



HAL
open science

Direct formation of HONO through aqueous-phase photolysis of organic nitrates

Juan Miguel González-Sánchez, Miquel Huix-Rotllant, Nicolas Brun, Julien Morin, Carine Demelas, Amandine Durand, Sylvain Ravier, Jean-Louis Clément, Anne Monod

► To cite this version:

Juan Miguel González-Sánchez, Miquel Huix-Rotllant, Nicolas Brun, Julien Morin, Carine Demelas, et al.. Direct formation of HONO through aqueous-phase photolysis of organic nitrates. 2023. hal-04333124v1

HAL Id: hal-04333124

<https://hal.science/hal-04333124v1>

Preprint submitted on 17 Nov 2023 (v1), last revised 9 Dec 2023 (v2)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License



Direct formation of HONO through aqueous-phase photolysis of organic nitrates

Juan Miguel González-Sánchez^{1,2}, Miquel Huix-Rotllant², Nicolas Brun^{1,2}, Julien Morin¹, Carine Demelas¹, Amandine Durand¹, Sylvain Ravier¹, Jean-Louis Clément², Anne Monod¹

5 ¹Aix Marseille Univ, CNRS, LCE, Marseille, France

²Aix Marseille Univ, CNRS, ICR, Marseille, France

Correspondence to: Juan Miguel González-Sánchez (juangonzalez.sc@proton.me) and Anne Monod (anne.monod@univ-amu.fr)

10 **Abstract.**

Organic nitrates (RONO₂) are secondary compounds whose fate is closely related to the transport and removal of NO_x in the atmosphere. Despite their ubiquitous presence in submicron aerosols, the photochemistry of RONO₂ has only been investigated in the gas phase, leaving their reactivity in condensed phases poorly explored. This work aims to address this gap by investigating, for the first time, the reaction products, and the mechanisms of aqueous-phase photolysis of four
15 RONO₂ (i.e., isopropyl nitrate, isobutyl nitrate, α-nitrooxyacetone, and 1-nitrooxy-2-propanol). The results show that the reactivity of RONO₂ in the aqueous phase differs significantly from that in the gas phase. In contrast to the gas phase, where RONO₂ releases NO_x upon photolysis, the aqueous phase photolysis of RONO₂ leads primarily to the direct formation of HONO, which was confirmed by quantum chemistry calculations. Hence, the aqueous-phase photolysis of RONO₂ represents both a NO_x sink and a source of atmospheric HONO, a significant precursor of ·OH and ·NO. These secondary
20 radicals (·OH and ·NO) are efficiently trapped in the aqueous phase, leading to the formation of HNO₃ and functionalized RONO₂. This reactivity can thus potentially contribute to the aging of Secondary Organic Aerosol (SOA) and serve as an additional source of aqueous-phase SOA.

1 Introduction

Organic nitrates are secondary compounds, formed through NO_x + VOC reactions, that play an essential role in the transport and removal of NO_x in the atmosphere. These compounds can have long lifetimes, lasting from a few hours to several days,
25 which allow them to travel to remote regions (Shepson, 1999). During their long-range transport, they can undergo reactions such as gas-phase photolysis and/or ·OH oxidation, which can release NO_x back into the atmosphere. As a result, RONO₂ molecules are responsible for a more uniform distribution of NO_x and thus, are indirectly responsible for the transport of other pollutants such as O₃ and SOA (Perring et al., 2013).



30 Furthermore, NO_x removal from the atmosphere can occur via either RONO_2 deposition to the Earth's surface or by transformation into a less reactive chemical compound, such as nitric acid (Hu et al., 2011; Nguyen et al., 2015). Therefore, their atmospheric reactivity and fate must be considered to accurately predict pollution transport on a regional scale. This is especially important for world regions, such as Europe and North America, where the relative importance of RONO_2 in NO_x transport and removal is increasing due to the overall transformation of NO_x into RONO_2 (Romer Present et al., 2020).

35 RONO_2 are not only present in the gas phase, as some of them have low volatility and can partition into condensed phases. As a result, RONO_2 account for a significant fraction of submicron organic aerosol, ranging from 5% to 77% (Kiendler-Scharr et al., 2016; Ng et al., 2017). RONO_2 reactivity in condensed phases may differ from that in the gas phase and may affect their role as NO_x reservoirs. For instance, it is well-established that the hydrolysis of tertiary and allylic RONO_2 serves as a fast and permanent sink of NO_x in the atmosphere, as the nitrate group is transformed into nitric acid (Darer et al., 2011; Hu et al., 2011; Rindelaub et al., 2015). However, only a small fraction of RONO_2 (between 9 % and 34 % for α - and β -pinene related RONO_2) undergoes hydrolysis (Takeuchi and Ng, 2018; Wang et al., 2021). Other aqueous-phase reactions are thus to be considered: photolysis and $\cdot\text{OH}$ oxidation. Our previous studies have emphasized the significance of aqueous-phase reactivity for atmospherically relevant RONO_2 , such as isoprene and terpene nitrates, with intermediate to high water solubilities (González-Sánchez et al., 2021, 2023). At typical cloud/fog conditions (liquid water content, LWC, of 0.35 g m^{-3}), the aqueous-phase photoreactivity can act as a major sink ($> 50 \%$) for water-soluble RONO_2 ($K_H > 10^5 \text{ M atm}^{-1}$), while at very low LWC ($3 \cdot 10^{-5} \text{ g m}^{-3}$), it can serve as a major sink for very highly water-soluble RONO_2 ($K_H > 10^9 \text{ M atm}^{-1}$). Nevertheless, the fate of the nitrate group during these processes is still unknown, and it is uncertain whether this reactivity acts as a NO_x sink or as an additional transport mechanism.

This work intends to address these questions for the aqueous-phase photolysis of RONO_2 . To do so, the fate of four RONO_2 (i.e., isopropyl nitrate, isobutyl nitrate, α -nitrooxyacetone, and 1-nitrooxy-2-propanol) was experimentally investigated. The aqueous-phase photolysis primary and secondary reaction products were identified and quantified, and the fate of the nitrate group was elucidated with support from theoretical calculations. The atmospheric implications of these findings are discussed.

2 Materials and methods

55 2.1 Experimental setup

The aqueous-phase photolysis experiments were conducted using the experimental setup previously described in detail by González-Sánchez et al., (2023). Briefly, a 450 cm^3 double-wall Pyrex aqueous-phase photoreactor filled with 400 mL of aqueous solution and covered by a quartz lid was used. It was equipped with four apertures for reagent injections, sampling, and an Optical IDS dissolved oxygen sensor FDO® 925 (WTW) which included temperature monitoring. The reactor was thermostated at 298 K and continuously stirred. Irradiation was provided by an arc light source (LOT Quantum Design) equipped with a 1000 W arc Xe lamp. Wavelengths below 290 nm were removed using an ASTM 892 AM1.5 standard filter



(see lamp spectra in González-Sánchez et al., 2023). A constant distance of 18.4 cm between the lamp and the water surface was carefully maintained in all experiments.

2.2 Photolysis experiments

- 65 Prior to each photolysis experiment, the photoreactor was filled with mili-Q water and the RONO₂ was added. The solution was stirred for 30 min in the dark to ensure complete dilution of the RONO₂. Meanwhile, the lamp was turned on for 10 min to stabilize the light beam. The first aliquot was sampled when the reactor was placed under the light beam, marking the reaction time zero. Photolysis reactions were performed for 4 to 7 h at 298.0 ± 0.2 K. The specific experimental conditions of all photolysis experiments are appended in Table 1.
- 70 During the reaction, aliquots were regularly sampled for offline analyses. The pH of the reaction mixture was measured using a 9110DJWP pH Probe (Thermo Scientific). UHPLC-UV analyses were performed to monitor the RONO₂ decay or to identify and quantify carbonyl compounds after DNPH derivatization. HPIC-CD analyses were conducted to quantify HNO₂, HNO₃ and organic acids. At the end of the reaction, the remaining volume was used to perform liquid-liquid extraction and GC-MS analyses to identify the formed oxidized RONO₂. In experiment 1, the headspace of the reactor was monitored with
- 75 a NO_x analyzer to investigate the possible formation of these compounds.

Table 1: Initial conditions and analytical instruments used during the photolysis experiments of 4 individual RONO₂ molecules.

Nº	RONO ₂	[RONO ₂] ₀ / mM	Reaction time / h	UHPLC-UV	DNPH ^a	HPIC	GC-MS	NO _x Analyzer
1	Isopropyl nitrate	1.00	4					X
2	Isopropyl nitrate	0.93	7	X	X	X	X	
3	Isopropyl nitrate	1.81	7	X	X			
4	Isopropyl nitrate	1.71	5	X	X	X		
5	Isobutyl nitrate	0.60	7	X				
6	Isobutyl nitrate	0.59	7	X				
7	Isobutyl nitrate	0.53	7	X			X	
8	Isobutyl nitrate	0.55	7	X	X	X		
9	Isobutyl nitrate	0.49	7	X	X			
10	α-Nitrooxyacetone	1.18	7	X	X	X	X	
11	1-Nitrooxy-2-propanol	0.72	7	X	X	X	X	
12	1-Nitrooxy-2-propanol	0.38	7	X	X	X		

^aUHPLC-UV analyses after DNPH derivatization of the sample were used to identify and quantify carbonyl compounds. All experiments were performed at 298.0 ± 0.2 K.



2.3 Analytical instruments

2.3.1 UHPLC-UV

An Ultra-High Performance Liquid Chromatography (UHPLC) with an Ultra-Violet detector (UV) (Thermo Scientific Accela) equipped with a Hypersil Gold C18 column (50 x 2.1 mm) with a particle size of 1.9 μm and an injection loop of 5 μL was used to quantify carbonyl compounds after 2,4-dinitrophenylhydrazine (DNPH) derivatization and RONO_2 .

a) Measurements of RONO_2 .

A binary eluent of H_2O and CH_3CN was used for all analyses, with a flow rate of $400 \mu\text{L min}^{-1}$. Two gradients were used depending on the polarity of the compounds. For isopropyl nitrate and isobutyl nitrate, the gradient started at $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ 80/20 (v/v) and was gradually adjusted to 50/50 (v/v) over 3 min, held at this proportion for 1 min, and then set back to 80/20 (v/v) within 10 s until the end of the run at 5 min. For more polar compounds, i.e., α -nitrooxyacetone and 1-nitrooxy-2-propanol, a similar gradient was employed but the initial and final proportions were adjusted to $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ 90/10 (v/v) to optimize their retention times (rt). All RONO_2 were detected at their maximum absorbance wavelength at 200 nm (González-Sánchez et al., 2023).

Calibration curves were linear (as determined by the Mandel test) between $5 \cdot 10^{-5}$ and $1 \cdot 10^{-3} \text{ mol L}^{-1}$ with $R^2 > 0.9995$. Aliquots with expected concentrations higher than $1 \cdot 10^{-3} \text{ mol L}^{-1}$ were diluted before analyses. The retention times were 0.9, 1.2, 2.4, and 3.3 min for 1-nitrooxy-2-propanol, α -nitrooxyacetone, isopropyl nitrate, and isobutyl nitrate, respectively (Figure S1). Limits of detection (LOD) were $9 \cdot 10^{-6} \text{ mol L}^{-1}$ for isopropyl nitrate and $1 \cdot 10^{-5} \text{ mol L}^{-1}$ for the 3 other compounds.

b) Measurements of carbonyl compounds.

To derivatize the carbonyl compounds, $500 \mu\text{L}$ of the aqueous sample was mixed with $450 \mu\text{L}$ of 0.005 M DNPH and $50 \mu\text{L}$ of 0.1 M HCl. The mixture was allowed to react for 24 hours to achieve high yields. A specific method was developed for separating and quantifying the formed hydrazones. The gradient, with a flow rate of $400 \mu\text{L min}^{-1}$, started from $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ 80/20 (v/v) for 1 min, then was gradually adjusted to 30/70 (v/v) over 6 min, held at this proportion for 1 min, and then set back to 80/20 (v/v) within 10 s until the end of the run, at 9 min.

The resulting hydrazones from formaldehyde, acetaldehyde, acetone, hydroxyacetone, and isobutyraldehyde were identified and quantified at 360 nm. External calibrations were performed to quantify carbonyl compounds with concentrations ranging from $5 \cdot 10^{-6}$ to $1 \cdot 10^{-3} \text{ M}$ and $R^2 > 0.9995$. Their retention times were 4.4, 5.1, 5.8, 3.8, and 6.8 min, respectively. LOD were 4.1, 2.1, 1.5, 4.2, and $5.3 \cdot 10^{-6} \text{ M}$, respectively.



2.3.2 HPIC-CD

The formation of HNO₂ and HNO₃ and organic acids such as formic acid and acetic acid was quantified using a DIONEX ICS-3000 High-Performance Ionic Chromatography (HPIC) with a DIONEX IonPac™ AG11-HC precolumn (4 x 50 mm) and a DIONEX IonPac™ AS11-HC column (4 x 250 mm) coupled to a CD25 conductivity detector.

- 115 A binary eluent gradient method composed of H₂O and NaOH 0.1 mol L⁻¹ aqueous solution was optimized to separate the formed organic acids at relatively short retention times. At a flow rate of 1 mL min⁻¹, the gradient started at H₂O/NaOH 0.1 mol L⁻¹ 96/4 (v/v) for 10 min, then gradually to 50/50 (v/v) during 12 min, then went back within a minute to 96/4 (v/v), and was held at this proportion until the end of the analyses at 25 min. The injection volume was 200 μL, and a constant flow of H₂SO₄ 0.05 M continuously passed through the suppressor at a flow rate of 3 mL min⁻¹.
- 120 The retention times of acetate, formate, NO₂⁻ and NO₃⁻ were 5.9, 7.2, 17.3, and 21.9 min, respectively. Calibration curves were optimized to obtain good linearity and low LOD (within the concentrations range expected). LOD were 4.3 · 10⁻⁶, 3.5 · 10⁻⁶, 6 · 10⁻⁷ and 5 · 10⁻⁷ M for acetic acid, formic acid, NO₂⁻ and NO₃⁻, respectively.

2.3.3 GC-MS

- A Clarus® 680 Gas Chromatograph (GC, Perkin Elmer) equipped with an Elite-5MS Capillary Column (Perkin Elmer) with
125 30 m length, 0.25 mm diameter, and 0.25 μm of film thickness coupled to an AxION® iQT™ Quadrupole/Time of Flight-Mass Spectrometer (MS, Perkin Elmer) was used to qualitatively detect and identify oxidized RONO₂ formed during the aqueous-phase photolysis experiments. RONO₂ were extracted and preconcentrated from the remaining solution after the end of each photolysis experiment. The remaining solutions were stored at ~4 °C for up to 48 h before the analyses.

- 100 mL of the remaining solution were extracted using 3 x 20 mL of dichloromethane in a separatory funnel. UHPLC-UV
130 analyses of the aqueous phase before and after the extraction confirmed that all RONO₂ efficiently partitioned to dichloromethane. The extracts were washed with 20 mL of mili-Q water and were concentrated in a TurboVap II system (Biotage). The concentration workstation used a nitrogen flow at 11 psi and a water bath at 30 °C to evaporate dichloromethane until a 500 μL sample was obtained.

- One μL of the concentrated extract was then injected into the GC-MS. The carrier gas was helium at a flow rate of 1 mL
135 min⁻¹. A split of 20:1 was used due to the high concentration of the compounds. The injector temperature was set to increase from 60 °C to 200 °C within 1 min to prevent RONO₂ thermolysis. The following program was set in the oven: 30 °C for 10 min; increase until 300 °C at a 15 °C min⁻¹ rate; and hold for 10 min at 300 °C before the end of the analyses.

- The analytes were detected with a Time-of-Flight Mass Spectrometer using electron impact ionization with an electron
140 energy of 70 eV and an ion source temperature of 250 °C. The ion source was turned on 5 – 7 minutes after the analysis started, to avoid the saturation of the source due to the solvent signal. The detector performed full scan measurements from m/z = 30 to 300 amu. The mass-to-charge ratio of the ion NO₂⁺ (m/z = 46), specific to RONO₂, was extracted to detect these



compounds. Seven known RONO_2 were analyzed by GC-MS to investigate their retention times and fragmentation patterns (Section S1).

2.3.4 NO_x analyzer in the reactor's headspace

145 A CLD 88p Ecophysics NO_x analyzer was used to determine if $\cdot\text{NO}$ and $\cdot\text{NO}_2$ were formed and partitioned into the gas-phase headspace of the solution during the photolysis of isopropyl nitrate. Indeed, both $\cdot\text{NO}$ and $\cdot\text{NO}_2$ are highly volatile compounds ($K_H = 1.8 \cdot 10^{-3} \text{ M atm}^{-1}$ and $K_H = 2.0 \cdot 10^{-2} \text{ M atm}^{-1}$, respectively, Sander, 2015) i.e. from 30 to 10^7 times more volatile than the investigated RONO_2 . Therefore, if any $\cdot\text{NO}$ or $\cdot\text{NO}_2$ were formed during the aqueous-phase photolysis, they would have partitioned to the reactor's headspace.

150 As the NO_x analyzer monitored the headspace of the reactor, a specific experimental setup consisting of a hermetic one-liter three-neck round-bottom flask was used (Fig. S2). It was irradiated by the lamplight beam on its side. Note that since the reactor's headspace was also illuminated, photolysis of isopropyl nitrate could occur in the reactor's headspace. However, although isopropyl nitrate is highly volatile, most of the compound remained in the aqueous phase in the time scale of the experiments (only 3 % of isopropyl nitrate partitioned into the reactor's headspace after 7 h, González-Sánchez et al., 2023).

155 The NO_x Analyzer LOD is 0.1 ppbv for both $\cdot\text{NO}$ and $\cdot\text{NO}_2$. Considering the gas phase dilutions performed downward the reactor, $\cdot\text{NO}_x$ could be detected, if formed, at concentrations higher than ~ 2 ppbv using this set-up. Although the CLD 88p Ecophysics NO_x analyzer uses a photolytic converter, interferences with the RONO_2 were observed. A slight proportion (less than 0.6 %) of gas-phase isopropyl nitrate was detected as $\cdot\text{NO}_2$. Further details are given in Section S2.

In addition, a control experiment was performed to test the efficiency of the gas-phase $\cdot\text{NO}_2$ photolysis and conversion to
160 $\cdot\text{NO}$ under our experimental conditions by bubbling gas-phase $\cdot\text{NO}_2$ into the reactor's aqueous phase and photolyzing it with the lamplight. The experimental setup is depicted in Fig. S3.

2.4 Molar yield determinations

The molar yields of the primary reaction products were determined by plotting their concentrations against $\Delta[\text{RONO}_2]$, that represents the consumption of the parent organic nitrate (Eq. 1).

165
$$\text{yield (\%)} = \frac{[\text{product}]}{\Delta[\text{RONO}_2]} \cdot 100\% \quad (1)$$

Since the reaction products were susceptible to undergo photolysis over time, the yields were calculated for the initial aliquots, sampled during the first 1–2 h of reaction. The evaporation rate of some RONO_2 could be non-negligible compared to photolysis (González-Sánchez et al., 2023), $\Delta[\text{RONO}_2]$ was thus systematically corrected from evaporation using Eq. (2-3).

170
$$[\text{RONO}_2]_{\text{reac}} = [\text{RONO}_2]_0 e^{(-k_{\text{exp}} + k_{\text{vap}}) \cdot t} \quad (2)$$

$$\Delta[\text{RONO}_2] = [\text{RONO}_2]_0 - [\text{RONO}_2]_{\text{reac}}, \quad (3)$$



where $[RONO_2]_0$ is the initial concentration, and k_{exp} the pseudo-first-order decay, determined by fitting of the $RONO_2$ concentrations ($[RONO_2]_t$) versus time (t) following Eq. (4).

$$[RONO_2]_t = [RONO_2]_0 e^{(-k_{exp}) \cdot t} \quad (4)$$

175 The evaporation rate constant, k_{vap} , was determined by control experiments reported in González-Sánchez et al., (2023).

2.5 Theoretical calculations

Theoretical simulations of the photolysis reaction of isopropyl nitrate photolysis were performed in a model of aqueous solution and in the gas phase. For building the model in the gas phase, snapshots from a 10 ps QM MD dynamics were performed using a thermostat at 300 K. For building the model in aqueous solution, a water box of $(22.5 \text{ Angstrom})^3$ was
180 built and equilibrated using Amber99 TIP3P water parameters. Isopropyl nitrate was then soaked in the boxed, and re-equilibrated in the following protocol (see Section S3): 1) An NVT MM MD at fixed isopropyl geometry during 125 ps; 2) An NPT MM MD at fixed isopropyl during 1 ns; and 3) An NPT B3LYP/6-31G**//Amber99 QM/MM PBC MD relaxing the full system for 12 ps (Bonfrate et al., 2023). The snapshots were taken from the latter, discarding the first 2 ps. For each
185 snapshot, a water droplet of 10 Angstrom was extracted, including a spherical wall potential to avoid evaporation of water during the excited-state dynamics. In each snapshot (gas phase and aqueous solution), non-adiabatic excited state molecular dynamics were operated using Tully's fewest switch surface hopping algorithm (Huix-Rotllant et al., 2023). The trajectories were started from the second excited state (S_2). Excited states were computed using mixed-reference time-dependent density-functional theory, which can describe the multi-configuration character of wavefunctions during photolysis at the cost of a density-functional theory calculation (Huix-Rotllant et al., 2023; Lee et al., 2018).

190 3 Results

The results of aqueous phase photolysis of organic nitrates are presented stepwise. Since NO_x are the known major primary products formed in the gas-phase photolysis of $RONO_2$, this process is first examined in Section 3.1 which describes the attempt to measure any formation and partitioning of NO_x to the headspace of the reactor. Sections 3.2, 3.3, and 3.4 present the identified reaction products in the aqueous phase including HNO_2 , HNO_3 , carbonyls, organic acids, and oxidized
195 $RONO_2$, and their associated yields. All results are reported in Table S1. Finally, Section 4 provides a detailed discussion of the mechanisms involved focusing on the fate of the nitrate group.

3.1 Absence of NO_x in the reactor's headspace

Experiment 1 investigated isopropyl nitrate (1 mM) photolysis by analyzing the reactor's gas-phase headspace with a NO_x analyzer (Fig. 1a). Prior to turning on the lamp, $\cdot NO_2$ signal increased up to ~ 150 ppb, corresponding to a fraction of gas-
200 phase isopropyl nitrate that was photolyzed inside the NO_x analyzer photolytic converter (see Section S2 for further details).



Once the lamp was turned on (shown in shaded blue in Fig. 1a), the aqueous-phase photolysis of isopropyl nitrate started, but no $\cdot\text{NO}$ signal was detected, while the $\cdot\text{NO}_2$ signal peaked at 800 ppb within ~ 10 min of photolysis. However, this signal did not correspond to $\cdot\text{NO}_2$, as demonstrated by the control experiment where ~ 800 ppb of $\cdot\text{NO}_{2(g)}$ were bubbled through the same volume of ultrapure water. When the lamp was turned on (shown in shaded blue in Fig. 1b), $\cdot\text{NO}_{2(g)}$ was effectively photolyzed, forming $\cdot\text{NO}_{(g)}$. In this experiment, barely any $\cdot\text{NO}_{2(g)}$ partitioned to the aqueous phase (confirmed by the absence of aqueous-phase HNO_2 or HNO_3 , measured by HPIC), and thus the photolysis of $\cdot\text{NO}_{2(g)}$ exclusively occurred in the reactor's headspace. From this control experiment, it was concluded that if the measured $\cdot\text{NO}_2$ signal represented actual $\cdot\text{NO}_{2(g)}$ directly formed in Experiment 1, it would be photolyzed to produce measurable amounts of $\cdot\text{NO}_{(g)}$. Since no $\cdot\text{NO}_{(g)}$ was observed when the lamp was turned on in Experiment 1 (Fig. 1a), one can conclude that no substantial amounts of $\cdot\text{NO}_{2(g)}$ were present in the system. The signal detected as $\cdot\text{NO}_{2(g)}$ likely corresponded to another volatile N-containing compound that was detected by the NO_x analyzer as $\cdot\text{NO}_2$ signal (as isopropyl nitrate does).

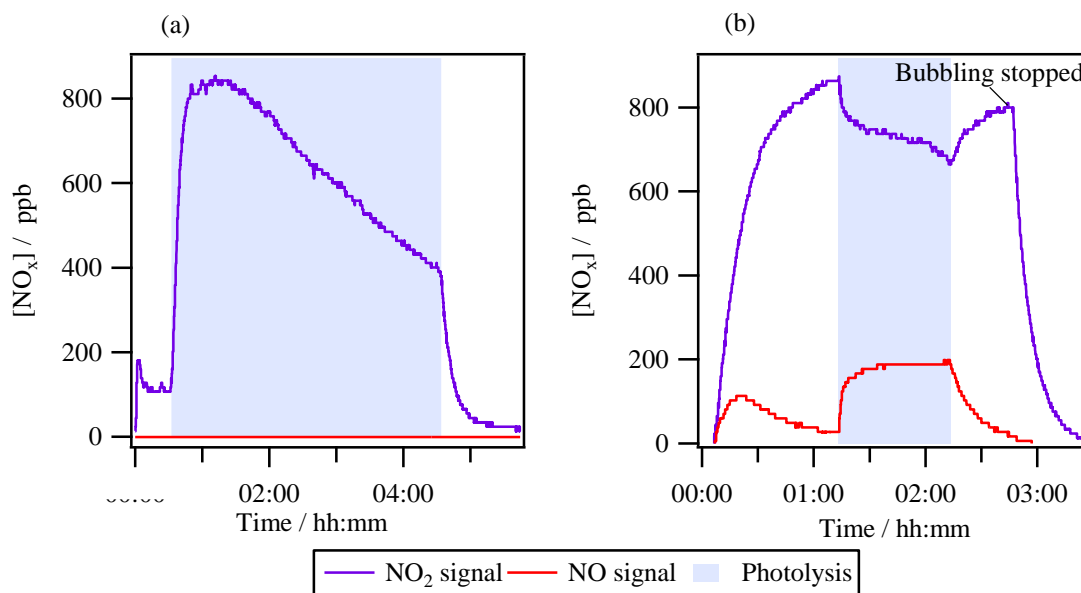


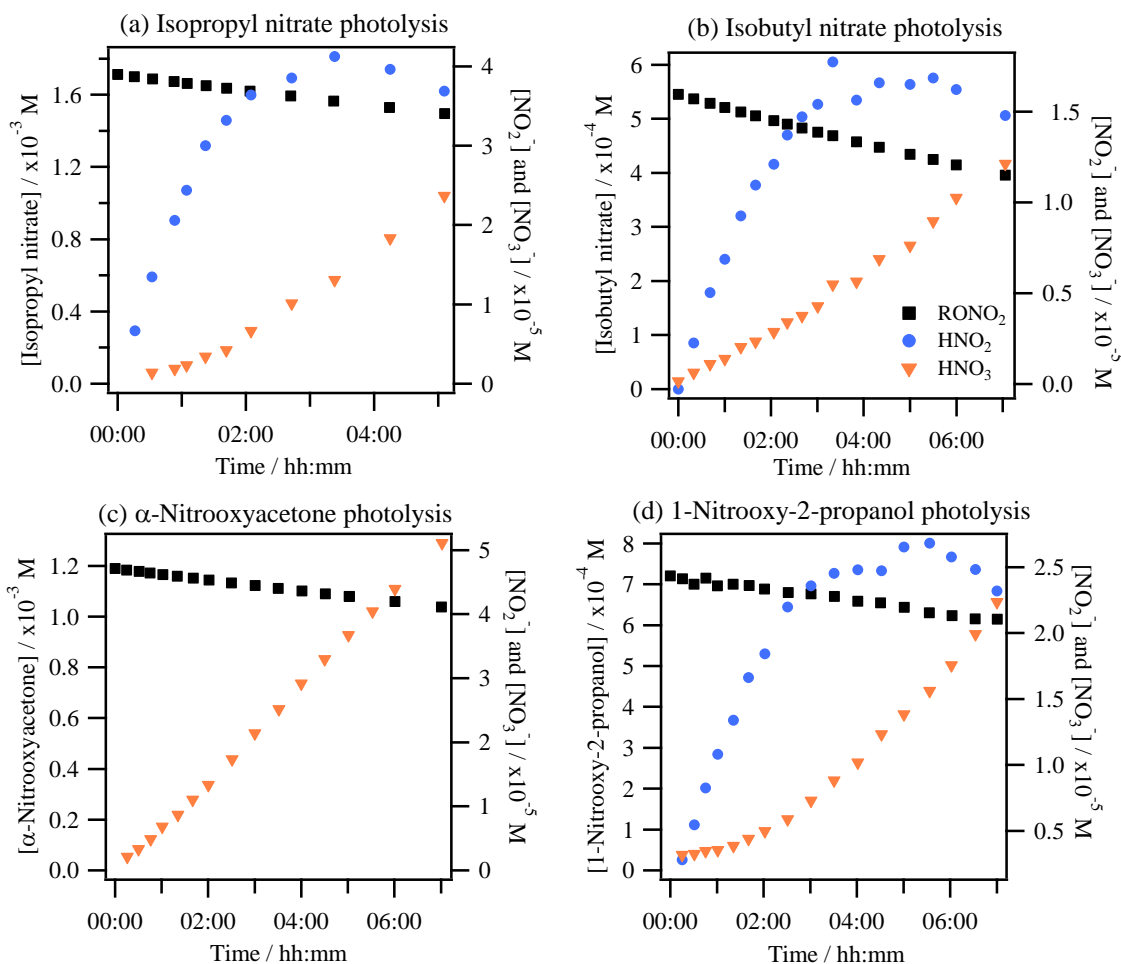
Figure 1: Headspace time profiles of $\cdot\text{NO}_{(g)}$ and $\cdot\text{NO}_{2(g)}$ signals during a) aqueous-phase photolysis of isopropyl nitrate with $[\text{RONO}_2]_0 = 10^{-3}$ M (Exp. 1 in Table 1); and b) photolysis of $\cdot\text{NO}_{2(g)}$ bubbled in water.

215 3.2 Formation of HNO_2 and HNO_3

HNO_2 and HNO_3 were formed during RONO_2 aqueous-phase photolysis. Both compounds were detected as NO_2^- , and NO_3^- using HPIC-CD but their formation as acids was inferred by the observed fast decrease of pH (Fig. S4) and was confirmed by theoretical calculations (see Section 3.5).

Figure 2 shows an example of HNO_2 and HNO_3 time profiles during the photolysis experiments of isopropyl nitrate (Fig. 2a), isobutyl nitrate (Fig. 2b), α -nitrooxyacetone (Fig. 2c), and 1-nitrooxy-2-propanol (Fig. 2d). HNO_2 could not be

quantified during the aqueous-phase photolysis of α -nitrooxyacetone due to its fast hydrolysis in the HPIC system that used high pH eluents, where the molecule decomposes into lactate and NO_2^- (Brun et al., 2023).



225 **Figure 2: RONO₂ photolysis experiments: time profiles of RONO₂, HNO₂, and HNO₃ for (a) isopropyl nitrate (Exp. 4), (b) isobutyl nitrate (Exp. 8), (c) α -nitrooxyacetone (Exp. 10), and (d) 1-nitrooxy-2-propanol (Exp. 11).**

The figure shows that HNO₂ was efficiently formed as a primary product during all RONO₂ aqueous-phase photolysis reactions. HNO₂ formation slowed down over time due to its fast oxidation to HNO₃ whose time profiles present exponential growth due to its secondary formation. Since this conversion is fast, HNO₃ formation of the first aliquots has been included in the HNO₂ primary yields, assuming that all HNO₃ was formed via HNO₂ oxidation. The detailed chemistry of HNO₂/HNO₃ that validates this approach is discussed in Section 3.5. The HNO₂ yields ranged from 40 to 59 % for isopropyl nitrate (Exp 2 and 4), 59 to 62 % for 1-nitrooxy-2-propanol (Exp. 11 and 12), was of 31 ± 7 % for isobutyl nitrate (Exp. 8) and was higher than 28 % for α -nitrooxyacetone (Exp. 10).

230

3.3 Formation of carbonyl compounds and organic acids

235 The formation of primary and secondary carbonyl compounds and organic acids was observed during the aqueous-phase photolysis of RONO_2 (Fig. 3).

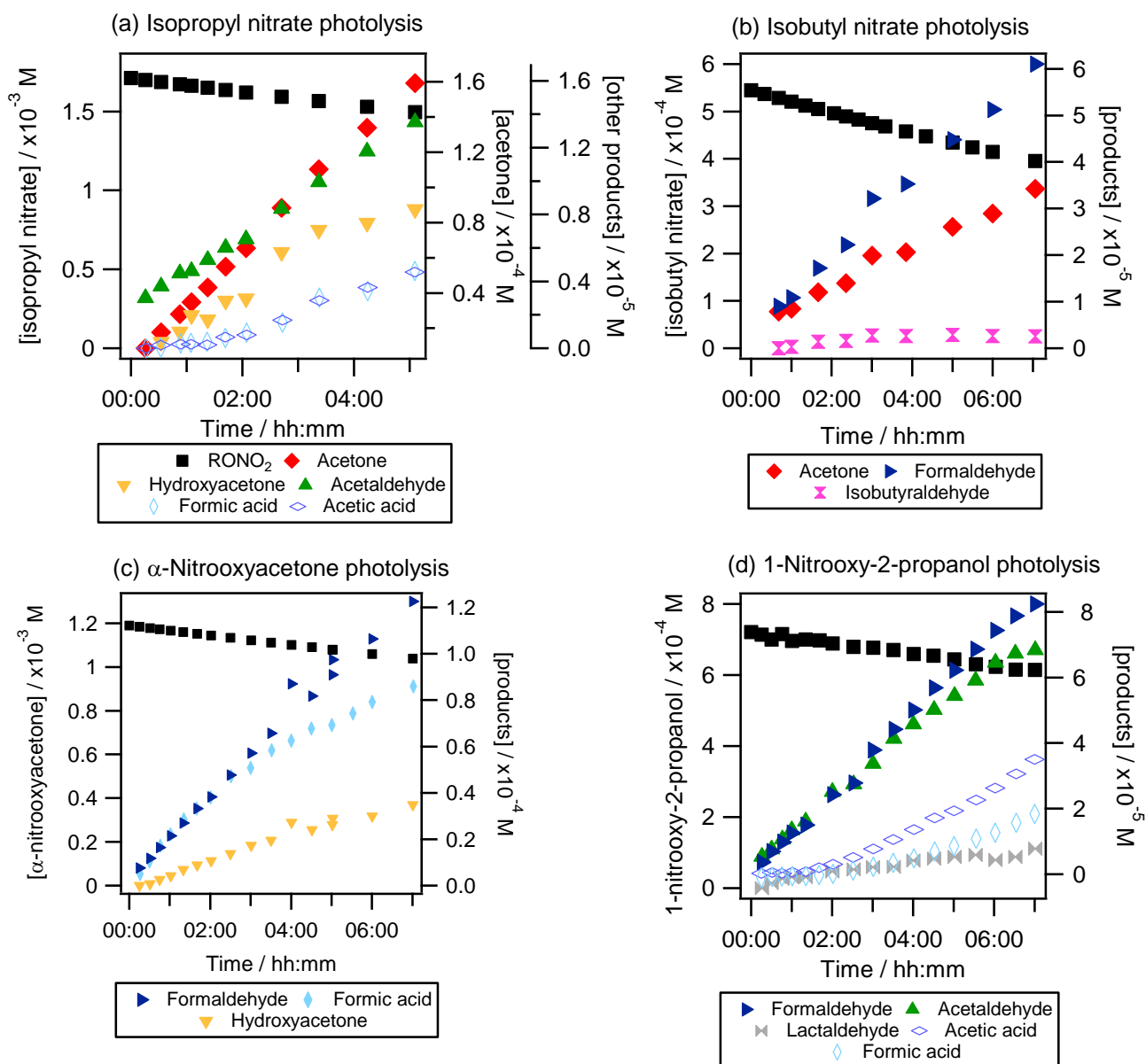


Figure 3: RONO_2 photolysis experiments: time profiles of RONO_2 , carbonyl compounds and organic acids for (a) isopropyl nitrate (Exp. 4), (b) isobutyl nitrate (Exp. 8), (c) α -nitrooxyacetone (Exp. 10), and (d) 1-nitrooxy-2-propanol (Exp. 11). Plain markers are used for primary products.

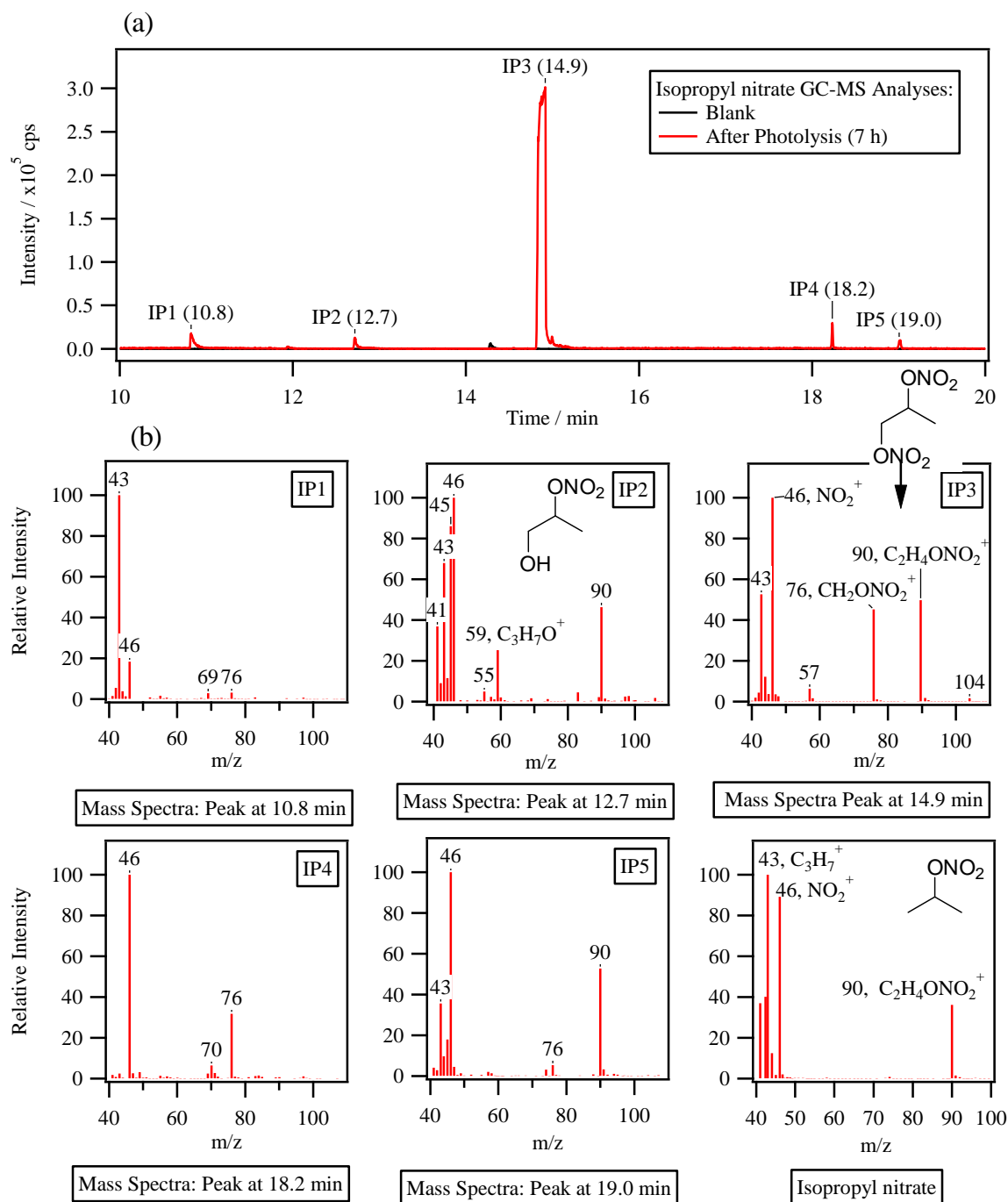


240 For isopropyl nitrate (Fig. 3a), the main primary reaction product was acetone with yields ranging from 32 to 88 % (Exp. 2–
4) and acetaldehyde was formed primarily with lower yields (5 %). Additionally, hydroxyacetone, formic acid and acetic
acid were formed as secondary products. These compounds were likely formed via acetone photooxidation (Poulain et al.,
2010). For isobutyl nitrate (Fig. 3b), formaldehyde and acetone were the main non-nitrogen-containing photolysis products
(primary yields of 37 – 39 % and 20 – 32 %, respectively, Exp. 8–9). Additionally, isobutyraldehyde was detected as a minor
245 product (with a primary yield of 4 – 5 %). For α -nitrooxyacetone (Fig. 3c), formaldehyde and formic acid appeared as
primary products while hydroxyacetone and acetaldehyde were likely secondary products. The formation yields were found
to be 96 ± 5 % and 79 ± 3 % for formic acid and formaldehyde, respectively. Other reaction products such as acetic acid and
methylglyoxal were identified but not quantified due to interferences in the analyzers, caused by hydrolysis of α -
nitrooxyacetone or oligomerization of methylglyoxal (see Section S4). For 1-nitrooxy-2-propanol (Fig. 3d), formaldehyde
250 and acetaldehyde were identified as the main primary reaction products with yields of 63 – 71 % and 50 – 70 %,
respectively. Furthermore, lactaldehyde was detected as a primary product with a minor yield of 8 – 14 %. Formic acid and
acetic acid were observed as secondary products, likely formed via the photooxidation of formaldehyde and acetaldehyde.

3.4 Secondary formation of oxidized RONO_2

GC-MS analyses at the end of each reaction were performed to seek for nitrogen-containing organic products. For isopropyl
255 nitrate, Fig. 4a compares the gas chromatograms obtained for the sample analyzed after 7 h of photolysis with one obtained
during a control experiment of isopropyl nitrate in the dark. In both chromatograms, $m/z = 46$ (which corresponds to NO_2^+
fragment) was extracted to display chromatographic peaks related to RONO_2 compounds. The figure shows the formation of
at least 5 oxidized RONO_2 molecules (IP1, IP2, IP3, IP4, and IP5), with IP3 presenting an intensity of one magnitude higher
than the others.

260 The observed compounds were less volatile than isopropyl nitrate (which $rt = 6$ min, not shown in Fig. 4a) given their higher
retention times and thus were probably oxidized species. The mass spectra of IP1 to IP5 confirm that all compounds were
 RONO_2 with similar chemical structures as isopropyl nitrate (included in Fig. 4b bottom right for comparison). Apart from
the NO_2^+ fragment, other fragments observed for isopropyl nitrate were detected. Fragments such as C_3H_7^+ ($m/z = 43$), and
 $\text{C}_2\text{H}_4\text{ONO}_2^+$ ($m/z = 90$) were observed in IP2, IP3, and IP5 (and also IP1 for $m/z = 43$). Note that $m/z = 43$ can also
265 correspond to an oxygenated fragment ($\text{C}_2\text{H}_3\text{O}^+$) but the resolution of 1 amu did not allow for separation from C_3H_7^+
fragments. Additionally, a specific fragment of a RONO_2 bearing its nitrate group on a primary carbon atom ($\text{CH}_2\text{ONO}_2^+$ at
 $m/z = 76$) was observed for IP1, IP3, IP4, and IP5. Since IP3 and IP5 combine this fragment with a fragment specific for the
secondary nitrate group ($\text{C}_2\text{H}_4\text{ONO}_2^+$ at $m/z = 90$), these compounds might be dinitrates. This is the case for the most intense
chromatographic peak (IP3). IP3 was thus assigned to the 1,2-propyl dinitrate molecule due to its mass spectra. Additionally,
270 IP2 was assigned to 2-nitrooxy-1-propanol due to the $\text{C}_3\text{H}_7\text{O}^+$ and $\text{C}_2\text{H}_5\text{ONO}_2^+$ fragments ($m/z = 59$ and $m/z = 90$,
respectively). These identifications are consistent with the proposed mechanism (see Section 4.2). However, the absence of
standards prevented from precise identification and quantification of these compounds.



275 **Figure 4: Isopropyl nitrate photolysis:** (a) gas chromatogram (extracted for $m/z = 46, \text{NO}_2^+$) of the “end of reaction” of Exp 2 in Table 1 (after 7 hours of photolysis) and blank (isopropyl nitrate in water); (b) Mass spectra of the detected peaks.



Hints of the formation of an oxidized RONO_2 were also observed in the non-derivatized UHPLC-UV analyses. An unidentified peak was detected at a retention time close to isopropyl nitrate (2.7 vs. 2.4 min). The peak presented similar UV absorption spectra to the RONO_2 standards (Figure S5) and was thus assigned to be IP3 (1,2-propyl dinitrate) due to its major concentrations). The compound was a secondary product since its occurrence started after 2 hours of reaction. A rough estimation of its concentration was performed using average calibration curve parameters obtained for isopropyl nitrate, isobutyl nitrate, α -nitrooxyacetone, and 1-nitrooxy-2-propanol. Assuming that IP3 was a dinitrate, it represented 9 % of the consumed nitrogen at the end of the reaction.

The secondary formation of oxidized RONO_2 was also confirmed for isobutyl nitrate and 1-nitrooxy-2-propanol. For isobutyl nitrate, two unidentified peaks assigned to oxidized RONO_2 (IB1 and IB2) were observed by UHPLC-UV. Both compounds present UV-Vis absorption spectra identical to isobutyl nitrate at lower retention times (1.6 min for IB1 and 3.1 min for IB2 vs 3.4 min for isobutyl nitrate) related to a higher polarity of the molecules. Their time profiles show that both compounds were formed through secondary reactions (Fig. S6). GC-MS analyses (performed after preconcentration of the sample) allowed for the detection of up to 9 oxidized RONO_2 . For 1-nitrooxy-2-propanol, four oxidized RONO_2 , including α -nitrooxyacetone, were observed by GC-MS. The chromatograms and mass spectra as well as comments on the identification of the formed molecules are presented in SI (Section S5).

For α -nitrooxyacetone, no oxidized RONO_2 were found neither in UHPLC-UV analyses nor in GC-MS analyses.

4 Discussion

4.1 N budget during aqueous-phase RONO_2 photolysis

Gas-phase photolysis of RONO_2 is known to induce homolytic rupture of the RO-NO_2 bond releasing $\cdot\text{NO}_2$ to the atmosphere with yields close to 100 % (Talukdar et al., 1997; Carbajo and Orr-Ewing, 2010). This reactivity turns RONO_2 into NO_x reservoirs and shifts pollution transportation from the local to the regional scale. Our results show that, in the aqueous phase, a primarily formation of HNO_2 (with yields ranging from 31 to 62 %) is followed by a secondary formation of HNO_3 . Therefore, one of the main questions about the aqueous-phase photolysis of RONO_2 is if they can (or not) regenerate NO_x that would partition to the gas phase.

To address this question, we explored the viability of two different chemical pathways that lead to $\text{NO}_2^-/\text{HNO}_2$ and $\text{NO}_3^-/\text{HNO}_3$ in the aqueous phase. The first explored pathway was the direct formation of $\cdot\text{NO}_{2,(aq)}$ followed by its known aqueous reactivity (i.e., hydrolysis and reactivity towards other radicals). This pathway was rejected since $\cdot\text{NO}$ and $\cdot\text{NO}_2$ should be observable in the system under this scenario (see details in Section S6). The second explored pathway was the direct formation of HNO_2 in the aqueous phase. This pathway was confirmed by theoretical calculations for isopropyl nitrate aqueous-phase photolysis. Herein, the discussion focuses on this pathway and the secondary chemistry of the photolysis products in our system. Finally, a conclusion is given with proposed mechanisms of aqueous phase photolysis reactions of



isopropyl nitrate, isobutyl nitrate, 1-nitrooxy-2-propanol, and α -nitrooxyacetone, including a detailed discussion for
310 isopropyl nitrate.

4.1.1 Direct formation of HNO_2 in the aqueous phase

Theoretical calculations were performed to evaluate if the direct formation of HNO_2 is possible in the aqueous phase. The
results showed that the formation of HNO_2 is thermodynamically favorable. Figure 5 represents the relative energy diagram
of isopropyl nitrate aqueous-phase photolysis, showing that it is indeed a possible reaction. Upon photon absorption,
315 isopropyl nitrate is in the first excited state (1) and relaxes rapidly to the minimum of this state (at $74.72 \text{ kcal mol}^{-1}$). From
the excited state, it undergoes an internal conversion to the ground state through a degenerated point between the excited and
the ground state, a conical intersection (2). The $-\text{ONO}_2$ presents a pyramidal structure (instead of triangular) in the conical
intersection. The process is very fast since the energy barrier is $5.47 \text{ kcal mol}^{-1}$ while there is an excess of $\sim 36 \text{ kcal mol}^{-1}$ of
nuclei kinetic energy. From there, the molecule can come back to the ground state. However, there is enough energy to cross
320 the transition state (4) and undergo dissociation into acetone and HNO_2 .

To further investigate the reaction intermediates, excited state non-adiabatic have been performed. In Fig. 6, a reactive
trajectory in the excited state is depicted. Initially, the R-ONO_2 is in a trigonal planar conformation. Once the photon is
absorbed, the group displays a pyramidal conformation that allows a non-radiative conversion from the excited to the ground
state via a conical intersection. This leads directly to the dissociation of $\cdot\text{NO}_2$, which diffuses towards water. Interaction of
325 $\cdot\text{NO}_2$ with water favors the 180-degree twist, in which nitrogen is pointing towards water molecules, favoring thus a
conformation in which a proton transfer is favored, occurring in less than 1 ps. Despite this happening to be the main
reaction channel, other reactions are possible in which direct formation of acetaldehyde or dissociation of HNO_2 in $\cdot\text{OH}$ and
 $\cdot\text{NO}$ are observed. This is due to the excess of vibrational energy of the photoproducts encapsulated in a water cavity of a
diameter around 7 \AA , which prevents their diffusion. Still, in longer timescales the photoproducts will either react with water
330 or dissipate the energy to the solvent.

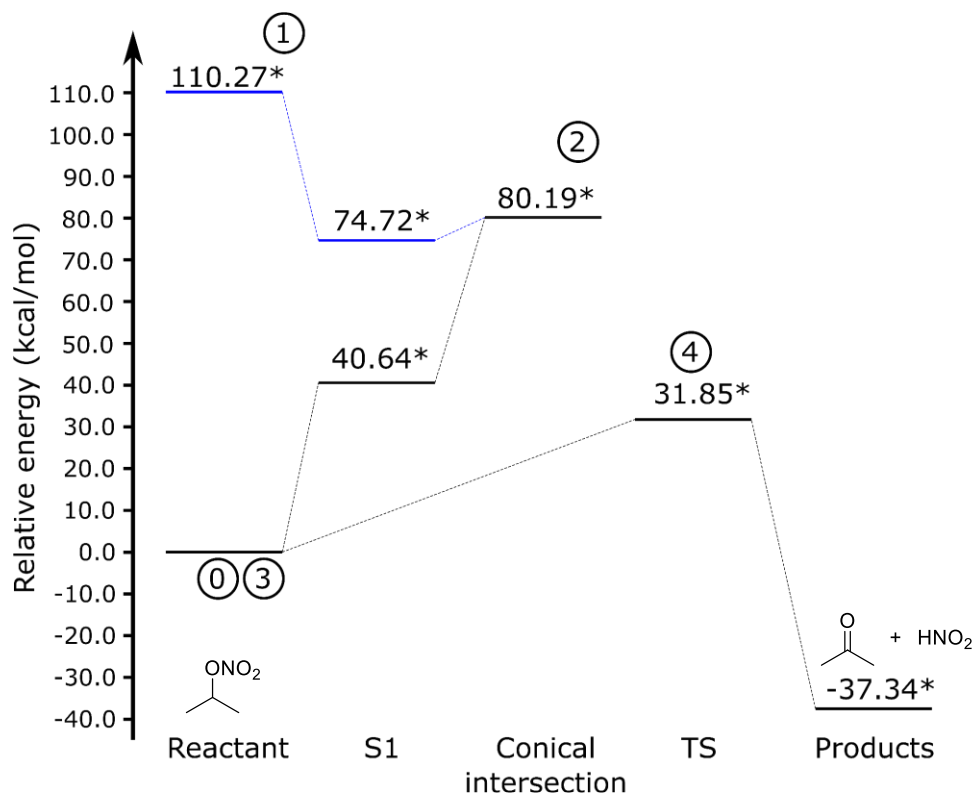
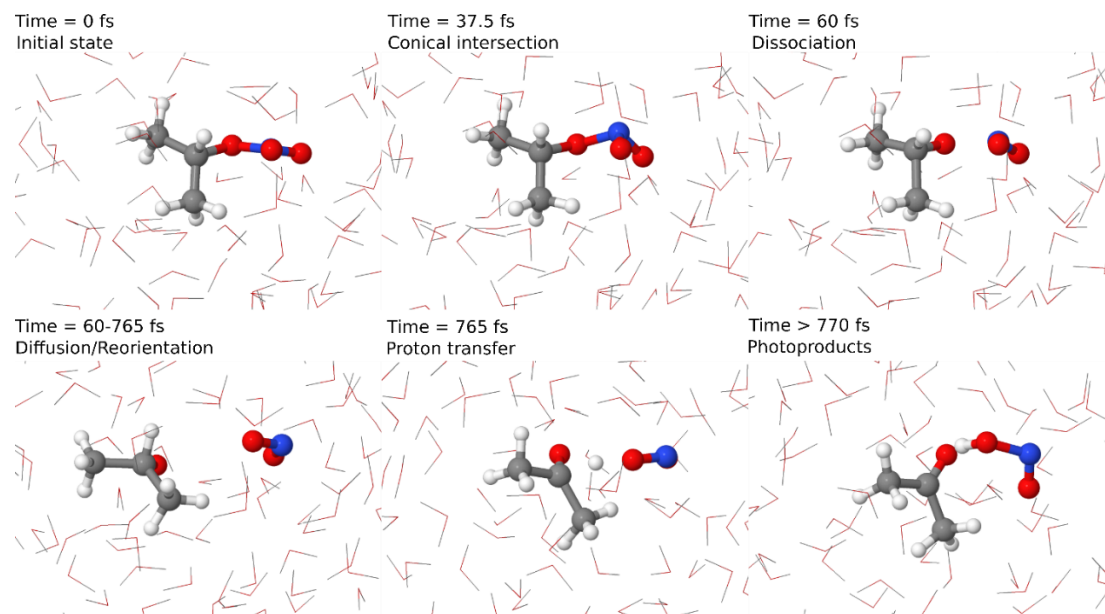


Figure 5: Relative energy diagram of isopropyl nitrate photolysis surrounded by a sphere of 900 water molecules. The reactant's energy has been arbitrarily placed at 0.0 kcal/mol. Calculations were performed using a DFT model.

335 Using the same type of dynamics, it was calculated that the initial $\cdot\text{NO}_2$ radical formation mechanisms also occurs during the gas-phase photolysis of isopropyl nitrate. Likely, the energy dissipation through collisions with other molecules does not take place fast enough in the gas phase due to the absence of a cavity that keeps the fragments together. Therefore, in the gas-phase, the great amount of energy ($\sim 110 \text{ kcal mol}^{-1}$) held by the RONO_2 upon photon absorption provokes the dissociation of the O–N bond and a subsequent diffusion of the resulting fragments as in aqueous solution. The main

340 difference lies in the fact that the diffusion separates the resulting fragments at large distance, without the possibility of proton transfer. This explains the observed direct formation of $\cdot\text{NO}_{2(g)}$ (Talukdar et al., 1997). In contrast, in the cavity, collisions with the solvent are frequent, and thus, the photolysis likely follows the pathway with the minimum energy barrier, that leads to the formation of HNO_2 and acetone.



345 **Figure 6: Representative reactive trajectories for the formation of acetone and HNO₂ with the main reaction steps depicted. Timescales are just indicative.**

These calculations agree with our observations where the photolysis of isopropyl nitrate provided the direct concomitant formation of HNO₂ and acetone as shown in Fig. 7. Furthermore, minor trajectories where the carbon backbone structure of isopropyl nitrate breaks leading to the formation of acetaldehyde and other species have been also experimentally observed

350 since acetaldehyde was determined to be a primary product with low yields (~4 %).

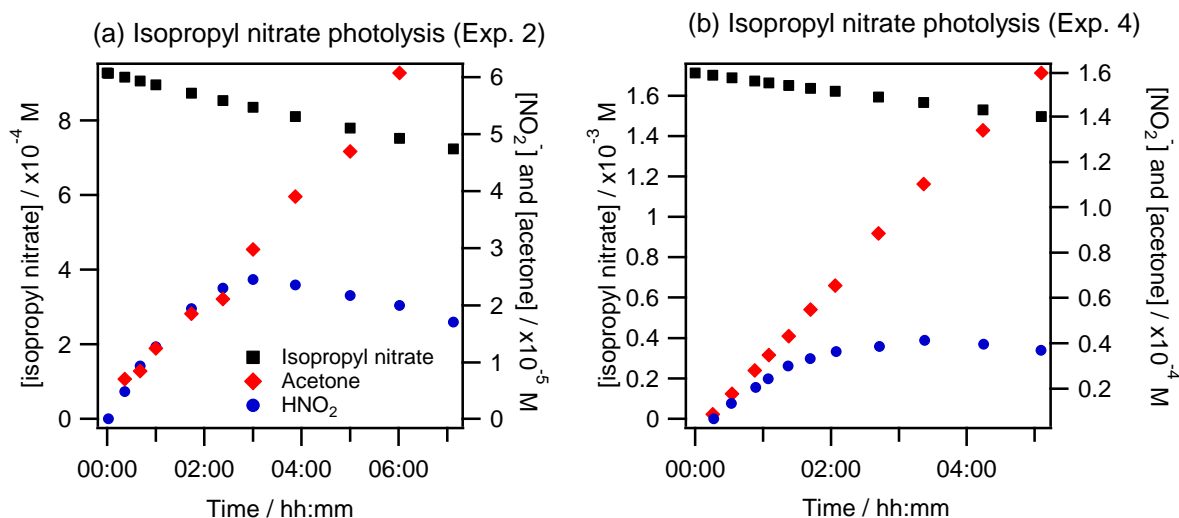


Figure 7: Concomitant acetone and HNO₂ formation during isopropyl nitrate photolysis at two different initial concentrations (a) 0.57 mM (Exp.2) and (b) 1.42 mM (Exp. 4).



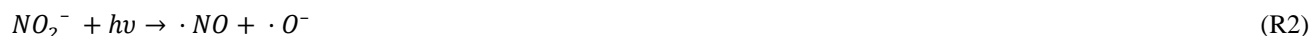
4.1.2 Secondary chemistry of HNO₂ in the aqueous phase

355 Once formed in the solution, HNO₂ was highly reactive as shown by its time profiles (in Fig. 7). It may disproportionate to yield ·NO and ·NO₂ (R1).

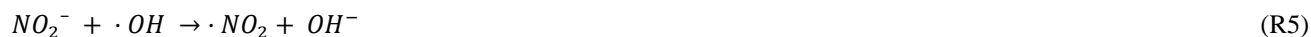


However, this reaction is quite slow under our experimental conditions (rate constant of 28.6 M⁻¹ s⁻¹, Vione et al., 2004).

360 Nevertheless, considering the lamp actinic flux, the photolysis/photooxidation of HNO₂ was likely its major sink. The photolysis of HNO₂ and NO₂⁻ is known to form ·NO and a ·OH radical (R2–4) (Mack and Bolton, 1999; Fischer and Warneck, 1996; Kim et al., 2014). HNO₂ can also decompose due to the additional energy of the RONO₂ photolysis.



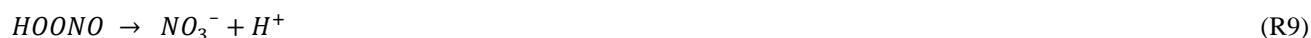
365 Additionally, ·OH radicals readily react with NO₂⁻ and with HNO₂ (rate constants of 1.0 ·10¹⁰ and 2.6 ·10⁹ M⁻¹ s⁻¹, respectively) (Mack and Bolton, 1999; Kim et al., 2014).



HNO₃ can then be formed through ·NO₂ hydrolysis (R7) (Finlayson-Pitts and Pitts Jr., 2000).



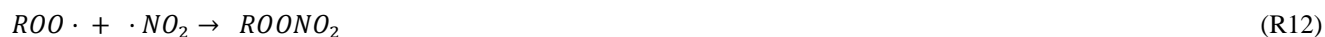
Another pathway can be initiated by the reaction of ·NO with HO₂· radicals to yield peroxyxynitrite (R8). The latter can isomerize into HNO₃/NO₃⁻ (R9) or decompose yielding ·NO₂ and ·OH radicals (R10).



HO₂· radicals were likely formed by the photooxidation of organic compounds. Since ·OH radicals were formed through HNO₂/NO₂⁻ photolysis they could attack the organic molecules present in the photoreactor (i.e., the RONO₂, as no scavenger was used). Upon oxygen addition, the ·OH attack yielded peroxy radicals. The formation of peroxy radicals was confirmed by the dissolved oxygen time profiles: during each photolysis experiment, dissolved [O₂] underwent slight decay due to the

380 reaction of alkyl radicals (R·) and oxygen (Fig. S7).

Peroxy radicals can readily react with ·NO to form peroxyxynitrites (ROONO) that can isomerize to RONO₂ (R11). Additionally, peroxy radicals react with ·NO₂ forming peroxyxynitrates (ROONO₂) (Goldstein et al., 2004).



385 The rate constants observed for reactions R11 and R12 range, respectively, from 2.8 ·10⁹ to 3.5 ·10⁹ M⁻¹ s⁻¹ (with R being (CH₃)₂CCH₂- and CH₃-), and from 0.7 to 1.5 ·10⁹ M⁻¹ s⁻¹ (with R = (CH₃)₂CCH₂-, CH₃-, and c-C₅H₉-). Therefore, these



reactions could readily occur under our experimental conditions, but not in the first step as they would be limited by the formation of $\cdot\text{OH}$ radicals to be initiated.

In our experiments, the formation of oxidized RONO_2 during isopropyl nitrate and isobutyl nitrate photolysis was confirmed by GC-MS, and UHPLC-UV analyses (Fig. 4 and Section S4). The possibility to form oxidized RONO_2 via the aforementioned reactions is consistent with the substantial number of compounds displaying the NO_2^+ fragment found by GC-MS analyses (up to 6 compounds for isopropyl nitrate photolysis and up to 8 for isobutyl nitrate). Nevertheless, ROONO_2 , if formed, were not detected due to their thermolysis during the analysis.

During isopropyl nitrate photolysis, the main formed oxidized RONO_2 (IP3 in Fig. 4) was suspected to be a dinitrate (1,2-propyldinitrate) since its mass spectra conjugate mass fragments that correspond to both primary ($m/z = 76, \text{CH}_2\text{ONO}_2^+$) and secondary nitrate groups ($m/z = 90, \text{CH}(\text{ONO}_2)\text{CH}_3^+$). The formation of this compound through secondary photochemistry of $\text{HNO}_2/\text{NO}_2^-$ agrees well with the observed secondary time profile of this product. An equivalent compound was observed during isobutyl nitrate photolysis (IB6 in Fig. S4.1).

4.2 Proposed chemical mechanisms

4.2.1 Isopropyl nitrate aqueous-phase photolysis proposed mechanism

Conjugating all the reactions mentioned in the discussion, Fig. 8 proposes a complete mechanism of isopropyl nitrate aqueous-phase photolysis.

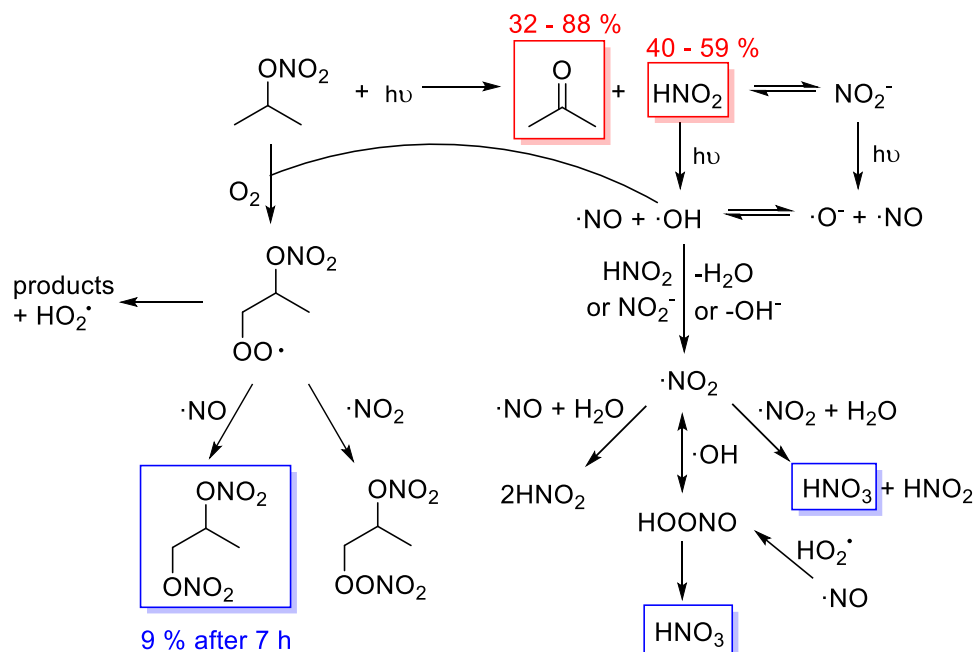


Figure 8: Proposed mechanism of isopropyl nitrate photolysis in the aqueous phase. In red are the measured primary products with their molar yields. In blue are the measured secondary products.



Isopropyl nitrate photolyzes into acetone and nitrous acid. Nitrous acid undergoes equilibrium in the aqueous phase with nitrite. Both HNO_2 and NO_2^- can undergo photolysis yielding $\cdot\text{NO}$ and $\cdot\text{OH}$ radicals (R5 to 7). $\cdot\text{OH}$ radicals can react with isopropyl nitrate yielding an alkyl radical that upon oxygen addition forms a peroxy radical. The peroxy radical can decompose into products (i.e., acetone, formic acid, acetic acid, hydroxy acetone, and acetaldehyde which also could be issued from acetone photooxidation), or react with $\cdot\text{NO}$ or $\cdot\text{NO}_2$, to form a dinitrate or a peroxyxynitrate. The dinitrate likely corresponds to the compound detected by GC-MS (IP3 in Fig. 4) and is formed secondarily in agreement with the proposed mechanism. Additionally, IP3 was estimated to account for 18 % of the reactive N at the end of the reaction, in agreement with the 20 % of isopropyl nitrate estimated to undergo $\cdot\text{OH}$ oxidation. Furthermore, HNO_3 is formed through secondary reactions such as $\cdot\text{NO}_2$ hydrolysis (R1) or peroxyxynitrite isomerization (R11).

4.2.2 Isobutyl nitrate and 1-nitrooxy-2-propanol aqueous-phase photolysis proposed mechanism

The primary formation of HNO_2 was also observed during the photolysis of isobutyl nitrate and 1-nitrooxy-2-propanol in the aqueous phase (Fig. 2). The determined yields were 31 % and 59–62 %, for isobutyl nitrate (Fig. 9a), and 1-nitrooxy-2-propanol (Fig. 9b), respectively. Although no DFT calculations were performed specifically for these molecules, they likely undergo a similar photolysis process to the one detailed for isopropyl nitrate, where an adjacent hydrogen atom is captured by the $-\text{NO}_2$ leaving moiety (as shown in Fig. 6).

Nevertheless, the formation of carbonyl products concomitant to HNO_2 was different from those expected from the main isopropyl nitrate mechanism. The corresponding carbonyl compounds were only observed in minor proportions: yields of 5 % isobutyraldehyde and 8–10 % lactaldehyde were obtained respectively for isobutyl nitrate and 1-nitrooxy-2-propanol. The major carbonyl products were formed after the breakdown of the organic chain, probably due to the excess energy the molecules have after light absorption. This pathway has been observed during the isopropyl nitrate calculations although as a minor pathway, leading to the formation of acetaldehyde. Figure S8 clearly shows that the carbonyl products formed concomitantly to HNO_2 were acetone and formaldehyde (yields of 20–32 % and 37–39 %, respectively) during isobutyl nitrate photolysis, and formaldehyde and acetaldehyde (yields of 63–71 % and 50–70%, respectively) during 1-nitrooxy-2-propanol photolysis.

The proposed pathways for their photolysis are given in Fig. 9. Further studies should be conducted to understand the breakdown of the organic chain.

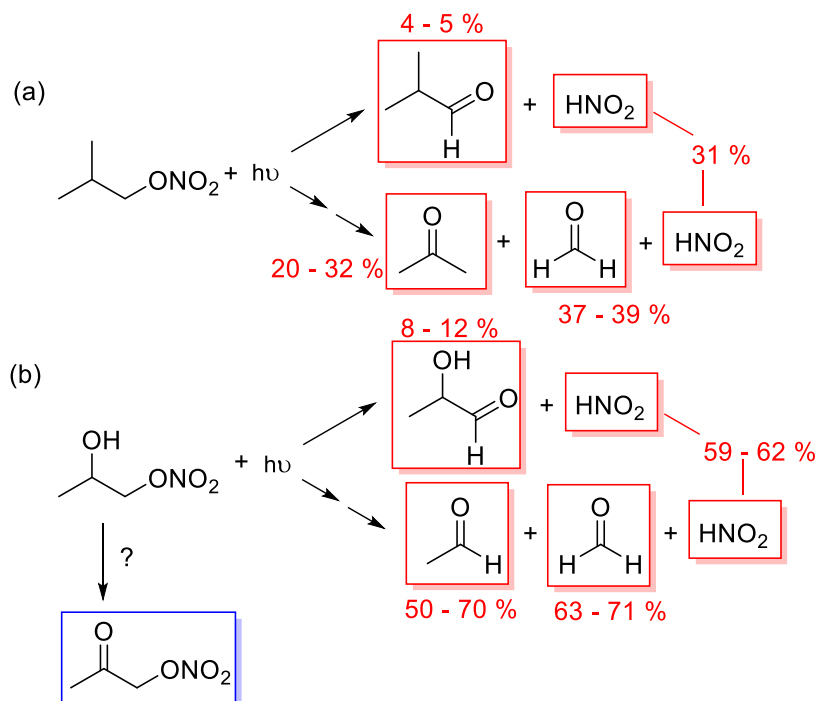
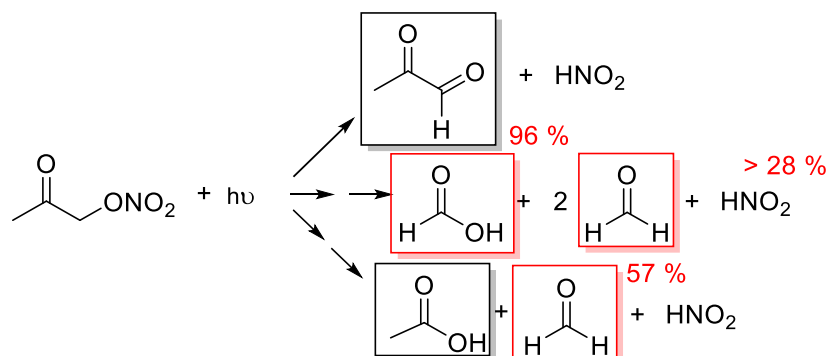


Figure 9: Proposed mechanisms of aqueous-phase photolysis of (a) isobutyl nitrate, and (b) 1-nitrooxy-2-propanol. In red are the measured primary products, and in blue, the detected secondary products.

435 During isobutyl nitrate photolysis, two oxidized RONO_2 were observed, these compounds were likely formed through the $\cdot\text{OH}$ oxidation of isobutyl nitrate initiated by $\text{HNO}_2/\text{NO}_2^-$ aqueous-phase photochemistry (as it occurs in isopropyl nitrate photolysis). During 1-nitrooxy-2-propanol photolysis, the secondary formation of α -nitrooxyacetone was observed (Fig. 9b).

4.2.3 α -Nitrooxyacetone aqueous-phase photolysis proposed mechanism

440 During α -nitrooxyacetone photolysis, NO_2^- could not be measured due to its base-catalyzed hydrolysis in the HPIC system (at $\text{pH} = 12$, Brun et al., 2023), but NO_3^- was quantified and showed a secondary formation. Primary formation of HNO_2 was thus expected with a minimum yield of 28 %. Due to the formation of various carbonyl compounds, the photolysis mechanism was likely following various pathways (Fig. 10).



445 **Figure 10: Proposed mechanisms for α -nitrooxyacetone aqueous-phase photolysis. In red are the measured primary products, and in black, other identified products.**

4 Conclusions and atmospheric implications

This work has investigated the fate of the nitrate group during the aqueous-phase photolysis of four RONO₂ species: isopropyl nitrate, isobutyl nitrate, 1-nitrooxy-2-propanol, and α -nitrooxyacetone. Our findings suggest a completely different reactivity from the gas phase one. While RONO₂ releases NO_x back to the atmosphere upon photolysis in the gas phase, HNO₂ is directly formed in the aqueous phase.

HNO₂ was detected as a primary compound along with other primary products such as carbonyl compounds or organic acids. The direct formation of HNO₂ by aqueous-phase photolysis was confirmed by DFT theoretical calculations and was supported by the absence of direct \cdot NO₂ formation.

Therefore, aqueous-phase photolysis of RONO₂ represents both a sink of NO_x and a source of atmospheric HNO₂ (or HONO). The latter is an important precursor of \cdot OH and \cdot NO radicals. During our experiments, these secondarily formed radicals were shown to be trapped in the aqueous phase, producing HNO₃ and functionalized RONO₂. In the atmosphere, this reactivity can potentially contribute to the sink of NO_x, a source of \cdot OH radicals in condensed phases, and an additional source of SOA_{aq}. Aqueous-phase photolysis has been reported to be negligible in the RONO₂ sinks in the atmosphere due to the hindering effect of the “solvent cage” (González-Sánchez et al., 2023). Nevertheless, the mechanisms of this reactivity might be relevant for more significant reactions such as the aqueous-phase \cdot OH oxidation of RONO₂, or potentially their heterogeneous photolysis. Therefore, further work should be done to better assess the role of RONO₂ in NO_x sink and transport, in the formation of atmospheric HONO and SOA.

Data and code availability. Data related to this article are available at <https://doi.org/10.7910/DVN/USWU6V> (González-Sánchez, 2023). Data related to the theoretical calculations can be requested from Miquel Huix-Rotllant (miquel.huixrotllant@univ-amu.fr).



Author contributions. JMGS performed all experiments and treated all experimental data. MHR developed the quantum chemistry model and conducted the calculations. JMGS, NB, and CD developed the HPIC-CD method. JM build the NO_x analyzer experimental setup. JMGS and SR developed the UHPLC-UV method. JMGS and AD developed the GC-MS method. JMGS and JLC performed the organic synthesis of RONO₂. AM and JLC coordinated the work. JMGS, MHR and AM wrote the article with inputs from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

Financial support. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie (grant no. 713750). It has been carried out with the financial support of the Regional Council of Provence-Alpes-Côte d'Azur and with the financial support of the A*MIDEX (grant no. ANR- 11-IDEX-0001-02), funded by the Investissements d'Avenir project funded by the French Government, managed by the French National Research Agency (ANR). This study also received funding from the French CNRS-LEFE-CHAT (Programme National-Les Enveloppes Fluides et l'Environnement-Chimie Atmosphérique – Project “MULTINITRATES”) and from the program ANR-PRCI (ANR-18-CE92-0038-02) – Project “ARAMOUNT”.

References

- Atkinson, R., Aschmann, S. M., and Winer, A. M.: Alkyl nitrate formation from the reaction of a series of branched RO₂ radicals with NO as a function of temperature and pressure, *J Atmos Chem*, 5, 91–102, <https://doi.org/10.1007/BF00192505>, 1987.
- Biswal, J., Paul, J., Naik, D. B., Sarkar, S. K., and Sabharwal, S.: Radiolytic degradation of 4-nitrophenol in aqueous solutions: Pulse and steady state radiolysis study, *Radiation Physics and Chemistry*, 85, 161–166, <https://doi.org/10.1016/j.radphyschem.2013.01.003>, 2013.
- Brun, N., González-Sánchez, J. M., Demelas, C., Clément, J.-L., and Monod, A.: A fast and efficient method for the analysis of α -dicarbonyl compounds in aqueous solutions: Development and application, *Chemosphere*, 137977, <https://doi.org/10.1016/J.CHEMOSPHERE.2023.137977>, 2023.
- Carbajo, P. G. and Orr-Ewing, A. J.: NO₂ quantum yields from ultraviolet photodissociation of methyl and isopropyl nitrate, *Physical Chemistry Chemical Physics*, 12, 6084–6091, <https://doi.org/10.1039/c001425g>, 2010.
- Clemittshaw, K. C., Williams, J., Rattigan, O. v., Shallcross, D. E., Law, K. S., and Anthony Cox, R.: Gas-phase ultraviolet absorption cross-sections and atmospheric lifetimes of several C₂-C₅ alkyl nitrates, *J Photochem Photobiol A Chem*, 102, 117–126, [https://doi.org/10.1016/S1010-6030\(96\)04458-9](https://doi.org/10.1016/S1010-6030(96)04458-9), 1997.
- Finlayson-Pitts, B. J. and Pitts Jr., J. N.: *Chemistry of the Upper and Lower Atmosphere*, Academic P., Elsevier, <https://doi.org/10.1016/b978-0-12-257060-5.x5000-x>, 2000.



- 500 Fischer, M. and Warneck, P.: Photodecomposition of nitrite and undissociated nitrous acid in aqueous solution, *Journal of Physical Chemistry*, 100, 18749–18756, <https://doi.org/10.1021/jp961692+>, 1996.
- Goldstein, S., Lind, J., and Merenyi, G.: Reaction of Organic Peroxyl Radicals with NO₂ and NO in Aqueous Solution: Intermediacy of Organic Peroxynitrate and Peroxynitrite Species, *Journal of Physical Chemistry A*, 108, 1719–1725, <https://doi.org/10.1021/jp037431z>, 2004.
- 505 González-Sánchez, J. M., Brun, N., Wu, J., Ravier, S., Clément, J.-L., and Monod, A.: On the importance of multiphase photolysis of organic nitrates on their global atmospheric removal, *EGUsphere*, 2023, 1–28, <https://doi.org/10.5194/egusphere-2023-37>, 2023.
- Hu, K. S., Darer, A. I., and Elrod, M. J.: Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates, *Atmos Chem Phys*, 11, 8307–8320, <https://doi.org/10.5194/acp-11-8307-2011>, 2011.
- 510 Kim, D. H., Lee, J., Ryu, J., Kim, K., and Choi, W.: Arsenite oxidation initiated by the uv photolysis of nitrite and nitrate, *Environ Sci Technol*, 48, 4030–4037, <https://doi.org/10.1021/es500001q>, 2014.
- Kroflič, A., Grilc, M., and Grgić, I.: Unraveling Pathways of Guaiacol Nitration in Atmospheric Waters: Nitrite, A Source of Reactive Nitronium Ion in the Atmosphere, *Environ Sci Technol*, 49, 9150–9158, <https://doi.org/10.1021/acs.est.5b01811>, 2015.
- 515 Mack, J. and Bolton, J. R.: Photochemistry of nitrite and nitrate in aqueous solution: a review, *J Photochem Photobiol A Chem*, 128, 1–13, [https://doi.org/10.1016/S1010-6030\(99\)00155-0](https://doi.org/10.1016/S1010-6030(99)00155-0), 1999.
- Madronich, S. and Flocke, S.: *The Role of Solar Radiation in Atmospheric Chemistry*, Springer, Berlin, Heidelberg, 1–26, https://doi.org/10.1007/978-3-540-69044-3_1, 1999.
- Merényi, G., Lind, J., and Goldstein, S.: The rate of homolysis of adducts of peroxynitrite to the C=O double bond, *J Am Chem Soc*, 124, 40–48, <https://doi.org/10.1021/ja011799x>, 2002.
- 520 Nguyen, T. B., Crounse, J. D., Teng, A. P., Clair, J. M. S., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, *Proc Natl Acad Sci U S A*, 112, E392–E401, <https://doi.org/10.1073/pnas.1418702112>, 2015.
- Pang, H., Zhang, Q., Lu, X., Li, K., Chen, H., Chen, J., Yang, X., Ma, Y., Ma, J., and Huang, C.: Nitrite-Mediated
- 525 Photooxidation of Vanillin in the Atmospheric Aqueous Phase, *Environ Sci Technol*, 53, 14253–14263, <https://doi.org/10.1021/acs.est.9b03649>, 2019.
- Perring, A. E., Pusede, S. E., and Cohen, R. C.: An observational perspective on the atmospheric impacts of alkyl and multifunctional nitrates on ozone and secondary organic aerosol, *Chem Rev*, 113, 5848–5870, <https://doi.org/10.1021/cr300520x>, 2013.
- 530 Poulain, L., Katrib, Y., Isikli, E., Liu, Y., Wortham, H., Mirabel, P., Le Calvé, S., and Monod, A.: In-cloud multiphase behaviour of acetone in the troposphere: Gas uptake, Henry’s law equilibrium and aqueous phase photooxidation, <https://doi.org/10.1016/j.chemosphere.2010.07.032>, 2010.



- Roberts, J. M. and Fajer, R. W.: UV Absorption Cross Sections of Organic Nitrates of Potential Atmospheric Importance and Estimation of Atmospheric Lifetimes, *Environ Sci Technol*, 23, 945–951, <https://doi.org/10.1021/es00066a003>, 1989.
- 535 Romer Present, P. S., Zare, A., and Cohen, R. C.: The changing role of organic nitrates in the removal and transport of NO_x, *Atmos Chem Phys*, 20, 267–279, <https://doi.org/10.5194/acp-20-267-2020>, 2020.
- Sander, R.: Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Database, 20, 107, <https://doi.org/10.1017/CBO9781107415324.004>, 1999.
- Sander, R.: Compilation of Henry's law constants (version 4.0) for water as solvent, *Atmos Chem Phys*, 15, 4399–4981, 540 <https://doi.org/10.5194/acp-15-4399-2015>, 2015.
- Shepson, P. B.: Organic nitrates, Blackwell Publishing Ltd, Oxford, UK, 58–63 pp., <https://doi.org/10.1358/dnp.1999.12.1.863615>, 1999.
- Talukdar, R. K., Burkholder, J. B., Hunter, M., Gilles, M. K., Roberts, J. M., and Ravishankara, A. R.: Atmospheric fate of several alkyl nitrates: Part 2. UV absorption cross-sections and photodissociation quantum yields, *Journal of the Chemical Society - Faraday Transactions*, 93, 2797–2805, <https://doi.org/10.1039/a701781b>, 1997.
- 545 Vione, D., Maurino, V., Minero, C., Vincenti, M., and Pelizzetti, E.: Aromatic photonitration in homogeneous and heterogeneous aqueous systems, *Environmental Science and Pollution Research*, 10, 321–324, <https://doi.org/10.1065/espr2001.12.104.1>, 2003.
- Vione, D., Belmondo, S., and Carnino, L.: A kinetic study of phenol nitration and nitrosation with nitrous acid in the dark, 550 *Environ Chem Lett*, 2, 135–139, <https://doi.org/10.1007/s10311-004-0088-1>, 2004.
- Vione, D., Maurino, V., Minero, C., and Pelizzetti, E.: Nitration and photonitration of naphthalene in aqueous systems, *Environ Sci Technol*, 39, 1101–1110, <https://doi.org/10.1021/es048855p>, 2005.