given in Thomson units; 1 Th = \(u/e\), where \(e\) is elementary charge and \(u\) is the atomic mass unit.
Due to cyclohexenes symmetric ring structure with no substituents around the double bond, it produces two aldehyde functionalities containing primary oxidation products as illustrated in Figure 1. In these compounds the aldehydic hydrogens have the lowest C-H bond energies, and thus further oxidation, autoxidation or stepwise, will inevitably lead into further acylperoxy radicals. Also, cyclohexene’s carbon chain length enables close to optimal H-shift transition states and facilitate the formation of a pool of secondary acylperoxy radicals. In Scheme S1 further examples for acylperoxy radical formation during the oxidation sequence have been gathered.

Scheme S1 Further potential acylperoxy formation pathways, and interconversions, during cyclohexene autoxidation. Acylperoxy radicals have been marked with red color.

The pool of different RC(O)O$_2$ will combine with NO$_2$ forming a collection of peroxyacylnitrate (PAN) species (R(C)O$_2$NO$_2$). Potential PAN structures detected in the current work have been collected in Figure S2.
Figure S2 Potential peroxyacylnitrate (PAN) product structures detected in this work. Acylperoxy radicals have been marked with red color.

**Suppression reaction kinetics**

The suppressing reaction RC(O)O₂ + NO₂ must happen faster than the unimolecular hydrogen shifts progressing the oxidation chain reaction. Previously it has been estimated that H-shift rates of above 0.1 s⁻¹ can compete with other RO₂ loss processes (mainly reactions with HO₂ and NO) even under moderately polluted atmospheres. The exact concentration at which NO₂ will suppress depends on the rate of the RO₂ + NO₂ reaction, and thus on the specific RO₂. The experimental rate determinations for RO₂ + NO₂ are scarce, especially for the larger RO₂ as relevant for the current investigation, and hence, the exact values cannot be used. However, the limiting
concentrations at which the NO$_2$ reaction becomes competitive with the unimolecular propagation reaction can be estimated using hypothetical rate coefficient values. In Table S2 the concentration of NO$_2$ that is needed for the RC(O)O$_2$ + NO$_2$ reaction to outcompete an H-shift rate of 0.1 s$^{-1}$ and 10 s$^{-1}$ have been calculated assuming general and previously determined rate coefficient values. In Figure 3, a similar analysis was illustrated in graphical format with general assumed reaction rate $k$(RC(O)O$_2$+NO$_2$) between 10$^{-10}$ cm$^3$s$^{-1}$ and 10$^{-13}$ cm$^3$s$^{-1}$ depicted as a function of [NO$_2$].

**Table S2** NO$_2$ concentration needed to outcompete H-shift rates of 0.1 s$^{-1}$ and 10 s$^{-1}$; competition of unimolecular H-shift and bimolecular RC(O)O$_2$ + NO$_2$ reaction rates.

| [NO$_2$] / cm$^{-3}$ (ppb) | $k$(RC(O)O$_2$+NO$_2$) / cm$^3$s$^{-1}$ | $k'$(RC(O)O$_2$+NO$_2$) / s$^{-1}$ | Comment |
|---------------------------|---------------------------------|---------------------------------|---------|
| 10$^{12}$ (40.7)          | 1 x 10$^{-13}$                  | 0.1                             | Slowish $k$ value |
| 10$^{14}$ (4065)          | 1 x 10$^{-13}$                  | 10                              |         |
| 10$^{11}$ (4.1)           | 1 x 10$^{-12}$                  | 0.1                             |         |
| 10$^{13}$ (406.5)         | 1 x 10$^{-12}$                  | 10                              |         |
| 1.14 x 10$^{10}$ (0.46)   | 8.8 x 10$^{-12}$                | 0.1                             | $k$(C$_2$H$_5$O$_2$+NO$_2$) used |
| 1.14 x 10$^{12}$ (46.2)   | 8.8 x 10$^{-12}$                | 10                              |         |
| 6.67 x 10$^9$ (0.27)      | 1.5 x 10$^{-11}$                | 0.1                             | $k$(CH$_3$C(O)O$_2$+NO$_2$) used |
| 6.67 x 10$^{11}$ (27.1)   | 1.5 x 10$^{-11}$                | 10                              |         |
| 1.11 x 10$^9$ (0.05)      | 9 x 10$^{-11}$                  | 0.1                             | $k$ close to collision limit |
| 1.11 x 10$^{11}$ (4.51)   | 9 x 10$^{-11}$                  | 10                              |         |
According to the simple comparison procedure above it was estimated with previously measured \( \text{RC(O)O}_2 + \text{NO}_2 \)
and \( \text{RO}_2 + \text{NO}_2 \) rate coefficients that already below 1 ppb of \( \text{NO}_2 \), corresponding to very clean environmental conditions, can influence the oxidation sequence. With a moderate rate coefficient of \( k(\text{RC(O)O}_2 + \text{NO}_2) = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), over 50\% of the acylperoxy radicals would be lost to PAN formation if the potential secondary chemistry is omitted. At a hundred-fold higher \( \text{NO}_2 \) concentration, corresponding to polluted urban environments around the world, most of the \( \text{RC(O)O}_2 \) would be more likely to form PAN than HOM, in this simple analysis.

**NO’s enhancing influence**

In contrast to \( \text{RO}_2 + \text{NO}_2 \) reaction, \( \text{RO}_2 + \text{NO} \) reaction can also propagate the radical chain by reactive RO generation. In experiments where the NO’s influence was investigated, an enhanced \( \text{C}_6\text{H}_8\text{O}_8 \) product formation was observed after NO was introduced into the gas flow, whereas larger oxidation products were strongly depleted (Figure S3). The amplification of RO chemistry due to NO could lead to species with C5 and C11 structures, i.e., to compounds which have lost a CO or CO\(_2\) during the oxidation sequence. Whereas a C5 compound was observed to increase with the NO addition (see Figure S3), all the dimer compounds were depleted as a function of \([\text{NO}_x]\), and thus this dependence could not be observed for C11 compounds. Due to the cyclic nature of the oxidation chain reaction, yet further NO addition interfered the oxidation at an even earlier stage, and resulted also in reduction of the observed nitrate formation (Figure S4).
Figure S3 $\text{C}_6\text{H}_8\text{O}_8$ product formation is aided by NO addition. Note also that $\text{C}_6\text{H}_8\text{O}_7$ is produced in bigger proportion, whereas the $\text{C}_6\text{H}_9\text{O}_8$ radical and $\text{C}_6\text{H}_8\text{O}_9$ closed shell product are strongly depleted.

Figure S4 even the observed nitrate signals were plummeting at highest NO or NO$_2$ additions.
The addition of NO$_x$ during various instances of the oxidation sequence is illustrated in Figure S5, where example spectra obtained at several [NO$_2$] and [RO$_2$] combinations are shown.
Figure S5 Panels a) to e) illustrate how NOx addition happens during various times of the oxidation sequence. The experiments were performed in 2.4 cm i.d. and either 80 or 200 cm long Quartz reactor, with [O3] = 11 ppb and [O2] = 4.5 %. The spectra were obtained at: a) [NO2] = 0 and low [RO2] ([CH] = 3 × 10^{13} cm^{-3}) at 2.2 s reaction time; b) [NO2] = 50 ppb, and moderate [RO2] ([CH] = 1.3 × 10^{14} cm^{-3}) at 5.9 second reaction time; c) [NO2] = 0 and high [RO2] ([CH] = 6.6 × 10^{14} cm^{-3}) at 5.9 second reaction time; d) [NO2] = 500 ppb and high [RO2] ([CH] = 6.6 × 10^{14} cm^{-3}) at 5.9 second reaction time; and e) [NO2] = 2600 ppb and high [RO2] ([CH] = 6.6 × 10^{14} cm^{-3}) at 5.9 second reaction time. Bg stands for a background peak.

With the highest NOx additions, the oxidation suppression was observed even earlier in the oxidation chain, which resulted in decrease of all the product species detected with the utilized nitrate ionization technique (See Figures S4 and S5 above). In the experiments with very high RO2 and NOx concentrations, it was impossible to even qualitatively quantify the extent of NO2 suppression, as removing NO2 from the gas flow resulted in strong
depletion of the reagent ion signals (indicating formation of a very large number of products), and thus rendered the CIMS concentration determination unreliable. However, when a sufficient NO₂ flow was added back to the reacting gas mixture, the HOM formation (except few PAN-HOM) practically ceased, and the reagent ion signals recovered (see Figure 2).

Also, in experiments with high [RO₂] and [NOₓ], apparent highly oxidized nitrates with two N-atoms attached were observed and could potentially indicate formation by NO₃ initiated and NOₓ terminated reactions [i.e., C₆H₁₀O₆NO₃NO₂(*NO₃⁻) at 348.017 Th, see Table 1 and Figure S5]. However, product charged by the reagent ion dimer would be observed with a similar composition {i.e., m/z[C₆H₉O₆NO₂(*HNO₃NO₃⁻)] = m/z[C₆H₁₀O₆NO₃NO₂(*NO₃⁻)]} and seems far more likely, already as the NO₃ is not expected to live long enough here to perturb the oxidation system. Also, from Figure S5 e it can be seen that when most of the compounds have been depleted due to high [NO₂] in the flow, the two peaks that are well resolvable in the spectrum, and have about similar intensity, could correspond to C₆H₉O₆NO₂ charged by NO₃⁻ and HNO₃NO₃⁻.

Also in other experiments, the apparently two nitrogen containing compounds were coincident with the highest PAN signals and could be explained with these PAN species clustering with the reagent dimer; similar observations of potential dimer charging were absent from experiments conducted without NOₓ. Finally, it seems that the nitrate functionality containing products could potentially cluster more efficiently with NO₃⁻, and thus potentially also by HNO₃NO₃⁻, as the PAN signals seem to increase somewhat more than the HOM signals decrease, indicating a potential positive bias in their detection.

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