A four carbon organonitrate as a significant product of secondary isoprene chemistry

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Introduction

Details on the isoprene oxidation experiments in the atmospheric simulation chamber SAPHIR are provided in section S1. Sensitivities for the quantification of the organonitrates are discussed in section S2. Section S3 provides details on the ambient measurements. Section S4 discusses the updated chemical mechanism of the C4H7NO5. The last section, S5, gives details on the complimentary experiments at the Go:PAM flow reactor.

Text S1. Experiments in the atmospheric simulation chamber SAPHIR

The experiments were conducted in the atmospheric simulation chamber SAPHIR (Rohrer et al., 2005; Fuchs et al., 2017) in Jülich, Germany, in August 2018 to improve our knowledge on the gas and particle phase products of isoprene oxidation by NO3 radicals (Dewald et al., 2020; Brownwood et al., 2021; Wu et al., 2021; Vereecken et al., 2021). Here we selected four experiments to scrutinize the formation of ONs (Table S1). The major loss of peroxy radicals was the reaction with HO2. However, different chemical conditions enhanced different chemical regimes (Brownwood et al., 2021). In experiment 1 HO2 formation was enhanced by propene ozonolysis and CO addition to favor the RO2 + HO2 regime, whereas experiment 2 favored the RO2 + RO2 regime. In the other two experiments we simulated nighttime to daytime transition exposing the nighttime products to OH oxidation and photolysis in exp. 3 and only to photolysis in exp. 4 where CO was added as an OH scavenger before the opening of chamber’s roof. For all experiments the NO3 radicals were formed in the chamber by the addition of ozone and NO2. The reaction was initiated by isoprene injection. 1.5 to 2 hours after the first injection when most of the isoprene was consumed, additional NO2, O3, and isoprene were introduced in the chamber to propagate the chemistry. This injection of isoprene was repeated one more time in all 4 experiments (Figure 1, Table S1). In a last step, after total isoprene consumption, only ozone and NO2 were added to enhance further oxidation of the products (exp. 1 and exp. 2). In exp. 3 and 4 the chamber roof was open to test the daytime effect on the products after the third injection. The potential aerosol contributions of isoprene products were scrutinized by addition of ammonium sulfate as aerosol seeds in exp. 3. However, the focus on the present study is on the gas-phase processes where a high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS, Aerodyne Research Inc.) (hereafter I-CIMS) using iodide as the primary reagent ion (Lee et al., 2014) was used to measure the gas-phase oxidation products. A filter inlet for gases and aerosols (FIGAERO) (Lopez-Hilfiker et al., 2014) was also coupled to the I-CIMS during the experiment with aerosol seeds to measure the particle phase oxidation products. For clarity, the particle data was removed from the time trends shown in Figure 1c. The I-CIMS was placed in an air-conditioned container under the chamber. A four-meter long PFA (Swagelok, 6mm diameter) line and four-meter long copper tubing (12mm diameter) were used as gas and particle inlets respectively. Both were insulated to avoid condensation in the lines. The measured signal of the 64 identified ONs was corrected for background, normalized to iodide signal and converted to ppt using a bulk sensitivity of 4.8 ncps ppt⁻¹ for all measured
ONs (see Section S2). No loss corrections have been applied to the data set. A CIMS using bromide as the reagent ion and coupled with a customized inlet (Albrecht et al., 2019) attached directly at the bottom of the chamber was also deployed (Wu et al., 2021).

**Table S1. Experimental conditions in the atmosphere simulation chamber SAPHIR.**

| Conditions          | Exp. 1 (9 August) | Exp. 2 (13 August) | Exp. 3 (16 August) | Exp. 4 (12 August) |
|---------------------|-------------------|--------------------|--------------------|--------------------|
| Favored chemical regimes | RO₂ + HO₂         | RO₂ enhanced       | Isomerization enhanced | RO₂ enhanced       |
| Roof                | Closed            | Closed             | Closed + open      | Closed + open      |
| Seeds               | No                | No                 | Yes                | No                 |
| Humidity            | Dry               | Dry                | Wet                | Dry                |
| Isoprene / ppbv     | 3 / 3 / 1.5       | 6 / 8 / 7          | 2 / 1.5 / 2        | 2.5 / 2 / 2.5      |
| O₃ / ppbv           | 100 / 47 / 28 / 32| 105 / 20 / 12 / 37 | 100/ 30 / -        | 80 / 46 / 13       |
| NO₂ / ppbv          | 5 / 3 / 3 / 2.5   | 23 / 12.5 / 7 / 13 | 4 / 2.5 / 2.5      | 12 / - / 1         |
| Propene / ppbv      | 100 / 40          | -                  | -                  | -                  |
| CO / ppmv           | 120               | 0                  | 0.02               | 120                |

The yields of the total measured ONs, C₄H₇NO₅, and the sum of the major primary products C₃H₅NO₅ (hydroperoxide nitrates, INP), C₃H₇NO₄ (carbonyl nitrates, ICN), and C₅H₉NO₄ (hydroxy nitrates, IHN) were estimated based on isoprene consumption (Table S2). The measured ONs signal was converted to ppt using a bulk ON calibration factor of 4.8 ncps ppt⁻¹ with a standard deviation of 0.7 ncps ppt⁻¹ (Figure S1). The consumed isoprene was modeled and predicted based on measurements of isoprene, ozone, OH radicals, and dilution during the experiments. The OH concentration was below the detection limit during the experiments while the amount of isoprene reacted with NO₃ was calculated to be around 90% (Brownwood et al., 2021).
**Table S2.** Estimated yields of the total measured ONs, C₄H₇NO₅, and the sum of the major primary products (C₅H₈NO₅, C₅H₇NO₄, and C₃H₈NO₄). The yields were estimated when all isoprene had been consumed. The yields in experiments 3 and 4 were calculated only for the dark period. An error of 30%, corresponding to an uncertainty of 2σ has been applied.

| Experiment | Total measured ONs yield (%) | C₄H₇NO₅ yield (%) | Major C₅ yield (%) |
|------------|-----------------------------|-------------------|-------------------|
| 1 (9 Aug)  | 108.8 ± 32.6                | 3.4± 1.0          | 41.6 ± 12.5       |
| 2 (13 Aug) | 97.6 ± 29.3                 | 9.7 ± 2.9         | 51.6 ± 15.5       |
| 3 (16 Aug) | 32.4 ± 9.7                  | 5.3 ± 1.6         | 13.1 ± 3.9        |
| 4 (12 Aug) | 76.7 ± 23.0                 | 7.6 ± 2.8         | 38.6 ± 11.6       |

**Text S2. Sensitivity estimates**

Recently, Zhang and Zhang (2021) showed that secondary chemistry processes in the ion molecule reaction (IMR) chamber of CIMS under high O₃ conditions can lead to adduct formation of organic molecules with IOₓ⁻, instead of making a cluster with I⁻. This can lead to misinterpretations of the identified chemical formulas. However, the assignment of C₄H₇NO₅ formula as an adduct with iodide ((I)C₄H₇NO₅⁻) and not as an adduct with IOₓ⁻ ((IO)C₄H₇NO₄⁻) are supported by the following three reasons.

A test experiment was conducted in the SAPHIR chamber in which pre-synthesized N₂O₅ was used as the source of NO₃ radicals. Thus, ozone was not present preventing formation of IOₓ⁻. The N₂O₅ was flowing continuously into the chamber while isoprene was injected four times. The chemical conditions of the experiment were in line with the experiments 2 and 4 (Figure 1b & 1d). In absence of ozone, a very similar formation rate of the C₄H₇NO₅ was observed. The relative contribution of C₄H₇NO₅ to the total measured ONs was slightly higher than 10%, similar to experiments 2 and 4. The test experiment is in support of the assignment as (I)C₄H₇NO₅⁻. Furthermore, in another phase of the test experiment ozone was added after all isoprene had been consumed by NO₃ and MVK was also injected. The goal was to observe if MVK could produce C₄H₇NO₅ but the observations were too complicated due to additional secondary reaction and this experiment was not analyzed further. However, the addition of ozone caused an instant increase of the IOₓ⁻ signals induced by ozone chemistry in the chemical ionization inlet. An instant signal increase, was observed for 8 minor ON products out of the total 64 identified ONs. For the target species C₃H₈NO₅ there were no indications of an instant increase but rather a much slower increase was observed which was attributed to further oxidation of primary products due to the additions of ozone and MVK. This test confirms very limited influence of potential IOₓ⁻ effects on the targeted species described in this paper.

Secondly, similar results were observed during NO₃-initiated isoprene oxidation experiments in the Go:PAM flow reactor. In these experiments NO₃ radicals were produced only via the dissociation of synthesized N₂O₅. C₃H₈NO₅ formed with lower contribution as the residence time and the chemical conditions favored the primary products during these
experiments. Finally, the C4H7NO5 formula was also observed by a Br-CIMS. The Br-CIMS C4H7NO5 signal was showing a similar time profile as the I-CIMS signal.

The ion counts, i.e. normalized counts per second (ncps), derived for each species using the I-CIMS can be converted to concentration units using appropriate instrumental sensitivities, which can be derived from standards. Unfortunately, for the detected ONs there is a lack of standards making direct quantification difficult. However, two methods to derive limits on sensitivities were applied, i.e. using bulk sensitivity or relative sensitivity. These two methods constrain and strengthen the various conclusions of the overall and relative importance of the various organonitrates discussed in this work.

To derive bulk-sensitivities for the ONs a Thermal Dissociation Cavity Ring-down Spectrometer (TD-CRDS) was deployed during the experiments in the atmospheric simulation chamber SAPHIR (Brownwood et al., 2021). The comparison of the sum of ONs measured by the I-CIMS versus the total alkyl nitrates measured by the TD-CRDS provides an estimation of the bulk sensitivity for the ONs (Figure S1). The mean average bulk ON sensitivity of the four experiments was 4.8 ncps ppt⁻¹ with a standard deviation of 0.7 ncps ppt⁻¹. This bulk sensitivity factor of 4.8 ncps ppt⁻¹ was used to convert to concentrations all the data collected using the University of Gothenburg CIMS (GU-CIMS) in this study.

Figure S1. Total ONs signal detected by I-CIMS versus total alkyl nitrates measured by the TD-CRDS.
**Figure S2.** An averaged spectrum at nominal mass-to-charge (m/z) 276 Th during the exp. 4 (Figure 1d). The C₄H₇NO₅ is the dominant peak at this nominal mass.

In addition, a comparison with the C₄H₇NO₅ measurements using Br-CIMS are depicted in Figure S3. The comparison of normalized signal shows very good agreement between the two instruments, especially at the early oxidation stages, during experiments 1, 4 and the nighttime period of experiment 3. The discrepancy in experiment 3 after transition to the daytime might be attributed to different isomer distribution, because of OH oxidation. Experiment 2 is not shown since there were operation problems of the Br-CIMS that day.

**Figure S3.** Comparison of C₄H₇NO₅ measurements by I-CIMS and Br-CIMS.
For differences in individual ON sensitivities the voltage scanning (VS) technique can be utilized to estimate an upper limit sensitivity. This will give a lower limit of concentration of the corresponding species, that is based on the collision limit of iodide ion adducts (Lopez-Hilfiker et al., 2016; Iyer et al., 2016). It should be noted that the I-CIMS can only provide the molecular formulas of the measured ions, which can consist of several different isomers. The iodide ionization can have isomer dependent sensitivities (e.g. IHN (Lee et al., 2016; Lee et al., 2014)) but this has not been considered here. During the VS technique the voltage difference (dV) of the interface between two quadrupoles in CIMS is increasing stepwise. The VS allows the determination of the voltage where half of the I-cluster signal is left (i.e. dV_{50}). The dV_{50} value is then a measure of the stability of I-clusters which is an important property for its sensitivity.

We can estimate a relative sensitivity for different iodide adducts using a characterized compound concentration in conjunction with VS (Ye et al., 2021). We have characterized a dinitrogen pentoxide (N_2O_5) diffusion source via NO titration, and we obtained a calibration factor of 21 ncp ppm^{-1} which was used to determine the relative sensitivity. The N_2O_5 reacts with iodide ions at the collision limit and it can be used for the determination of the upper limit sensitivity (Lopez-Hilfiker et al., 2016). For the estimation of N_2O_5 the sum of NO_3^{-} (m/z 62) and IN_2O_5^{-} (m/z 235) signals were used. Recently, Dörich et al. (2021) observed deprotonation of HNO_3 under high ozone mixing ratios by IO_2^{-} clusters in a similar mechanism to acetic acid CIMS measurements (Veres et al., 2008). This provides additional nitrate anions NO_3^{-} (m/z 62) that may lead to an overestimation of N_2O_5. However, in our work the calibration experiments and VS were done using pre-synthesized N_2O_5 in the absence of ozone, thus there was no formation of IO_2^{-} clusters that could deprotonate HNO_3. We performed oxidation experiments of isoprene and NO_3 using the Go:PAM flow reactor in conjunction with VS. The NO_3 radicals were introduced by dissociation of N_2O_5 via the characterized diffusion source. Then, we used the N_2O_5 calibration factor as the maximum sensitivity to estimate the relative sensitivity of products of interest.

It should be noted, that the VS experiments with the characterized N_2O_5 source were conducted after a general instrument refurbishment. This means that the instrument performance has been optimized compared to the period that the previous experiments took place (SAPHIR experiments and ambient measurements using the GU-CIMS). Thus, we expect higher sensitivities. However, we can derive useful information about the maximum sensitivity of specific products as well as any differences on their sensitivities. The relative sensitivities of C_4H_7NO_5, C_5H_9NO_5 (INP), C_5H_7NO_4 (ICN), and C_5H_9NO_4 (IHN) were estimated using VS in five experiments. The average relative sensitivities and the standard deviations are given in the Table S3. The values of C_4H_7NO_5, C_5H_9NO_5, and C_5H_7NO_4 are similar indicating similar sensitivities, although the C_5H_7NO_4 value has higher uncertainty. The C_5H_9NO_4 relative sensitivity is lower than the others but closer to values that has been reported before using synthesized standards of different C_5H_9NO_4 (IHN) isomers (Lee et al., 2014). This difference indicates that we may underestimate the C_5H_9NO_4 concentration. It should be noted that the relative sensitivities were estimated to understand the potential variability of I-CIMS sensitivity to the different ONs. The bulk ON calibration factor of 4.8
ncps ppt\(^{-1}\) with a standard deviation of 0.7 ncps ppt\(^{-1}\) was utilized for all conversions to ppt using GU-CIMS.

Table S3. The estimated relative sensitivities of the ONs used for analysis based on the \(N_2O_5\) calibration factor.

| Relative sensitivity (ncps ppt\(^{-1}\)) |
|----------------------------------------|
| \(C_4H_7NO_5\)                       | 17.6 ± 1.7 |
| \(C_5H_9NO_5\)                       | 18.3 ± 2.9 |
| \(C_5H_7NO_4\)                       | 18.9 ± 6.7 |
| \(C_5H_9NO_4\)                       | 5.4 ± 3.4  |

Text S3. Ambient measurements

Data sets using an I-CIMS at six different locations around the globe have been used. University of Gothenburg CIMS (GU-CIMS) was used in Gothenburg, Sweden (2014), in Changping (near Beijing), China (2016), in Hong Kong (2018) and in Jülich, Germany (2019). The University of Washington instrument (UW-CIMS) was used in Centreville, Alabama, USA (2013). Finally, the University of Manchester CIMS (UMan-CIMS) was deployed in the Amazon rainforest, Brazil (2016).

The measured ONs signal has been converted using the bulk sensitivity factor for the ONs (4.8 ncps ppt\(^{-1}\)) at the locations where the GU-CIMS has been used. The measurements by the UW-CIMS used a weighted IHN (\(C_5H_9NO_4\)) isomer distribution as reported by Wennberg et al. (2018) and measured by Lee et al. (2014) as a proxy calibrant, while the UMan-CIMS used the isoprene-derived IEPOX as a proxy calibrant to convert the counts per seconds (cps) to ppt.

The measurements in Gothenburg, Sweden, took place in the city’s port in October, 2014. The measurement in Changping and Hong Kong were part of the project “Photochemical smog in China” (Hallquist et al., 2016). The measurement site during the first campaign was located at a semi-rural area 40km north-east of downtown Beijing close to Changping town (Le Breton et al., 2018), while the second one was situated at the Hok Tsui Tsuen area, south-east on the Hong Kong island. The Changping measurements were conducted during May-June, 2016, while the Hong Kong ones during November-December, 2018. The measurements in Jülich took place in April-May, 2019 during the Jülich Atmospheric Chemistry Project campaign (JULIAC) at Forschungszentrum Jülich (FZJ), Germany. Here, ambient air was continuously sampled from an inlet at 50 m height above ground and then transferred to the atmospheric simulation chamber SAPHIR where all instruments sampled the air. The GU-CIMS was located in a container below SAPHIR.

The measurements in USA were part of the Southern Oxidant and Aerosol Study (SOAS) during June-July, 2013. The UW-CIMS was placed a few meters above the ground (Lee et al., 2016).
The Amazon campaign took place in June-July, 2016 in Central Amazonia, at a site located 60 km northwest of Manaus (0.235680° S, 60.12560° W, 110 m above sea level) facing a huge area (1600 km²) of nearly pristine forest to the east. The UMan-CIMS was situated just above the canopy (~35 m height above ground).

Figure S4 shows the corresponding time-trends of the ON and NOx shown as diurnal trends in Figure 2. The low NOx levels observed could explain why isoprene-rich regions like Amazon and SE USA report relatively lower levels of selected ON. The ozone concentrations and operational characteristics of CIMS during each campaign are also depicted in Table S5 and Table S6, respectively.

Table S4. Correlation slopes and R squared between C_{4}H_{7}NO_{5} vs C_{5}H_{9}NO_{5}, C_{5}H_{7}NO_{4}, and C_{5}H_{9}NO_{4} at the different measurement sites.

|                | Gothenburg | Amazon | Hong Kong | Changping | Jülich | Alabama |
|----------------|------------|--------|-----------|-----------|--------|---------|
|                | Cor. slope | R²     | Cor. slope | R²     | Cor. slope | R²     | Cor. slope | R²     | Cor. slope | R²     | Cor. slope | R²     |
| C_{5}H_{9}NO_{3} Day | 0.94      | 0.99   | 1.30      | 0.32     | 1.54    | 0.68   | 0.62      | 0.30     | 1.27      | 0.99   | 4.50      | 0.69   |
| Night          | 0.99      | 0.96   | 1.80      | 0.31     | 1.90    | 0.91   | 3.23      | 0.74     | 1.26      | 0.97   | 1.76      | 0.76   |
| C_{5}H_{7}NO_{4} Day | 1.86      | 0.94   | 5.53      | 0.60     | 24.77   | 0.65   | 0.84      | 0.0006   | 6.29      | 0.33   | 151.98    | 0.31   |
| Night          | 1.90      | 0.80   | 4.26      | 0.12     | 19.87   | 0.57   | 16.42     | 0.25     | 2.57      | 0.07   | 21.58     | 0.37   |
| C_{5}H_{9}NO_{4} Day | -        | -      | 3.19      | 0.74     | 9.99    | 0.88   | -0.23     | 0.0015   | 6.95      | 0.45   | 4.49      | 0.78   |
| Night          | -         | -      | 4.07      | 0.38     | 6.81    | 0.70   | 2.97      | 0.07     | 7.60      | 0.50   | 3.63      | 0.92   |
**Figure S4.** The time series of the major isoprene nitrates and NO$_x$ in a) Gothenburg, Sweden, b) Central Amazonia, Brazil, c) Hong Kong, d) Changping, China, e) Jülich, Germany, and f) Centreville, Alabama, USA. Note that only the NO$_2$ concentration is depicted in Amazonia.
**Figure S5.** (Top) The time series of the major isoprene nitrates in Hong Kong. The relative contribution represents the ratio of \( C_4H_7NO_5 \) over the total isoprene-derived nitrates that measured via the I-CIMS during the campaign. (Bottom) Median diurnal profile of the \( C_4H_7NO_5 \) and \( NO_x \) with the 10\(^{th}\), 25\(^{th}\), 75\(^{th}\) and 90\(^{th}\) percentile, in Hong Kong during the
period with higher ONs formation (between 14-25/11). The grey areas in the plot indicate the nighttime period.

**Table S5.** Mean, median, min and max ozone concentrations during the ambient observations at the different measurement sites.

| Ozone (ppb) | Gothenburg | Amazon | Hong Kong | Changping | Jülich | Alabama |
|-------------|------------|--------|-----------|-----------|--------|---------|
| Mean        | 22         | 12     | 53        | 58        | 41     | 27      |
| Median      | 22         | 13     | 54        | 52        | 39     | 25      |
| Min         | 2          | 0.1    | 3         | 0.6       | 6      | 0.3     |
| Max         | 39         | 26     | 95        | 185       | 85     | 69      |

**Table S6.** Operation characteristics of I-CIMS at the different measurement sites.

|                  | Gothenburg, GU-CIMS | Amazon, UMan-CIMS | Hong Kong, GU-CIMS | Changping, GU-CIMS | Jülich, GU-CIMS | Alabama, UW-CIMS |
|------------------|----------------------|-------------------|--------------------|--------------------|----------------|------------------|
| IMR a pressure (mbar) | 190-199              | -                 | 147-248            | 418-441            | 165-220        | -                |
| SSQ b pressure (mbar) | 1.79-1.80            | -                 | 0.85-1.0           | 1.77-1.78          | 1.05-1.1       | -                |
| Gas inflow (sccm)  | ~2000                | ~2000             | ~2000              | ~2000              | ~2050          | ~2000            |
| Ionization        | $^{210}$Po           | $^{210}$Po        | $^{210}$Po         | X-ray              | $^{210}$Po     | $^{210}$Po       |

aIMR stands for ion molecule reaction. bSSQ stands for short segmented quadrupole.

**Text S4. Chemical mechanism**

The oxidation products with the chemical formula C$_4$H$_7$NO$_5$ consist of different isomers. The chemical structure of most relevant isomers and the naming convention using the Master Chemical Mechanism (MCM) are depicted in Table S7. The FZJ-NO3-isoprene mechanism was published recently in the study by Vereecken et al. (2021). There, the focus was on the initial reaction of isoprene with the NO$_3$ radical and the resulting peroxy- and alkoxy-radicals. This also leads to additional sources of HC4ACHO and HC4CCHO (names as in the MCM, structures see Figures S5), for which plausible mechanisms for the formation of C$_4$H$_7$NO$_5$ can be formulated. With the help of structure activity relationships, the mechanisms shown in the Figure S5 were constructed. The rate of the reaction with NO$_3$ was calculated as shown in (Kerdouci et al., 2014), with a 65% preference for addition on the secondary carbon as used for the detailed description of the addition reaction in the MCM. The rate coefficients and branching ratios for the
bimolecular peroxy radical reaction pathways (reaction with NO, NO₃, HO₂ and other RO₂) are calculated according to (Jenkin et al., 2019), the unimolecular reactions as given in (Vereecken and Nozière, 2020). The rates for the alkoxy radicals are calculated as given in (Vereecken and Peeters, 2009; Novelli et al., 2021), with only the competitive reactions implemented. It should be noted that this is the first expansion of the FZJ-NO₃-isoprene mechanism to such late-stage chemistry. The mechanism expansion itself with all relevant reactions are given below in EASY format:

\[
\begin{align*}
\text{k}[HC_4CCHO + NO3 \rightarrow ISOP1CO2O3N4OH] &= \text{CONST}(1.05E-14*0.65) \\
\text{k}[HC_4CCHO + NO3 \rightarrow ISOP1OH2O3N4CO] &= \text{CONST}(1.05E-14*0.35) \\
\text{k}[HC_4ACHO + NO3 \rightarrow ISOP1OH2O3N4CO] &= \text{CONST}(1.05E-14*0.65) \\
\text{k}[HC_4ACHO + NO3 \rightarrow ISOP1OH2N3O4CO] &= \text{CONST}(1.05E-14*0.35) \\
\text{k}[ISOP1CO2O3N4OH \rightarrow MVKNO3 + CO + OH] &= \text{CONST}(2.54E-63*T@(24.25)*\text{EXP}(1605/T)) \\
\text{k}[ISOP1CO2O3N4OH + NO \rightarrow ISOP1CO2O3N4OH + NO2] &= \text{CONST}(KRO2NO*0.93) \\
\text{k}[ISOP1CO2O3N4OH + NO \rightarrow ISOP1CO2O3N4OH + NO2] &= \text{CONST}(KRO2NO*0.07) \\
\text{k}[ISOP1CO2O3N4OH \rightarrow ISOP1CO2O3N4OH] &= \text{CONST}(1.0E-13*\text{EXP}(-324/T)*0.3*RO2) \\
\text{k}[ISOP1CO2O3N4OH \rightarrow ISOP1CO2O3N4OH] &= \text{CONST}(1.0E-13*\text{EXP}(-324/T)*0.7*RO2) \\
\text{k}[ISOP1OH2O3N4CO + NO \rightarrow ISOP1OH2O3N4CO + NO2] &= \text{CONST}(KRO2NO*0.84) \\
\text{k}[ISOP1OH2O3N4CO + NO \rightarrow ISOP1OH2O3N4CO + NO2] &= \text{CONST}(KRO2NO*0.16) \\
\text{k}[ISOP1CO2O3N4CO + NO3 \rightarrow ISOP1CO2N3O4CO + NO2] &= \text{CONST}(KRO2NO3) \\
\text{k}[ISOP1CO2O3N4CO + NO3 \rightarrow ISOP1CO2N3O4CO + NO2] &= \text{CONST}(KRO2NO3) \\
\text{k}[ISOP1OH2O3N4CO + NO \rightarrow ISOP1OH2O3N4CO + NO2] &= \text{CONST}(KRO2NO*0.84) \\
\text{k}[ISOP1OH2O3N4CO + NO \rightarrow ISOP1OH2O3N4CO + NO2] &= \text{CONST}(KRO2NO*0.16) \\
\text{k}[ISOP1OH2O3N4CO \rightarrow ISOP1OH2O3N4CO] &= \text{CONST}(1.0E-13*\text{EXP}(-221/T)*0.3*RO2) \\
\text{k}[ISOP1OH2O3N4CO \rightarrow ISOP1OH2O3N4CO] &= \text{CONST}(1.0E-13*\text{EXP}(-221/T)*0.7*RO2) \\
\text{k}[ISOP1OH2N3O4CO + NO2 \rightarrow ISOP1OH2N3O4CO + NO2] &= \text{CONST}(KRO2NO*0.84) \\
\text{k}[ISOP1OH2N3O4CO + NO2 \rightarrow ISOP1OH2N3O4CO + NO2] &= \text{CONST}(KRO2NO*0.16) \\
\text{k}[ISOP1OH2N3O4CO + O2 \rightarrow ISOP1OH2N3O4CO + NO2] &= \text{CONST}(KRO2NO*0.84) \\
\text{k}[ISOP1OH2N3O4CO + O2 \rightarrow ISOP1OH2N3O4CO + NO2] &= \text{CONST}(KRO2NO*0.16) \\
\text{k}[ISOP1OH2N3O4CO + NO3 \rightarrow ISOP1OH2N3O4CO + NO2] &= \text{CONST}(KRO2NO3) \\
\text{k}[ISOP1OH2N3O4CO + NO3 \rightarrow ISOP1OH2N3O4CO + NO2] &= \text{CONST}(KRO2NO3) \\
\end{align*}
\]
Table S7. Molecular structure of the different isomers with chemical formula C₄H₇NO₅ and their corresponding MCM name.

| Molecular Structure | MCM name  |
|---------------------|-----------|
| ![Structure 1](image1) | MACRNB    |
| ![Structure 2](image2) | MACRNO3   |
| ![Structure 3](image3) | HMVKANO3  |
| ![Structure 4](image4) | MVKNO3    |
Figure S6. (Top) Analytical formation pathways of C₄H₇NO₅ isomer by HC₄CCHO (reaction R6 in the main text). (Bottom) Analytical formation pathways of C₄H₇NO₅ isomer by HC₄ACHO (reaction R7 in the main text).
The comparison of the modeled and the measured C₄H₇NO₅ time profiles are in good agreement for experiments 2 and 3 (Figure S7 and S8) (see also Figure 3 and Table S1). However, the estimated concentrations differ between the model and the measurements. The discrepancy varies depending on the experiment by a factor of 10 to 22. The lowest difference was observed for experiment 2 (a factor of 10). One may note that in experiment 1 there was addition of propene. The model has not been utilized for the additional propene chemistry, thus there is higher discrepancy for experiment 1 compared to the others.

**Figure S7.** Comparison of the measured (black) and modeled (green) C₄H₇NO₅ formation during exp. 1 (enhanced RO₂ + HO₂, addition of propene). The sum “full FZJ-NO₃-isoprene” of the four main isomers is compared against the I-CIMS measurements.
Figure S8. Comparison of the measured (black) and modeled (green) $C_6H_7NO_5$ formation during exp. 2 (enhanced RO2). The sum "full FZJ-NO$_3$-isoprene" of the four main isomers is compared against the I-CIMS measurements.

Figure S9. Comparison of the measured (black) and modeled (green) $C_6H_7NO_5$ formation during exp. 3 (nighttime to daytime transition). The sum "full FZJ-NO$_3$-isoprene" of the four main isomers is compared against the I-CIMS measurements.
**Text S5. Go:PAM experiments**

Oxidation experiments of MVK by NO$_3$ radicals were conducted using the laminar-flow Go:PAM reactor (Tsiligiannis et al., 2019; Watne et al., 2018) and the I-CIMS. The NO$_3$ radicals were introduced by dissociation of N$_2$O$_5$ via a continuous diffusion source. N$_2$O$_5$ was synthesized by reacting pure NO$_2$ with excess ozone in a glass vessel. The formed N$_2$O$_5$ was collected passing through a cold trap (-78.5 °C) using dry ice and then transferred to a diffusion vial fitted with a capillary tube (Faxon et al., 2018). The transfer took place in a dry glove box to minimize the exposure to ambient moisture. The N$_2$O$_5$ diffusion source was kept in a water bath at a stable temperature, which was varied to control NO$_3$ concentration. The sum of the signals of NO$_3^-$ product at m/z 62 and the adduct ion of IN$_2$O$_5^-$ at m/z 235 was used to estimate the NO$_3$ concentration. The NO$_3$ was quantified introducing pure NO to titrate the NO$_3$ to NO$_2$ while it was monitored by a NO/NO$_x$ analyzer (CLD 700 AL chemiluminescence).

MVK was introduced via a second diffusion vial fitted with a capillary tube and held in a water bath to control the temperature. Here the diffusion flux was determined gravimetrically. Using the NO$_3$ loss due to MVK reaction and the produced amount of C$_4$H$_7$NO$_5$ as measured by the I-CIMS, an upper limit of the primary yield could be estimated to less than 5 ncps per ppb of NO$_3$ consumed (i.e., less than 0.01%) (Figure S10).

**Table S8. Experimental conditions of MVK oxidation by NO$_3$ radicals in the Go:PAM flow reactor.**

| [MVK]$_0$ (ppb) | [NO$_3$+N$_2$O$_5$]$_0$ (ppb) | Δ[NO$_3$+N$_2$O$_5$] (ppb) | C$_4$H$_7$NO$_5$ production (ncps) |
|-----------------|--------------------------------|---------------------------|----------------------------------|
| 1               | 200                            | 6                         | 0.57                             | 3.69                                    |
| 2               | 200                            | 30                        | 1.26                             | 11.87                                   |
| 3               | 200                            | 83                        | 2.60                             | 17.87                                   |
| 4               | 500                            | 6                         | 3.34                             | 4.63                                    |
| 5               | 500                            | 27                        | 7.41                             | 27.20                                   |
| 6               | 500                            | 30                        | 8.07                             | 28.84                                   |
| 7               | 500                            | 92                        | 11.80                            | 53.19                                   |
Figure S10. C₄H₇NO₅ formation versus the consumed oxidant during the oxidation of MVK by NO₃ radicals in the Go:PAM flow reactor. NO₃ was introduced using a N₂O₅ diffusion source with subsequent decomposition.

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