Supplementary information to “Direct formation of HONO through aqueous-phase photolysis of organic nitrates”

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Figure S1: UHPLC-UV chromatograms of 1-nitrooxy-2-propanol (black), isosorbide 5-mononitrate (red), α-nitrooxyacetone (green), isopropyl nitrate (blue), and isobutyl nitrate (violet) at 200 nm. All compounds were injected at 3 \( \times 10^{-4} \) mol L\(^{-1}\).
Section S1: Analytical performances of GC-MS analysis of RONO₂

GC-MS retention times and fragmentation patterns were investigated for isopropyl nitrate, isobutyl nitrate, α-nitrooxyacetone, 1-nitrooxy-2-propanol, isopentyl nitrate, 1-pentyl nitrate, and isosorbide 5-monomonitrate. Their retention times were 6.0, 7.1, 12.3, 12.4, 13.0, 14.0, 20.5 min, respectively. Note that isopropyl nitrate showed a retention time lower than time when the EI filament was turned on (at 7 min). For this compound, headspace analysis of a sample containing pure isopropyl nitrate was performed to prevent from saturating the source with any solvent. Figure S1.1 shows the GC-MS chromatographic peaks of isobutyl nitrate, isopentyl nitrate, 1-pentyl nitrate, and isosorbide 5-monomonitrate. The intensity of the chromatographic peaks is very sensitive to the volatility of the RONO₂ (i.e., significant amounts of isobutyl nitrate are lost during the sample preconcentration step), its polarity (i.e., only ~24% of isosorbide 5-monomonitrate is extracted during the CH₂Cl₂ extraction step) and its ionization efficiency. This complicates the quantification of these compounds. Nevertheless, RONO₂ can be detected at very low concentrations.

![Figure S1.1: Gas chromatogram for isobutyl nitrate, isopentyl nitrate, 1-pentyl nitrate, and isosorbide 5-monomonitrate. The compounds were extracted using the developed protocol (Section 2.3.3) from solutions containing 0.05 mM for alkyl nitrates, and 0.01 mM for isosorbide 5-monomonitrates. The m/z = 46 fragment (NO₂⁺) is extracted in each chromatogram.](image)

Figure S1.2 shows their mass spectra. All compounds present highly fragmented mass spectra, and the molecular ion RONO₂⁺ was not observed. In all analyses, the m/z = 46, corresponding to the ion NO₂⁺, was obtained, thus validating the methodology of extracting the mass-to-charge ratio 46 to identify RONO₂ compounds in the “end of reaction” solutions (Section 2.2). The m/z = 46 fragment can also be observed for nitro compounds or peroxynitrates. We assumed that during the RONO₂ photolysis no nitro compounds were formed. In contrast, peroxynitrates might be formed, however, these compounds are thermally unstable and thus, likely decompose during their injection or elution in GC-MS analyses.

Figure S1.3 shows that the smallest molecules (i.e., isopropyl nitrate, isobutyl nitrate, α-nitrooxyacetone, and 1-nitrooxy-2-propanol) present clear fragmentation patterns. For all compounds, the R⁺ fragment was observed: CH₃CHCH₃⁺, CH₃CH(CH₃)CH₂⁺, CH₃COCH₂⁺ and CH₃CH₂(OH)CH₂⁺ at m/z = 43, m/z = 57, m/z = 57 and m/z = 59 for isopropyl nitrate, isobutyl nitrate, α-nitrooxyacetone and 1-nitrooxy-2-propanol, respectively. Fragmentation of the R⁺ was also observed for the three latter ions providing the most intense peaks: CH₃CHCH₃⁺ for isobutyl nitrate (m/z = 43), CH₃CO⁺ for α-nitrooxyacetone (m/z = 43) and CH₃CH₂(OH)⁺ for 1-nitrooxy-2-propanol (m/z = 45). For all primary nitrates, m/z = 76 was detected, corresponding to CH₂ONO₂⁺ ion, while isopropyl nitrate showed the CH₃CHONO₂⁺ fragment, observed at m/z = 90.
Figure S1.2: Mass spectra analyzed by GC-MS for the standard and synthesized RONO₂.

For 1-pentyl nitrate, isopentyl nitrate, and isosorbide 5-mononitrate much more fragmentation were observed. Due to their similar structure, the same peaks were detected for 1-pentyl nitrate and isopentyl nitrate, with only
small changes in their relative intensities. The R⁺ fragment was detected at m/z = 71, as well for the CH₂ONO₂⁺ fragment (m/z = 76). Other fragments such as C₃H₇⁺ and C₄H₉⁺ were also detected at m/z = 43 and m/z = 57, respectively. For isosorbide 5-mononitrate, the detected m/z = 127, probably corresponds to the fragment obtained once NO₂ and a water molecule are lost. The most intense peak at m/z = 69, likely corresponds to a furane-unit.

In any case, the fragmentation observed for these RONO₂ offers precious informations for elucidating the structures of the detected molecules during isopropyl nitrate and isobutyl nitrate photolysis.
Figure S2: Experimental setup used for the detection of \( \cdot \text{NO}_2 \) and \( \cdot \text{NO}_3 \) in the reactor’s headspace during the aqueous-phase reactivity of RONO₂.
Figure S3: Experimental setup used for the NOx control experiment: ·NO2(g) was bubbled in the reactor’s aqueous phase and then photolyzed by exposing it to the lamplight.
Section S2: Interferences of RONO₂ in the NOₓ Analyzer

The CLD 88p Ecophysics measurements are based on the following principles. Ozone is generated photochemically and used to oxidize ·NO to the excited form of ·NO₂ (·NO₂∗). The latter can undergo photochemical relaxation emitting light with a maximum at 1200 nm. The light emitted is proportional to the ·NO concentration and is detected by photomultiplicators. Repeatedly, the sampled air is guided to a photolytic commercial converter (PCL 860 Ecophysics) where ·NO₂ is converted to ·NO by photolysis at 320 – 400 nm. The total ·NO is measured to obtain the NOₓ concentration and ·NO₂ concentration is obtained by subtraction.

In our experiments, interferences with the RONO₂ were observed. During the first 30 min of Experiment 1 (before photolysis, Table 1), an increase in the ·NO₂ signal was observed immediately after the injection of isopropyl nitrate into the reactor’s aqueous phase (Fig. S2.1). The signal stabilized at ~110 ppbv. Since no reactivity occurred at that moment, the signal was only generated by the conversion of isopropyl nitrate partitioned into the reactor’s headspace, into ·NO in the photolytic converter. The concentration of isopropyl nitrate in the reactor’s headspace was estimated to be ~1300 ppmv (considering its aqueous-phase concentration and K_H value). Therefore, the conversion of RONO₂ to ·NO is very low in good agreement with the fact that the photolytic converter filters light out of the 320 to 400 nm range to minimize interferences due to NO_y species and provoke interferences lower than 0.6 % (Ryerson et al., 2000).

![Figure S2.1: ·NO and ·NO₂ signal time profiles in the first 30 minutes of Exp. 1 when isopropyl nitrate (1 mM) is injected into the aqueous phase of the photoreactor, before photolysis.](image-url)
Section S3: Classical dynamics of isopropyl nitrate in water

Figure S3.1: MD dynamics for 125 ps (1 fs timestep) in an NVT ensemble at fixed isopropyl nitrate (black: energy value, blue: running average).

Figure S3.2: MD dynamics for 1 ns (1 fs timestep) in an NPT ensemble at fixed isopropyl nitrate (black: energy value, blue: running average).
Figure S3.3: B3LYP/6-31G*/Amber99 MD dynamics for 12 ps (1 fs timestep) in an NPT ensemble relaxing the full system (black: energy value, blue: running average).
Table S1: Initial conditions and yields of primary reaction products during the photolysis experiments. (sec. = secondary reaction products)

<table>
<thead>
<tr>
<th>Exp</th>
<th>RONO₂</th>
<th>[RONO₂]₀ (mM)</th>
<th>Decay (10⁻⁵ s⁻¹)</th>
<th>% cosumed at end</th>
<th>HNO₂</th>
<th>HNO₃</th>
<th>Isobutyraldehyde (%)</th>
<th>Acetone (%)</th>
<th>Hydroxyacetone (%)</th>
<th>Lactaldehyde (%)</th>
<th>Acetaldehyde (%)</th>
<th>Formaldehyde (%)</th>
<th>Acetic acid (%)</th>
<th>Formic acid (%)</th>
<th>IP3</th>
<th>IB1</th>
<th>IB2</th>
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<td>2</td>
<td>Isopropyl nitrate</td>
<td>0.93</td>
<td>1.9</td>
<td>38</td>
<td>40</td>
<td>sec.</td>
<td>32</td>
<td></td>
<td></td>
<td>5</td>
<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
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<tr>
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<td>Isopropyl nitrate</td>
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<td>1.4</td>
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<td></td>
<td></td>
<td>88</td>
<td>3</td>
<td></td>
<td>5</td>
<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
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<tr>
<td>4</td>
<td>Isopropyl nitrate</td>
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<td>1.0</td>
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<td>sec.</td>
<td>74</td>
<td>4</td>
<td></td>
<td>5</td>
<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
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<tr>
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<td></td>
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<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
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<td></td>
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<td>sec.</td>
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<td>sec.</td>
<td>sec.</td>
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<td>&gt;28</td>
<td>sec.</td>
<td></td>
<td></td>
<td>sec.</td>
<td>sec.</td>
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<td></td>
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<td></td>
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<tr>
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<td>0.6</td>
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<td>62</td>
<td>sec.</td>
<td></td>
<td></td>
<td>14</td>
<td>70</td>
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<td>sec.</td>
<td>sec.</td>
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</tr>
<tr>
<td>12</td>
<td>1-Nitrooxy-2-propanol</td>
<td>0.38</td>
<td>0.7</td>
<td>16</td>
<td>59</td>
<td>sec.</td>
<td></td>
<td></td>
<td>8</td>
<td>50</td>
<td>63</td>
<td>sec.</td>
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Figure S4: pH time profiles during the photolysis of isopropyl nitrate (Exp. 2), isobutyl nitrate (Exp. 8), and α-nitroxyacetone (Exp. 10).
Section S4: Observation of acetic acid and methylglyoxal formation during α-nitrooxyacetone aqueous-phase photolysis

As both lactate and acetate anions present very similar retention times in our analyses (5.7 vs 6.0 min), the occurrence of a large peak due to the lactate anion rendered impossible the quantification of the acetate carboxylate although the latter was identified as a significant reaction product (Fig. S4.1).

Figure S4.1: α-Nitrooxyacetone photolysis reaction products: ionic chromatogram of α-nitrooxyacetone in water before photolysis (blue) and after 7 h of photolysis (red). (Exp 10 in Table S1).

The quantification of methylglyoxal by DNPH derivatization and UHPLC-UV was impeded by oligomerization reactions (Fig. S4.2). The acidic conditions needed for the derivatization reaction with 1,4-DNPH provoked aldol condensation reactions of methylglyoxal. This reaction was observed on a solution containing 10⁻⁴ M of methylglyoxal and resulted in an unresolved broad peak at the end of the UHPLC-UV chromatogram (7 to 9 min in Fig. S4.2). This hump was also observed during α-nitrooxyacetone photolysis, and thus the formation of methylglyoxal was confirmed after 100 min of photolysis, but it could not be quantified.
Figure S4.2: $\alpha$-Nitrooxacetone photolysis reaction products: UHPLC-UV chromatograms of DNPH-derivatized samples at time 0 and 100 min of photolysis (Exp 10 in Table S1), compared to a solution of methylglyoxal ($10^{-4}$ M) at 360 nm.
Figure S5: UV absorbance spectra obtained from the UHPLC-UV analyses: (a) IP3 (observed in Exp 2) and (b) standards of RONO₂ at ~10⁻³ M.
Figure S6: Isobutyl nitrate photolysis: time profiles of oxidized RONO$_2$ detected by non-derivatized UHPLC-UV analyses (Exp. 8 in Table S2).
Section S5: GC-MS analyses of the “end of reaction” for isobutyl nitrate and 1-nitrooxy-2-propanol

Figure S5.1a shows the chromatogram of the “end of reaction” (after 7 h of photolysis) for isobutyl nitrate. Up to nine chromatographic peaks corresponding to oxidized RONO$_2$ were detected at significant intensities (> 2 ·10$^5$ cps), the peak at 7.1 min corresponds to isobutyl nitrate. The obtained mass spectra (Fig. S5.1b) confirmed chemical structures corresponding to RONO$_2$ with similarities with isobutyl nitrate mass spectra (i.e., C$_3$H$_7^+$, C$_4$H$_9^+$ CH$_2$ONO$_2^+$ fragments at m/z = 43, 57, and 76, respectively). Functionalization of the organic chain was demonstrated by the presence of multiple fragmentations, and retention times higher than that of isobutyl nitrate. The mass spectra of IB6 and its retention time were identical to IP3, which was assigned to 1,2-propyl dinitrate. Further identification of IB7 and IB8 was performed upon the interpretation of the mass spectra. Nevertheless, the lack of standards prevented more precise identification.

For 1-nitrooxy-2-propanol, GC-MS analyses of the “end of reaction” confirmed the formation of RONO$_2$, although much fewer compounds were determined than during isopropyl nitrate and isobutyl nitrate photolysis (Figure S5.2). Four oxidized RONO$_2$ were observed including α-nitrooxyacetone. Their mass spectra were found to be similar to those observed for other RONO$_2$, however, precise identification was not achieved.
Figure S5.1: Isobutyl nitrate photolysis: (a) gas chromatogram (extracted for m/z = 46, NO$_2$) of the “end of reaction” of Exp. 7 in Table S1 (after 7 hours of photolysis) and (b) mass spectra for all detected peaks.
Figure S5.2: 1-Nitrooxy-2-propanol photolysis: (a) gas chromatogram of the “end of reaction” after 7 hours of photolysis (Exp 11 in Table 1) and (b) mass spectra of all detected peaks.
Section S6. Rejected hypothesis: \( \cdot\text{NO}_2\) (aq) direct formation followed by fast reactivity

\( \cdot\text{NO}_2 \) could be formed during the aqueous-phase photolysis of \( \text{RONO}_2 \) and then, transformed into \( \text{HNO}_2 \) and \( \text{HNO}_3 \) by hydrolysis through a reaction reported by Finlayson-Pitts and Pitts Jr., 2000:

\[
2 \cdot\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3
\]  

(RS1)

with a reaction rate given by Eq. (S1):

\[
\frac{-1}{2} \frac{d[\cdot\text{NO}_2]}{dt} = k_2 [\cdot\text{NO}_2]^2 = \frac{d[\text{HNO}_2]}{dt} = \frac{d[\text{HNO}_3]}{dt} \quad k_2 = 7 \cdot 10^7 \text{ M}^{-1} \text{s}^{-1}
\]

(S1)

However, this reaction disagrees with our experiments where the formation of \( \text{HNO}_3 \) was exclusively observed as a secondary product (Fig. 2).

Another known pathway could be the aqueous-phase photolysis of \( \cdot\text{NO}_2\) (aq) forming \( \cdot\text{NO}_2\) (aq).\( \cdot\text{NO}_2\) (aq) + \( h\nu \rightarrow \cdot\text{NO} \) (aq) + \( 0(3\text{P}) \),

(RS2)

followed by the reaction of \( \cdot\text{NO} \) (aq) with \( \cdot\text{NO}_2\) (aq) in solution, yielding two molecules of \( \text{HNO}_2 \) (Finlayson-Pitts and Pitts Jr., 2000).

\[
\cdot\text{NO} + \cdot\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2
\]

(RS3)

with a reaction rate given by Eq. (S2):

\[
\frac{-d[\cdot\text{NO}]}{dt} = k_3 [\text{NO}][\cdot\text{NO}_2], \quad k_3 = 3 \cdot 10^7 \text{ M}^{-1} \text{s}^{-1}
\]

(S2)

This pathway is in better agreement with our observations of primary formation of \( \text{HNO}_2 \). Under this hypothesis, we calculated the steady-state concentrations of \( \cdot\text{NO}_2\), and \( \cdot\text{NO}_2\) (aq), and confronted the results with our experimental observations. To do so, we assumed that i) \( \text{RONO}_2 \) aqueous-phase photolysis yields 100 % \( \cdot\text{NO}_2\) (aq), and ii) \( J\) \( \cdot\text{NO}_2\) (aq) = \( \alpha \) \( J\) \( \text{RONO}_2\) (aq) where \( J\) \( \text{RONO}_2\) (aq) = 6 \cdot 10^{-6} \text{ s}^{-1} \) (obtained for isopropyl nitrate from (González-Sánchez et al., 2023)) and \( \alpha \) was varied from 10 to 6700 (which is the gas phase value, calculated from Clemishaw et al., 1997; Madronich and Flocke, 1999; Roberts and Fajer, 1989; Talukdar et al., 1997 data).

The steady-state concentrations of \( \cdot\text{NO}_2\) and \( \cdot\text{NO}_2\) (aq) were derived from Eq. (S3) and Eq. (S4).

\[
[\cdot\text{NO}_2] = \frac{-2\alpha J_{\text{RONO}_2} + \sqrt{(2\alpha J_{\text{RONO}_2})^2 + 8k_2 J_{\text{RONO}_2}}} {4k_2}
\]

(S3)

\[
[\cdot\text{NO}_2\text{ (aq)}] = \frac{\alpha J_{\text{RONO}_2}} {k_3}
\]

(S4)

Assuming \( \alpha = 6700 \) and considering the initial \( [\text{RONO}_2] \) of 1 mM, the aqueous-phase steady concentrations of \( \cdot\text{NO}_2\) and \( \cdot\text{NO}_2\) (aq) were 6.3 \cdot 10^{-9} \text{ M} and 1.3 \cdot 10^{-9} \text{ M}, respectively. Considering their high volatilities (\( K\) = 2.0 \cdot 10^{-3} and 1.8 \cdot 10^{-3} \text{ M atm}^{-1} \), respectively, Sander, 1999), and the volumes of the aqueous phase and the reactor’s headspace (400 and 600 mL, respectively), around 310 and 740 ppb of \( \cdot\text{NO} \) (g) and \( \cdot\text{NO}_2\) (g) would be observed in the reactor’s headspace. Hence, both compounds should be detectable in our system by the \( \text{NO}_x \) analyzer. Even assuming a much lower \( \alpha \) value of 10, concentrations of 330 ppb of \( \cdot\text{NO}_2\) (g) would be observable. Under this scenario, one-fourth of this \( \cdot\text{NO}_2\) (g) would be converted to \( \cdot\text{NO} \) through gas-phase photolysis.

Since no \( \cdot\text{NO}_2\) (g) nor \( \cdot\text{NO} \) (g) were detected in the reactor’s headspace during isopropyl nitrate photolysis (Fig. 1), hydrolysis of \( \text{NO}_x \) was thus rejected to explain the formation of \( \text{HNO}_2\) and \( \text{HNO}_3\) observed in our system.

Hydrolysis is not the only reaction that \( \text{NO}_x \) can undergo in the aqueous phase. Several studies have confirmed the nitration of aromatic compounds via \( \cdot\text{NO}_2 \) oxidation (Pang et al., 2019; Kroflíč et al., 2015; Vione et al., 2003; Biswal et al., 2013; Vione et al., 2005, 2004). More appropriate to our system, Goldstein et al., (2004)
confirmed that ·NO₂ and ·NO readily react with peroxy radicals (ROO·) in the aqueous phase to form peroxynitrates (ROONO₂) and peroxynitrites (ROONO), respectively.

On the one hand, peroxynitrates are semi-stable molecules that present relatively long lifetimes in the aqueous phase. On the other hand, peroxynitrites are very short-lived compounds (lifetimes < 10⁻⁶ s) that can either decompose back to RO⁻ and ·NO₂ or isomerize and form RONO₂. Due to the solvent cage effect, the yields of isomerization into RONO₂ are much enhanced compared to the gas phase reaction: around 84 – 89 % in the aqueous phase versus 1 – 35 % in the gas phase (Goldstein et al., 2004; Merényi et al., 2002; Atkinson et al., 1987).

However, even if the aqueous-phase photolysis of RONO₂ could directly form ·NO₂, no peroxy radicals could be directly formed in this system, preventing from any direct reaction ·NO₂ + RO₂·. Therefore, this hypothesis was rejected.
Figure S7: RONO\(_2\) photolysis: time profiles of RONO\(_2\) and the dissolved oxygen for (a) isopropyl nitrate (Exp. 2), (b) isobutyl nitrate (Exp. 8), (c) \(\alpha\)-nitrooxyacetone (Exp. 10), and (d) 1-nitrooxy-2-propanol (Exp. 12).
Figure S8: Primary carbonyl reaction products concomitant to HNO₂ + HNO₃ formation during photolysis of (a) isobutyl nitrate (Exp. 8) and (b) 1-nitrooxy-2-propanol (Exp. 11).