Photochemical reactions of methyl and ethyl nitrate: a dual role for alkyl nitrates in the nitrogen cycle

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Abstract. Alkyl nitrates (ANs) are important nitrogen-containing organic compounds and are usually considered to be temporary reservoirs of reactive nitrogen NO\(_x\) (NO\(_2\) and NO) in the atmosphere, although their atmospheric fates are incompletely understood. Here a laboratory study of the gas-phase photolysis and OH-initiated reactions of methyl nitrate (CH\(_3\)ONO\(_2\)) and ethyl nitrate (C\(_2\)H\(_5\)ONO\(_2\)), as models of atmospheric ANs, is reported with a focus on elucidating the detailed photochemical reaction mechanisms of ANs in the atmosphere. A series of intermediate and end products were well characterised for the first time from the photochemical reactions of methyl and ethyl nitrate conducted under simulated atmospheric conditions. Notably, for both the photolysis and OH-initiated reactions of CH\(_3\)ONO\(_2\) and C\(_2\)H\(_5\)ONO\(_2\), unexpectedly high yields of HNO\(_3\) (photochemically non-reactive nitrogen) were found and also unexpectedly high yields of peroxyacetyl nitrates (RC(O)OONO\(_2\), where R = H, CH\(_3\), CH\(_3\)CH\(_2\), ...) (reactive nitrogen) have been found as CH\(_3\)C(O)OONO\(_2\) in the C\(_2\)H\(_5\)ONO\(_2\) reaction or proposed as HC(O)OONO\(_2\) in the CH\(_3\)ONO\(_2\) reaction. Although the yields of HNO\(_3\) from the ANs under ambient conditions are likely variable and different from those obtained in the laboratory experiments reported here, the results imply that the ANs could potentially serve as a sink for reactive nitrogen in the atmosphere. The potential for this dual role of organic nitrates in the nitrogen cycle should be considered in the study of air quality and nitrogen exchange between the atmosphere and surface. Finally, an attempt was made to estimate the production of HNO\(_3\) and peroxyacetyl nitrates derived from NO\(_3\) by ANs as intermediates in the atmosphere.

Additional keywords: nitric acid, OH-initiated reaction, peroxyacetyl nitrate, photolysis.

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Introduction

Oxides of nitrogen (NO\(_x\)) (i.e. NO\(_2\) and NO) are usually considered as reactive nitrogen species and play an important role in atmospheric chemistry. The photolysis of NO\(_2\) can initiate a series of reactions and is the sole known anthropogenic source of ozone in the troposphere.\(^1\) NO\(_2\) can transform into a variety of inorganic and organic nitrogen-containing substances in the troposphere, including peroxyacetic acid (HOONO\(_2\)), dinitrogen pentoxide (N\(_2\)O\(_5\)), chlorine nitrate (ClONO\(_2\)), nitric acid (HNO\(_3\)), nitrous acid (HNO\(_2\)), aerosol nitrate (NO\(_3\)), peroxyacetyl nitrates (RC(O)OONO\(_2\), where R = H, CH\(_3\), CH\(_3\)CH\(_2\), ...) and alkyl nitrates (RONO\(_2\), ANs). These chemicals together with NO\(_x\) are collectively termed as ‘odd nitrogen’, namely, NO\(_x\). However, the observed levels of NO\(_x\) were greater than the sum of the individually measured species (\(\Sigma\)NO\(_x\) = NO\(_2\), NO\(_2\), HNO\(_3\), NO\(_3\) (aerosol) and peroxyacetyl nitrate (PAN, CH\(_3\)C(O)OONO\(_2\))), implying missing NO\(_x\) components in the field NO\(_x\) measurement.\(^2\) Recently, ANs have come under increased scrutiny because the large abundances of ANs might represent the ‘missing NO\(_x\)’ in the atmosphere.\(^3\)

The mixing ratios of ANs lie in the range of tens to hundreds of parts per trillion by volume (pptv) in the air of polluted and remote regions. It should be noted that the ANs defined in the present study include monofunctional and multifunctional AN compounds. In polluted air masses, for example, in La Porte, Texas, the daytime mixing ratio of total straight chain alkyl nitrates (\(\Sigma\)C\(_1\)–C\(_5\)) was found to range from 30 to 80 pptv\(^3\); a long-term observation in coastal New England indicated that the median mixing ratio of \(\Sigma\)C\(_1\)–C\(_5\) was 23–25 pptv in winter and 14–16 pptv in summer\(^4\); the maximum mixing ratio of \(\Sigma\)C\(_1\)–C\(_5\) was detected as 204 pptv in the Pearl River Delta, an industrial area of South China.\(^5\) In remote continental air masses, mixing ratios of the C\(_1\)–C\(_10\) ANs were observed as 10 to 200 pptv.\(^6\)–\(^13\) The measurements at a rural site in California over a full annual cycle showed that total ANs (\(\Sigma\)ANs) were routinely 10–20 % of NO\(_3\).\(^1\) Increasing evidence
suggests that the biogenic volatile organic compounds, especially isoprene and terpenes, can significantly contribute to AN production, including simple and complex ANs with higher molecular weight and multifunctional structure. The measured concentration of isoprene nitrates reached \( \sim 90 \text{ pptv} \) in a forest site at Pellston, Michigan, and as high as \( 150 \text{ pptv} \) in rural Tennessee. ANs were also detected in the lower stratosphere by the NASA ER-2 aircraft, covering a latitude range of \( 60^\circ \text{N} \) to \( 2^\circ \text{S} \), \( 115^\circ \text{W} \) to \( 155^\circ \text{W} \) and altitudes to 20.5 km. Methyl and ethyl nitrate account for \( \sim 20\% - 40\% \) of the total light ANs. Methyl and ethyl nitrate have been detected in Antarctica and their sum mixing ratio accounted for more than \( 50\% \) of the \( 70 \text{ ppt} \) of NO\(_2 \) over Antarctica during the summer.

To date, the determinations of the concentrations of atmospheric ANs are subject to uncertainties because of limitations of handling and measurement techniques. Nonetheless, the collective pool of measurements to date point to the fact that ANs may be a significant component of NO\(_2 \) in the atmosphere. Tropospheric ANs appear to be mainly produced from the oxidation of parent hydrocarbons, as follows:

\[
\begin{align*}
\text{RH} + \text{OH} &\rightarrow \text{R} + \text{H}_2\text{O} \\
\text{R} + \text{O}_2 &\rightarrow \text{RO}_2 \\
\text{RO}_2 + \text{NO} &\rightarrow \text{RO} + \text{NO}_2 \\
&\rightarrow \text{RONO}_2
\end{align*}
\]

The branching ratio of the RONO\(_2 \) formation pathway can range from one percent to tens of percent, depending on the R group. This pathway is important because it is the major route for the formation of ANs and terminates the cycle between NO and NO\(_2 \). A possible alternative pathway for RONO\(_2 \) formation under polluted conditions has been suggested by.

\[
\text{RO} + \text{NO}_2 + \text{M} \rightarrow \text{RONO}_2 + \text{M}
\]

where M represents the molecular N\(_2 \) or O\(_2 \) in air.

In a previous investigation, we established that the reaction of methyl hydroperoxide (CH\(_3\)OOH) and ethyl hydroperoxide (CH\(_3\text{CH}_2\text{OOH}) with NO\(_2 \) can respectively produce methyl nitrate and ethyl nitrate, although the rate coefficients are merely \( 10^{-20} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \) at 293 K. The heterogeneous reaction of HCHO and HNO\(_3 \) on concentrated sulfuric acid aerosols has also been suggested to be a pathway for methyl nitrate formation. In addition to chemical formation, the oceanic source of ANs, particularly for methyl and ethyl nitrate, has been known for over a decade. In this case, ANs may come from the photodissociation of C\(_2\text{H}_5\text{ONO}_2 \). However, most previous photolysis investigations were carried out in a He or N\(_2 \) bath gas, neglecting the presence and importance of O\(_2 \) in the real atmosphere. The reaction of ANs with OH radicals initiates a series of successive reactions in which ANs release products into the atmosphere:

\[
\text{RONO}_2 + \text{OH} \rightarrow \text{products}
\]

The rate coefficients of methyl and ethyl nitrate reactions with OH radicals have been determined in several studies. Two pathways for the reaction of ANs with OH have been proposed, namely, hydrogen-atom abstraction and OH addition. However, the specific products formed in the reaction of ANs with OH radicals are still unclear.

ANs are usually considered to be the temporary reservoir of reactive nitrogen species and they can regenerate NO\(_x \) through photolysis and oxidation. Because compared to NO\(_2 \), they have relatively long atmospheric lifetimes, ranging from several days to weeks. ANs may be transported large distances to remote regions of the atmosphere, potentially providing a source of NO\(_x \) to these areas and influencing O\(_3 \) chemistry. Therefore, ANs play a significant role in the NO\(_x \)-O\(_3\)-HO\(_x \) cycle in both polluted and remote atmospheres. However, to date, the current knowledge of the specific products and mechanisms for the transformation of ANs in the atmosphere has depended upon the speculations derived from the theory and limited experiments performed in the absence of O\(_2 \), which thus do not simulate real atmospheric conditions. The relationship between ANs and NO\(_x \) has been simplified in the current atmospheric models, possibly leading to large discrepancies in the simulation of the reactive nitrogen cycle. Detailed laboratory studies of the products and mechanisms in AN reactions under a simulated real atmosphere containing O\(_2 \) are urgently needed to better understand their roles in air quality and nitrogen exchange between the Earth's atmosphere and surface.

In the present study, we have selected methyl and ethyl nitrate as models of atmospheric ANs and have investigated their photochemical reactions under simulated atmospheric conditions. Our study is focussed on the specific products and mechanisms in the photolytic and OH-initiated reactions of ANs. Our experimental results have revealed a dual role for ANs in the reactive nitrogen cycle, thus providing useful information for atmospheric chemical models.
Experimental methods

Chemicals

Fuming nitric acid (95%, Beijing Lishui Chemical Reagent Factory, Beijing, China), methanol (≥99.5%, Fisher Chemical, Fair Lawn, NJ, USA), ethanol (≥99.9%, Beijing Chemical Reagent Factory) N2 (≥99.999%, Beijing Pray Applied Gas Company Limited, Beijing, China) and O2 (≥99.999%, Beijing Analytical Instrument Factory, Beijing, China) were used in this study. As methyl nitrate and ethyl nitrate are not commercially available, they were synthesised in our laboratory by the esterification of the corresponding alcohol and nitric acid with dehydration by sulfuric acid, and in the presence of a grain of urea, according to the procedures described by Desseigne et al.[48] The purities of the methyl and ethyl nitrate obtained were confirmed to be ≥95% by checking for possible impurities such as NO3, CH3ONO and C2H5ONO etc. using Fourier-transform infrared (FTIR) spectroscopy.

Instrumentation and methods

Laboratory simulations were carried out in a 28.5-L cylindrical quartz reaction chamber (Q-6-54X2-BA-AU model, Infrared Analysis Inc., Anaheim, CA, USA). This chamber was equipped with a digital thermometer, a piezometer to measure the gas pressure, a vacuum system and a White-mirror system. The equipment has been described in detail in our previous work.[49] A FTIR spectrometer (Nexus model, Thermo Nicolet, USA) was used to characterise the reactants and some of the products. There were five UV lamps (λmax = 254 nm, 40 W, low-pressure mercury lamp, Beijing Haidian Konghou Complex Factory, Beijing, China) and a stainless steel enclosure around the reactor. The FTIR facility was mounted with a KB beam splitter and a liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector. FTIR spectra were recorded by co-adding 64 scans at 1 cm⁻¹ spectroscopic resolution over the frequency region of 500–4000 cm⁻¹. The reaction temperature was controlled at 298 ± 2 K and the total pressure of the gas mixture was controlled at ~1.01 × 105 ± 1333 Pa (760 ± 10 Torr).

For the offline analysis of products by high performance liquid chromatography (HPLC) and ion chromatography (IC), gas (1.2 L) was drawn from the reactor by a pump and was collected with a Horibe tube in a cold trap of ethanol–liquid nitrogen to reach a total pressure of 1.01 × 105 Pa, resulting in the initial gaseous concentrations of 60–210 ppmv for methyl nitrate and 50–160 ppmv for ethyl nitrate. These values, which were approximately six orders of magnitude higher than those in the atmosphere, were used to better characterise the possible products formed. After the gases were homogenously mixed, the UV lamps were turned on and in-situ FTIR spectra were recorded to investigate the concentration changes of the reactants and products. The FTIR spectrometer collected a spectrum every 5 min during the reaction, allowing us to record reactant and product concentrations. The gaseous samples were drawn out of the reaction chamber and collected by a Horibe tube during the reaction, followed by HPLC and IC analysis. Two samplings were usually done at the reaction times of 40 and 80 min during each experiment and a 1.2-L sample of gas was drawn out for each sample. After each sampling process, N2 was quickly added into the reactor to keep the total pressure at ~1.01 × 105 Pa, resulting in a slight dilution of the reactants and products. In order to obtain a uniform plot of the temporal evolution of reactants and products, the gas concentrations used in the plot, after each sampling process, were corrected by multiplying the corresponding concentrations measured in the reactor by the dilution ratio of 28.5/(28.5–1.2).

OH-initiated oxidation

For this experiment, OH radicals were generated by UV photolysis of O3 in the presence of water vapour:

\[ \text{O}_3 \xrightarrow{h \nu} \text{O}(^1\text{D}) + \text{O}_2 \]  \hspace{1cm} (8)
\[ \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]  \hspace{1cm} (9)

The reactor was cleaned with N2 and evacuated four to five times before the experiment. Methyl nitrate (or ethyl nitrate) and water were introduced into the evacuated reactor in turn. After both had been evaporated completely, ozone in O2 gas, which was generated in a 5-L quartz cell beforehand, was added into the reactor, followed by addition of high-purity nitrogen to reach a total pressure of ~1.01 × 105 Pa of synthetic

analysed using an IC instrument with an ED50 conductivity detector (ICS-2500 model, Dionex Corporation, Sunnyvale, CA, USA). The details of the sample processing and analysis are described in our previous work.[50–52] Blanks were sampled and analysed using the same method before the reaction.
air (O₂ : N₂ = 1 : 4). The initial concentrations of methyl nitrate and ethyl nitrate were the same as in the photolysis experiment described above. The initial concentration of O₃ in the reactor was ~45 ppmv. The initial relative humidity in the reaction chamber was ~30%. After the gases were homogenously mixed, the UV lamps were turned on, immediately generating OH radicals. The methods for determining the reactants and products were the same as in the photolysis experiment described above.

### Results and discussion

#### Characterisation of products

##### Photolysis of CH₃ONO₂ and C₂H₅ONO₂

In the standard FTIR spectrum of CH₃ONO₂ (Fig. 1a), the absorbance peaks can be assigned as follows: 3014 cm⁻¹, stretching vibration of methyl (group); 2965 cm⁻¹, asymmetric stretching of methyl; 1469 cm⁻¹, the bending of methyl; 1178 and 1139 cm⁻¹, out of plane bend of methyl; 1675 cm⁻¹, asymmetric stretching of NO₂; 1291 cm⁻¹, symmetric stretching of NO₂; 1018 cm⁻¹, stretching of C–O; 855 cm⁻¹, stretching of N–O; 760 and 658 cm⁻¹, out of plane bend of NO₂.

C₂H₅ONO₂ has a similar structure, and thus, most of its characteristic IR absorption bands are similar to those of CH₃ONO₂ (Fig. 1b): 3004 cm⁻¹, stretching of methyl; 2996 cm⁻¹, asymmetric stretching of methyl; 2939 cm⁻¹, asymmetric stretching of methylene; 1652 cm⁻¹, nitro asymmetric stretching; 1287 cm⁻¹, nitro symmetric stretching; 1029 cm⁻¹, stretching of C–O; 852 cm⁻¹, stretching of NO₂; 760 and 668 cm⁻¹, out of plane bend of NO₂. C₂H₅ONO₂ has one more absorption band at 912 cm⁻¹, which has not been assigned in this work.

Fig. 2 shows the temporal evolution of FTIR spectra during the photolysis of (a) CH₃ONO₂ and (b) C₂H₅ONO₂ in air (O₂ : N₂ = 1 : 4). Because the mixture of gases before photolysis was selected as the spectroscopic background, the negative absorbance represents the reactant consumption and the positive absorbance represents the product formation. As the aerobic reaction proceeded, the concentration of CH₃ONO₂ or C₂H₅ONO₂ decreased and the products, which are indicated by the new peaks in the spectra, formed. On the basis of the subtraction analysis of the spectra, HNO₃, H₂O₂NO₂, CO, HCHO and H₂O(H)OH were identified as the products in the photolysis of both CH₃ONO₂ and C₂H₅ONO₂, with major absorption bands appearing at: 1711, 1326 and 879 cm⁻¹ for HNO₃; 1735, 1397, 1304 and 803 cm⁻¹ for H₂O₂NO₂; 2229–2050 cm⁻¹ for CO; 2926–2685 cm⁻¹ for HCHO; and 1776 and 1105 cm⁻¹ for H₂O(H)OH. Moreover, PAN was identified as a photolytic product of C₂H₅ONO₂, with major bands at 1843, 1740, 1303 and 1164 cm⁻¹. It is worth noting that the expected nitrogen-containing substances, including NO₂, N₂O₅, NO, HONO, CH₃ONO and C₂H₅ONO, were not detected when each of their standard spectra was used to make comparisons. However, HO₂NO₂, PAN and a non-reactive nitrogen-containing substance, namely HNO₃, were found in these reactions conducted in air.

In the samples photolysed in air, we also identified peroxides, carbonyl compounds and acid ions using offline HPLC and IC as described in the experimental methods section. In addition to HCHO, H₂O(H)OH and HNO₃ that were observed by in-situ FTIR spectroscopy as described above, hydrogen peroxide (H₂O₂) was detected as a product for the photolysis of both CH₃ONO₂ and C₂H₅ONO₂. In C₂H₅ONO₂ aerobic photolysis, four more products, CH₃CHO, CH₃C(O)OH, methyl hydroperoxide (MHP, CH₃OOH) and peroxyacetic acid (PAA, CH₃C(O)OOH), were detected.

We also investigated the UV photolysis of CH₃ONO₂ or C₂H₅ONO₂ in pure N₂ and found that the formed products included HCHO/CH₃CHO, CO, HONO and NO, but excluded PAN, HNO₃ and H₂O₂NO₂ products that were detected when the photolysis experiments were conducted in air. This result indicated that the presence of O₂ will lead to a series of different nitrogen-containing products. Because the photolysis of CH₃ONO₂ and C₂H₅ONO₂ in the pure N₂ does not reflect the real atmosphere, we will not include any further discussion of this experiment.

##### OH-initiated oxidation of CH₃ONO₂ and C₂H₅ONO₂

Fig. 3 shows the time series spectra of the OH-initiated oxidation of (a) CH₃ONO₂ and (b) C₂H₅ONO₂ in air. The spectra of the mixture of gases obtained before the reaction was used as the spectroscopic background, resulting in negative absorbance for the reactant consumed and positive absorbance for the product formed. Based on the analysis of spectroscopic subtractions, HNO₃, HO₂NO₂, CO, HCHO and H₂O(H)OH were detected as the main products for both CH₃ONO₂ and
C$_2$H$_5$ONO$_2$ reactions, and one more product, PAN, was also present for the C$_2$H$_5$ONO$_2$ reaction. As in the photolysis system in the presence of O$_2$, NO$_2$, NO, HONO, CH$_3$ONO and C$_2$H$_5$ONO were also not detected in the OH-initiated oxidation of both methyl and ethyl nitrate.

Offline HPLC and IC were employed to further identify the products formed. In addition to verification of the formation of HC(O)OH, HCHO and HNO$_3$, which were detected by in-situ FTIR spectroscopy, this offline analysis revealed that H$_2$O$_2$ was produced in the CH$_3$ONO$_2$ reaction, and H$_2$O$_2$, CH$_3$CHO, CH$_3$OOH, CH$_3$C(O)OOH and CH$_3$C(O)OH were produced in the C$_2$H$_5$ONO$_2$ reaction.

Quantification of products

Photolysis of CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$

We examined the temporal evolution of reactants and products in the UV photolysis of (a) ~200-ppmv CH$_3$ONO$_2$ and (b) ~150-ppmv C$_2$H$_5$ONO$_2$ conducted in dry air (Fig. 4). The alkyl nitrate concentration decreased by 42% at 40 min and 56% at 80 min for CH$_3$ONO$_2$ and by 53% at 40 min and 68% at 80 min for C$_2$H$_5$ONO$_2$. For both CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$ photolysis, the kinetic characterisations for several carbon-containing products were as follows: (i) the concentration of HCHO increased in the early part of the reaction and then decreased after ~40 min; (ii) the concentration of HC(O)OH increased gradually and then levelled to a constant value; and (iii) the concentration of CO increased steadily throughout the course of the study. For the nitrogen-containing products, the reaction intermediates were observed as follows: (i) the concentration of HO$_2$NO$_2$ remained at a low level, ~1–3 ppmv for CH$_3$ONO$_2$ photolysis and even lower for C$_2$H$_5$ONO$_2$ photolysis; (ii) HNO$_3$ increased gradually, approaching 82 and 62 ppmv for CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$ at 90 min; and (iii) the concentration of PAN in C$_2$H$_5$ONO$_2$ photolysis reached a maximum at ~50 min, and levelled off at a constant value 38 ppmv.

The combined data obtained by FTIR, IC and HPLC analyses were used to estimate the yields of the products. In this study, a yield is defined as the ratio of the molar amount of a product formed versus the molar amount of the reactant consumed. The time series for observed yields of HNO$_3$, HO$_2$NO$_2$ and PAN are displayed in Fig. 5. The yield of HNO$_3$ was nearly constant throughout the reaction process, with ~76% for CH$_3$ONO$_2$ photolysis and ~57% for C$_2$H$_5$ONO$_2$ photolysis. In order to estimate the wall effect of HNO$_3$, we investigated the loss rate of gaseous HNO$_3$ with ~100 ppmv in the reactor, under the same...
Fig. 3. FTIR spectra of OH-initiated reactions of (a) CH$_3$ONO$_2$ and (b) C$_2$H$_5$ONO$_2$ in humid air (O$_2$:N$_2$ = 1:4, relative humidity 30%). PAN, peroxyacetyl nitrate.

Fig. 4. Plots of the temporal evolution of reactants and products in the photolysis of (a) CH$_3$ONO$_2$ and (b) C$_2$H$_5$ONO$_2$ in dry air (O$_2$:N$_2$ = 1:4). PAN, peroxyacetyl nitrate.
reaction conditions as the photolysis reaction of CH$_3$ONO$_2$ or C$_2$H$_5$ONO$_2$. The result showed a loss of <5% of HNO$_3$ over 90 min, indicating that HNO$_3$ adsorption onto the wall was minor under dry air conditions. Thus, the yield of HNO$_3$ observed by FTIR spectroscopy in the photolysis of CH$_3$ONO$_2$ or C$_2$H$_5$ONO$_2$ was an accurate reflection of its actual yield. For CH$_3$ONO$_2$ photolysis, the yield of HO$_2$NO$_2$ reached 12% at 5 min and decreased to 2% at 90 min. For C$_2$H$_5$ONO$_2$ photolysis, the yield of PAN remained at ~40% throughout the reaction process. Peroxides were observed with low yields for both CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$ photolysis, probably because they are unstable and easily photodissociate by UV irradiation.

It is interesting that CH$_3$C(O)OH was not detected by FTIR spectroscopy in either the photolysis or the OH-initiated oxidation of C$_2$H$_5$ONO$_2$, but rather it was detected by IC at a level of ~40 ppmv, a much higher value than its detection limit by FTIR analysis. Moreover, the yield of CH$_3$C(O)OH was found to be close to that of PAN which was detected by FTIR spectroscopy. We therefore propose that the CH$_3$C(O)OH was a technical artefact produced by the hydrolysis of PAN collected in water for IC analysis, rather than by the reaction that occurred in the reactor.

The observed product yields and the carbon and nitrogen mass balances at 40 min are listed in Table 1. The experimental error represents 1σ (each experiment was repeated three to five times). It can be seen that the carbon balance was ~100% within experimental error for the photolysis of both CH$_3$ONO$_2$ (113 ± 13%) and C$_2$H$_5$ONO$_2$ (110 ± 15%), with major carbon products as HCHO, HC(O)OH and CO, whereas the C$_2$H$_5$ONO$_2$ photolysis generated two more products, namely CH$_3$CHO and PAN, both with high yields.

For C$_2$H$_5$ONO$_2$ photolysis, the nitrogen balance observed by FTIR spectroscopy was ~100% within experimental error (100 ± 12%), with HNO$_3$ and PAN as the main nitrogen-containing products; for CH$_3$ONO$_2$ photolysis, however, the nitrogen balance was only 79 ± 16%, with HNO$_3$ as the major product. To find the ‘missing’ nitrogen in this reaction, we employed IC to determine the HNO$_3$ and the result showed that this HNO$_3$ was higher than that detected by FTIR spectroscopy, affording a quantitative yield of HNO$_3$, within experimental error. This result suggests that the unknown nitrogen-containing compound, not distinguished in the mixture by FTIR analysis, was hydrolysed into HNO$_3$ during the sample preparation. By analogy with PAN formed in C$_2$H$_5$ONO$_2$ photolysis, we tentatively consider this unknown nitrogen-containing compound as the homologue of PAN, namely, peroxymethyl nitrate.

Table 1. Yields (%) of products and the carbon and nitrogen mass balance in the photolysis in dry air (O$_2$:N$_2$ = 1:4) and OH-initiated reactions of CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$ in humid air (O$_2$:N$_2$ = 1:4, relative humidity 30%)

<table>
<thead>
<tr>
<th>Product</th>
<th>CH$_3$ONO$_2$ + UV</th>
<th>C$_2$H$_5$ONO$_2$ + UV</th>
<th>CH$_3$ONO$_2$ + OH</th>
<th>C$_2$H$_5$ONO$_2$ + OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>33 ± 3</td>
<td>40 ± 5</td>
<td>65 ± 5</td>
<td>66 ± 6</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>–</td>
<td>–</td>
<td>6 ± 0.5</td>
<td>4 ± 0.4</td>
</tr>
<tr>
<td>HC(O)OH</td>
<td>17 ± 2</td>
<td>19 ± 4</td>
<td>15 ± 1</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>HCHO</td>
<td>63 ± 7</td>
<td>31 ± 3</td>
<td>18 ± 5</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>–</td>
<td>24 ± 4</td>
<td>–</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>MHP</td>
<td>–</td>
<td>1 ± 0.1</td>
<td>–</td>
<td>3 ± 0.2</td>
</tr>
<tr>
<td>PAA</td>
<td>–</td>
<td>1 ± 0.4</td>
<td>–</td>
<td>2 ± 0.1</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>1 ± 0.1</td>
<td>1 ± 0.1</td>
<td>1 ± 0.4</td>
<td>2 ± 0.2</td>
</tr>
<tr>
<td>PAN</td>
<td>–</td>
<td>40 ± 5</td>
<td>–</td>
<td>49 ± 5</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>76 ± 16$^a$</td>
<td>57 ± 6$^b$</td>
<td>52 ± 13$^c$</td>
<td>43 ± 4$^d$</td>
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<tr>
<td>H$_2$O$_2$</td>
<td>3 ± 1</td>
<td>3 ± 2</td>
<td>2 ± 1</td>
<td>1 ± 1</td>
</tr>
<tr>
<td>$\Sigma C$</td>
<td>113 ± 13$^b$</td>
<td>110 ± 15$^b$</td>
<td>104 ± 13$^b$</td>
<td>98 ± 10$^b$</td>
</tr>
<tr>
<td>$\Sigma N$</td>
<td>79 ± 16</td>
<td>100 ± 12</td>
<td>54 ± 13</td>
<td>93 ± 9</td>
</tr>
</tbody>
</table>

$^a$The estimated yield of CO$_2$ based on the observed CO yield and its oxidation rate.
$^b$The observed yield of HNO$_3$ by FTIR spectroscopy.
$^c$The estimated yield of HNO$_3$ based on the observed yield by FTIR spectroscopy and the loss rate of HNO$_3$.
$^d$The yield of the unknown nitrogen-containing compound (UN) was calculated by subtracting the HNO$_3$ yield detected by FTIR analysis from that by IC. The UN is proposed to be PFN.
We suggest that the difference between the yields of HNO₃ estimated by the FTIR spectroscopy because of the lack of its standard spectrum. We could not identify PFN by IC analysis, HC(O)OH might be overestimated by the absorption band overlap between the PFN and HC(O)OH, as both of them contain the HC(O) group. Contrastingly, for IC analysis, HC(O)OH might be produced by the hydrolysis of PFN in water. Obviously, the assumption of the formation of PFN is not convincing enough simply by the analogy with PAN, and further study is needed to identify this unknown nitrogen-containing compound.

**OH-initiated oxidation of CH₃ONO₂ and C₂H₅ONO₂**

Fig. 6 shows the plot of the temporal evolution of reactants and products in the OH-initiated oxidation of (a) ~200-ppmv CH₃ONO₂ and (b) ~150-ppmv C₂H₅ONO₂ in air with 30% relative humidity. The alkyl nitrate concentration decreased by 53% at 40 min and 74% at 80 min for CH₃ONO₂, and 60% at 40 min and 80% at 80 min for C₂H₅ONO₂. For both CH₃ONO₂ and C₂H₅ONO₂, CO increased gradually with time; and HC(O)OH increased gradually and levelled off. For CH₃ONO₂, HCHO reached a maximum at 40 min and then decreased gradually, whereas for C₂H₅ONO₂, HCHO was not evident in the FTIR spectra.

In the CH₃ONO₂ reaction, HO₂NO₂ was detected at low levels (~2 ppmv), and at even lower levels for the C₂H₅ONO₂ reaction. PAN formed in the CH₃ONO₂ reaction reached 59 ppmv at 90 min. HNO₃ formed in both CH₃ONO₂ and C₂H₅ONO₂ reactions was lower than that in their corresponding photolytic reactions, and obviously decreased with the reaction time. This result may imply that the rapid deposition of HNO₃ or the formation of a complex of HNO₃ with H₂O would occur during the reaction because water vapour with 30% relative humidity was present in the reactor; water was added to the chamber in order to generate OH. HNO₃ is a ‘sticky’ molecule and is readily adsorbed onto surfaces, particularly if water is present. The loss rate of gaseous HNO₃ is therefore much higher in humid air than in dry air.

The chemical fate of HNO₃ was examined under the same conditions that were applied to those for the OH radical studies with the two nitrates, as fully described in the Experimental methods section. The result showed that the HNO₃ could undergo a significant loss in the reactor under humid conditions. Combining the observed HNO₃ yield and its rate of loss under the same conditions, we estimated the actual yield of HNO₃ formed in the OH-initiated oxidation of CH₃ONO₂ and C₂H₅ONO₂ (Fig. 7). The estimated actual yields remained almost constant, with ~50% for the OH⁻ CH₃ONO₂ reaction and ~40% for the OH⁻ C₂H₅ONO₂ reaction, although the observed yields decreased gradually with reaction time because of the deposition of gaseous HNO₃.

The yields of HO₂NO₂ and PAN from CH₃ONO₂ or C₂H₅ONO₂ are also shown in Fig. 7. For the CH₃ONO₂ reaction, the yield of HO₂NO₂ decreased from 16% at 1 min to 1% at 70 min because of its instability (Fig. 7). For the C₂H₅ONO₂ reaction, the yield of PAN remained ~50% throughout the reaction process. Peroxides were observed in the OH-initiated reactions but with a minor yield.

CO₂ is potentially a product and should be estimated. Unfortunately, we could not detect its concentration directly by FTIR spectroscopy, because a part of the FTIR spectrometer’s optical path was exposed to the ambient air, resulting in an interference by ambient CO₂. However, CO₂ can be estimated by the kinetics of CO in the reactor, because CO₂ is usually considered to be produced by the oxidation of CO. We investigated the respective oxidation rate of CO by O₃ and OH radicals, under the same conditions as for the photolysis and OH-initiated oxidation of CH₃ONO₂ or C₂H₅ONO₂. The result
indicated that \( \sim 20\% \) of CO was oxidised by OH radicals in 60 min, whereas there was no obvious oxidation of CO in the CO + O\(_2\) reaction in 90 min. For the OH-initiated oxidation of CH\(_3\)ONO\(_2\) or C\(_2\)H\(_5\)ONO\(_2\), the CO\(_2\) yield was then estimated using a linear fit on the basis of the observed CO concentration and OH\(^+\) CO reaction rate (Table 1).

The yields of products and the carbon and nitrogen mass balances in the OH-initiated reactions are shown in Table 1. The carbon balance for reactions with both ANs approached 100\%, with high yields of CO, HCHO and HC(O)OH for the CH\(_3\)ONO\(_2\) reaction, and high yields of CO and PAN for the C\(_2\)H\(_5\)ONO\(_2\) reaction. The results of nitrogen mass balance in the OH-initiated reactions were similar to the corresponding photolysis reactions, as follows: for the OH\(^+\) C\(_2\)H\(_5\)ONO\(_2\) reaction, the main nitrogen-containing products were HNO\(_3\) and PAN; for the CH\(_3\)ONO\(_2\) reaction, HNO\(_3\) was detected as one main nitrogen-containing product, and PFN was proposed as another main nitrogen-containing product.

**Reaction mechanisms based on observed products**

**Photolysis mechanism**

For CH\(_3\)ONO\(_2\) photolysis, two possible cleavage pathways exist that produce two different fragments, namely NO\(_2\) and ONO\(_2\), as follows:

\[
\text{CH}_3\text{ONO}_2 + h\nu \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad (10a) \\
\rightarrow \text{CH}_3 + \text{ONO}_2 \quad (10b)
\]

If photolysis is dominated by the reaction 10a pathway and occurs in the absence of O\(_2\), HCHO, CO and HONO could be expected to form by the following reactions:

\[
\text{CH}_3\text{O} \rightarrow \text{HCHO} + \text{H} \quad (11) \\
\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{HCHO} + \text{HONO} \quad (12) \\
\text{HCHO} + h\nu \rightarrow \text{CO} + \text{H}_2 \quad (13a) \\
\rightarrow \text{HC(O)} + \text{H} \quad (13b)
\]

However, we observed HCHO, CO and HONO formation during CH\(_3\)ONO\(_2\) photolysis in pure N\(_2\). The formation of HONO cannot be explained by the reaction 10b pathway. If the two pathways 10a and 10b coexist, HNO\(_3\) would be produced by the combination of ONO\(_2\) with CH\(_3\)O or HCHO in the absence of O\(_2\):

\[
\text{CH}_3\text{O} + \text{ONO}_2 \rightarrow \text{HCHO} + \text{HONO}_2 \quad (14) \\
\text{HCHO} + \text{ONO}_2 \rightarrow \text{HC(O)} + \text{HONO}_2 \quad (15)
\]

However, this outcome is inconsistent with our experiment result which indicated no formation of HNO\(_3\) in the absence of O\(_2\). In summary, we suggest that the photolysis of CH\(_3\)ONO\(_2\) follows the reaction 10a pathway exclusively. This is in agreement with the recent report for a NO\(_2\) quantum yield of unity from photodissociation of methyl and isopropyl nitrate.\(^{58}\)

In the presence of O\(_2\), the H and HCO radicals formed from reactions 11 and 13b, will rapidly react with O\(_2\), resulting in the formation of HO\(_2\), H\(_2\)O\(_2\) and OH (reactions 16–18), and the oxidation of NO\(_2\) into HNO\(_3\) (reaction 20) and HO\(_2\)NO\(_2\) (reaction 21). HO\(_2\)NO\(_2\) was reported to be the intermediate product in the HCO + O\(_2\) reaction, and it can decompose rapidly to CO and HO\(_2\) because of its instability (reactions 19).\(^{59,60}\)

In the present reaction system, we suggest that part of the HC(O)O\(_2\) reacts with NO\(_2\) to give HC(O)O\(_2\)NO\(_2\) (PFN) before its decomposition (reaction 22):

\[
\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad (16) \\
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (17) \\
\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH} \quad (18) \\
\text{HC(O)} + \text{O}_2 \rightarrow \text{HC(O)}\text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \quad (19) \\
\text{OH} + \text{NO}_2 \rightarrow \text{HONO}_2 \quad (20) \\
\text{HO}_2 + \text{NO}_2 \rightarrow \text{HOONO}_2 \quad (21) \\
\text{HC(O)}\text{O}_2 + \text{NO}_2 \leftrightarrow \text{HC(O)}\text{O}_2\text{NO}_2 \quad (22)
\]

Like CH\(_3\)ONO\(_2\), C\(_2\)H\(_5\)ONO\(_2\) will undergo cleavage of the O–N bond, giving fragment pairs of CH\(_3\)CH\(_2\)O and NO\(_2\) (reaction 23). The subsequent set of reactions leads to the...
formation of HCHO, CH₃CHO, CO, HNO₃, HO₂NO₂, H₂O₂, etc. In addition, PAN, PAA and MHP are formed (reactions 28, 29a and 31).

\[ \text{CH}_3\text{CH}_2\text{ONO}_2 + h\nu \rightarrow \text{CH}_3\text{CH}_2\text{O} + \text{NO}_2 \]  \( (23) \)

\[ \text{CH}_3\text{CHO} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 \]  \( (24) \)

\[ \text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3 + \text{HCO} \]  \( (25a) \)

\[ \rightarrow \text{CH}_4 + \text{CO} \]  \( (25b) \)

\[ \text{CH}_3\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CH}_3\text{C}(\text{O}) + \text{H}_2\text{O} \]  \( (26) \)

\[ \text{CH}_3\text{C}(\text{O}) + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 \]  \( (27) \)

\[ \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \leftrightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2 \]  \( (28) \)

\[ \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH} + \text{O}_2 \]  \( (29a) \)

\[ \rightarrow \text{CH}_3\text{C}(\text{O})\text{OH} + \text{O}_3 \]  \( (29b) \)

\[ \rightarrow \text{CH}_3\text{C}(\text{O})\text{O} + \text{O}_2 + \text{OH} \]  \( (29c) \)

\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \]  \( (30) \)

\[ \text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{O}_2\text{OH} + \text{O}_2 \]  \( (31) \)

\[ 2\text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_3\text{O} + \text{O}_2 \]  \( (32) \)

\[ \text{CH}_3\text{O} \rightarrow \text{HCHO} + \text{H} \]  \( (33) \)

\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \]  \( (34) \)

For the photolysis of both CH₃ONO₂ and C₂H₅ONO₂, formic acid was observed. It appears to be formed from HCHO and a HO₂ radical[61].

\[ \text{HCHO} + \text{HO}_2 \leftrightarrow (\text{HOOCH}_2\text{O}) \leftrightarrow \text{HOCH}_2\text{OO} \]  \( (33) \)

\[ \text{HOCH}_2\text{OO} + \text{HO}_2 \rightarrow \text{HOCH}_2\text{OOH} + \text{O}_2 \]  \( (34) \)

\[ 2\text{HOCH}_2\text{OO} \rightarrow 2\text{HOCH}_2\text{O} + \text{O}_2 \]  \( (35) \)

\[ \text{HOCH}_2\text{O} + \text{O}_2 \rightarrow \text{HC}(\text{O})\text{OH} + \text{HO}_2 \]  \( (36) \)

The above mechanisms agree well with the products observed in our experiments, which gave the observed carbon and nitrogen mass balances, although PFN was not directly identified.

The low level of the observed HO₂NO₂ can be explained as follows. First, we estimated the reaction rates of HO₂ + NO₂ and HO₂ + HO₂. The rate constants are 1.4 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ for kHO₂⁺NO₂ and 2.9 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ for kHO₂⁺HO₂ at 1 atm and 298 K.[62] Because of the lack of experimental values, the concentrations of NO₂ and HO₂ in the CH₃ONO₂ photolysis were estimated using the same box model method as that for C₂H₅ONO₂ photolysis described below. The model output gave the concentrations of ~3.7 × 10¹¹ molecule cm⁻³ for NO₂ and ~2.2 × 10¹² molecule cm⁻³ for NO₂. Combining the concentrations with rate constants, the reaction rates are estimated as 1.1 × 10¹² molecule cm⁻³ s⁻¹ for the HO₂ + NO₂ reaction and 0.4 × 10¹² molecule cm⁻³ s⁻¹ for the HO₂ + HO₂ reaction. This result indicates that the formation of HO₂NO₂ will compete with that of HO₂. However, HO₂NO₂ will be rapidly lost by photodissociation[63] thermal decomposition[64] and reaction with OH[65] resulting in its low photostationary state concentration. This is verified by the model, which gives its photostationary state concentration as ~3 ppmv.

As shown in Table 1, the observed yields of peroxides, including H₂O₂, MHP and PAA, are considerably low (~1%) in the photolysis of C₂H₅ONO₂, owing to their instability. CH₃C(O)OH was not detected by FTIR spectroscopy, although it should be produced by the CH₃C(O)OH + HO₂ reaction (reaction 29b). This outcome implies that the branching ratio of reaction 29b is minor compared with that of reaction 29a and 29c.[66,67]

Although our instrument did not detect the NO₂ that was expected to form according to the proposed mechanism, we have simulated its concentration in the photolysis of C₂H₅ONO₂ using a box model on the basis of the Carbon Bond Mechanism-Version IV (CBM-IV) developed by Gery et al.[68] In the present study, we modified the CBM-IV mechanism by deleting some irrelevant reactions and adding the C₂H₅ONO₂-related reactions. We estimated the photon flux at 254 nm of the UV irradiation by the measured photolysis rate of C₂H₅ONO₂ (its cross-section is known from the literature) and then estimated the photolysis rates of the other species using this photon flux. The experimental initial reactant concentrations, namely, 155 ppmv for C₂H₅ONO₂ and 2 × 10⁷ ppmv for O₂, were input into the model. Fig. 8 shows the model results for the concentration variations of C₂H₅ONO₂ and the main nitrogen-containing products. The modelled concentrations of PAN (maximum ~80 ppmv) are higher than those measured in our experiments (maximum ~60 ppmv) and those of HNO₃ are lower (modelled ~35 ppmv, measured ~50 ppmv). This discrepancy may arise from the uncertainties in the kinetic parameters used in the model. Several of the rate constants used in the model are limited and uncertain, including those for the formation of PAN (kPAN,f) and NO (kFR,f). Obviously, decreasing kPAN,f or increasing kFR,f would improve the modelled results. It is evident that NO₂ was produced and then was rapidly transformed into PAN and HNO₃, resulting in a maximum level of ~2 ppmv for the photostationary state of NO₂, and a much lower NO level. The NO₂ photostationary state was achieved at ~40 min after the photolysis reaction began.
As a result, the FTIR analysis was not able to detect NO, at such a low level. Moreover, it is suggested that the initial excitation in the photodissociation of CH$_3$ONO$_2$ is located on the NO$_2$ moiety, and most of the available energy is deposited in it. It is worth mentioning that we carried out an additional experiment in which ~40 ppmv of NO$_2$ was added to the CH$_3$ONO$_2$ photolysis system. The result showed that the production rate of HNO$_3$ in this NO$_2$-supplemented system had no obvious changes, compared with the control system containing no NO$_2$. This result implies that the added NO$_2$ reacts much more slowly than does the NO$_2$ in the excited-state derived from the photodissociation of CH$_3$ONO$_2$. This outcome may also indicate that the reaction of excited-state NO$_2$ (NO$_2^*$) to form HNO$_3$ and peroxyacetyl nitrates is competitive with its quenching. Therefore, we suggest that the NO$_2^*$ fragment from the CH$_3$ONO$_2$ or C$_2$H$_5$ONO$_2$ photolysis may have extra energy (in an electronically excited state), making it much more reactive than ground state NO$_2$ in the atmosphere, resulting in the formation of more HNO$_3$ and peroxyacetyl nitrates (RC(O)OONO$_2$, PAN and the homologue of PAN). To our knowledge, we have not found specific reports on the amount of extra energy in the NO$_2^*$ formed in the photolysis of methyl and ethyl nitrates. Unfortunately, we currently cannot make an estimation on the extra energy in the NO$_2^*$ and the dominant modes.  

**OH-initiated oxidation mechanism**

In the OH-initiated oxidation of ANs, the OH radicals were produced by UV photolysis of O$_3$ in the presence of water vapour. Because of the use of UV irradiation, the photolytic reaction should occur simultaneously. However, we observed that the consumption rate of CH$_3$ONO$_2$ or C$_2$H$_5$ONO$_2$ in the OH-initiated oxidation was ~30% higher than that in the corresponding photolysis, indicating that the OH-initiated oxidation was the dominant pathway in the reaction system. 

For this study, the reactions of CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$ with OH radicals were carried out in simulated atmospheric conditions, and HNO$_3$ was detected as a major product. The OH reaction has two different pathways, namely, addition and H-atom abstraction. As the H-atom abstraction could produce bifunctional organic nitrates such as carbonyl-nitrates, rather than HNO$_3$ or PAN, we think that this pathway should not predominate. Alternatively, the OH addition is possibly the dominant pathway in these reactions, resulting in the formation of an unstable adduct (reactions 37 and 38). This view is supported by Nielsen et al.

The adduct has two routes for its decomposition: (1) the direct formation of HNO$_3$, accompanied by the formation of the alkoxy radical (reactions 37a and 38a); and (2) formation of the excited NO$_2^*$ and alkyl peroxides (reactions 37b and 38b). CH$_3$OOH and C$_2$H$_5$OOH, which are formed in reactions 37b and 38b, will be rapidly transformed into other products by their photodissociation and reactions with OH, leading to their low photostationary state concentrations. HNO$_3$, HO$_2$NO$_2$, PFN or PAN are produced in the subsequent reactions of NO$_2^*$. This mechanism is similar to the photolysis system described previously. 

PAN was observed with a high yield in the OH-initiated oxidation of C$_2$H$_5$ONO$_2$, and this implies that the excited NO$_2^*$ was produced by the second decomposition pathway for the adduct (reactions 37b and 38b) because no evidence was reported for the formation of PAN by direct decomposition of the adduct. However, Nielsen et al. suggested a pathway leading to the direct decomposition of the adduct into HNO$_3$ (reactions 37a and 38a). These two routes for the adduct decomposition likely coexist and the branch ratio possibly approaches 1:1, considering the observed HNO$_3$/peroxyacetyl nitrates ratio of ~1:1, as seen in Table 1. Unfortunately, we cannot determine the relative contributions of these two channels in the present experimental study.

\[
\begin{align*}
\text{CH}_3\text{ONO}_2 + \text{OH} &\rightarrow \text{CH}_3\text{O} + \text{HONO}_2 \\
\text{C}_2\text{H}_5\text{ONO}_2 + \text{OH} &\rightarrow \text{C}_2\text{H}_5\text{OO} + \text{HONO}_2
\end{align*}
\]

(37a) \hspace{2cm} (37b) \hspace{2cm} (38a) \hspace{2cm} (38b)

In summary, for the OH-initiated oxidation of ANs, there are two pathways to form HNO$_3$, namely, direct OH-adduct decomposition and OH+NO$_2^*$ reaction, whereas for the photolysis of ANs, the OH+NO$_2^*$ reaction is the only pathway. We note that the yield of the OH+NO$_2^*$ pathway leading to HNO$_3$ could be different between the laboratory conditions presented in this paper and atmospheric conditions. In the atmosphere, whether NO$_2^*$ competes effectively for OH to form HNO$_3$ very much depends on the atmospheric composition and conditions. In the photolytic reaction, small concentrations of OH radicals were produced by a series of reactions after the cleavage of the alkoxy nitrate O–N bond; in the OH-initiated reaction, the OH radicals were produced by the photolysis of O$_3$ in the presence of water vapour (reactions 8 and 9). It is expected that the OH radicals in the OH-reaction are much more abundant than those in the photolysis. This can also explain the discrepancy regarding the CH$_3$CHO and PAN concentrations observed between the photolysis and OH-initiated reaction of C$_2$H$_5$ONO$_2$ (Table 1). As mentioned above, acetaldehyde is transformed into PAN through the OH-initiated reactions (reactions 26–28). The higher OH level in the OH-initiated reactions of C$_2$H$_5$ONO$_2$ results in the lower CH$_3$CHO level as well as higher PAN level relative to those in the photolytic oxidation reaction of C$_2$H$_5$ONO$_2$.

**Conclusions and environmental implications**

Under simulated atmospheric conditions, we have for the first time carried out a laboratory study of the atmospheric photochemical reactions of CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$, which served as models of ANs. A series of intermediate and end products, including carbon- and nitrogen-containing compounds, were well characterised, and the carbon and nitrogen balances based on these observed compounds were ~100%, within experimental error (1σ) for the reactions. Notably, for both photolysis and OH-initiated reactions of CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$, HNO$_3$ was found to be a major nitrogen-containing product with a yield of ~50% or more, whereas PAN was observed in C$_2$H$_5$ONO$_2$ reactions and PFN was proposed as a product in CH$_3$ONO$_2$ reactions with significant yields. The detailed mechanisms of these reactions have been deduced based on...
the experimental results. Noticeably, we used a Hg lamp ($\lambda_{\text{max}} = 254\,\text{nm}$) as the light source because it can provide enough UV intensity to encompass the AN photolysis lifetime in one hour at a controlled temperature. We propose that this UV wavelength, which is shorter than that in the troposphere, would not significantly change the reaction mechanism of ANs, which is intensively concerned in the present study, although the reaction rates and the product yields would be different from that in the troposphere.

The present study has revealed that the photochemical reactions of CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$ in the atmosphere would ultimately produce PAN or PFN, a reactive nitrogen-containing substance, and HNO$_3$, a photochemically non-reactive nitrogen-containing substance. It is expected that the higher-weight ANs might undergo a similar atmospheric fate. This finding implies that ANs may serve as not only a reservoir but also as a sink for reactive nitrogen in the atmosphere. Such a dual role for ANs in the nitrogen cycle should be considered in the models in regard to air quality and nitrogen exchange between atmosphere and surface.

Herein, we have attempted to estimate the production of HNO$_3$ and peroxyacyl nitrates derived from NO$_y$ by way of ANs as intermediates in the atmosphere on the basis of their yields obtained by our experiments. The average yields from CH$_3$ONO$_2$ and C$_2$H$_5$ONO$_2$ photolytic and OH-initiated decompositions (Table 1) are 57% for HNO$_3$ and 36% for peroxyacyl nitrates. We assume that these experimental yields approximate their yields in the real atmosphere. Recent measurements indicated that $\sum$ANs comprise a large fraction of NO$_x$ [2,3,14]; the result from the model analysis also suggested that $\sum$ANs represent a large fraction of NO$_y$, with 5–42% for a rural scenario and 2–16% for an urban scenario [12]. Summarising the observed and model results, we suggest that $\sum$ANs comprise ~10% of the NO$_y$ in urban areas and ~20% in rural areas. As mentioned earlier, ANs in the continental atmosphere are mainly produced from the reactions of NO$_3$. This means that 10 and 20% of NO$_2$ is converted into ANs in urban and rural atmospheres. Combining the percentages of ANs in NO$_y$ transformation with HNO$_3$ and PAN yields from ANs, we estimate here that ANs account for the sink and reservoir fractions of NO$_y$ by two scenarios: (i) in the urban atmosphere, HNO$_3$ makes up ~6% of the nitrogen sink and ~4% of the nitrogen reservoir is composed of peroxyacyl nitrates; and (ii) in the rural atmosphere, HNO$_3$ comprises ~11% of the nitrogen sink and ~7% of the nitrogen reservoir is peroxyacyl nitrates. This estimation is illustrated in Fig. 9. These sink and reservoir contributions are significant for the total NO$_y$ cycle, especially in rural areas.

Recently, a modelling study on global atmospheric chemistry pointed out that PAN has increased globally by 9% from megacities under year 2000 conditions [23]. We hope our findings will be useful for a better understanding of this global PAN change.

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References

Dual role of ANs in the nitrogen cycle


