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Supplement of

Impact of ozone and inlet design on the quantification of isoprene-derived organic nitrates by thermal dissociation cavity ring-down spectroscopy (TD-CRDS)

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Supplement

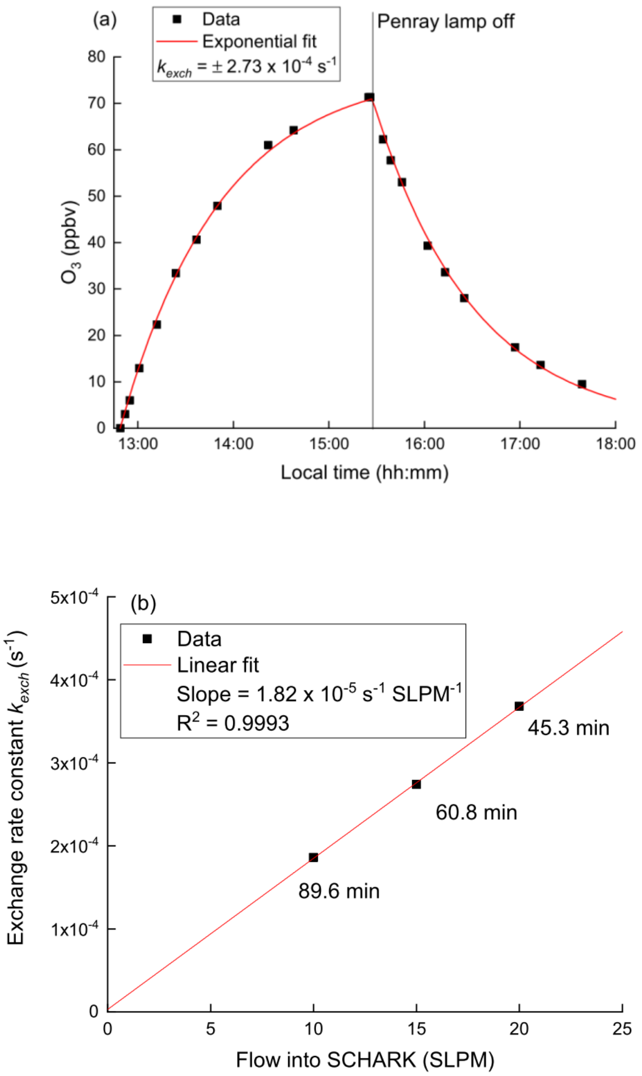

Figure S1: (a) Time-series of O_3 in the SCHARK at a flow rate of 15 SLPM dry zero-air. The Penray lamp used to generate O_3 was switched on at ~12:50 LT and switched off at 13:28 LT. The growth and depletion of the O_3 signal are reproduced by exponential expressions to derive the exchange constant (k_{exch}) **(b)** Dependence of k_{exch} on the total flow rate into the SCHARK. The linear regression indicates $k_{\text{exch}} = 1.82 \times 10^{-5}$ s^{-1} $SLPM^{-1}$.

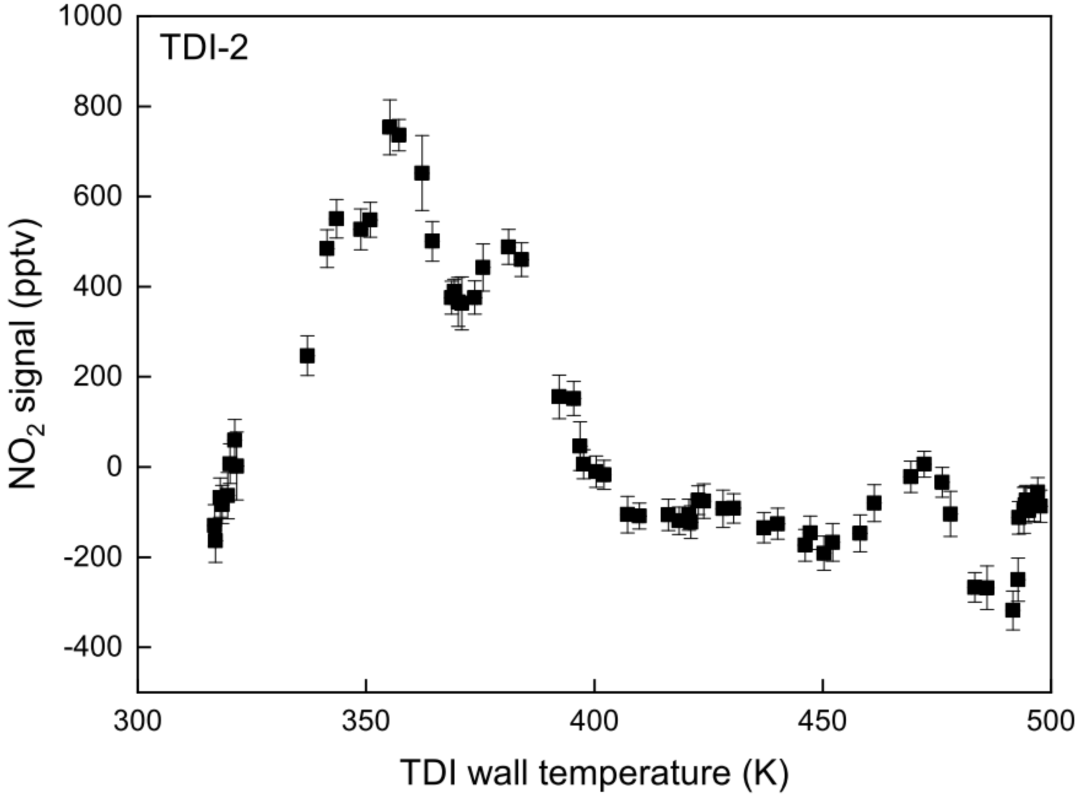

Figure S2: Dependence of NO_2 detection on TD temperature when sampling a mixture of 10.8 ppbv NO_2 in 15 SLPM humidified synthetic air (RH = 40%, 23°C) through TDI- 2. The NO_2 signal measured in the NO_2 cavity (unheated inlet) has been subtracted. The error bars represent standard deviation (1σ, 1 min) of the signal.

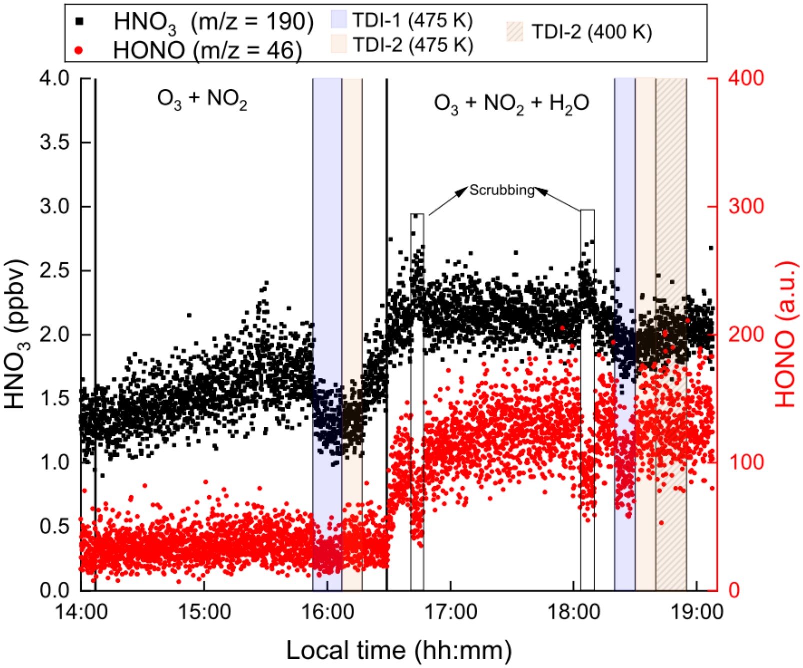

Figure S3: CIMS measurement of HNO_3 and HONO during an experiment in which NO_2 (10.8 ppbv) and O_3 (150 ppbv) were mixed in the SCHARK. At 16:30 LT the zero-air was humidified (RH = 23%, 23°C). Periods during which air from the SCHARK was first passed through TDI-1 or -2 prior to entering the CIMS are marked in blue and orange respectively. When the air was heated to 400 K while flowing through TDI-2 (yellow hatched) no effect was observed in the signal.

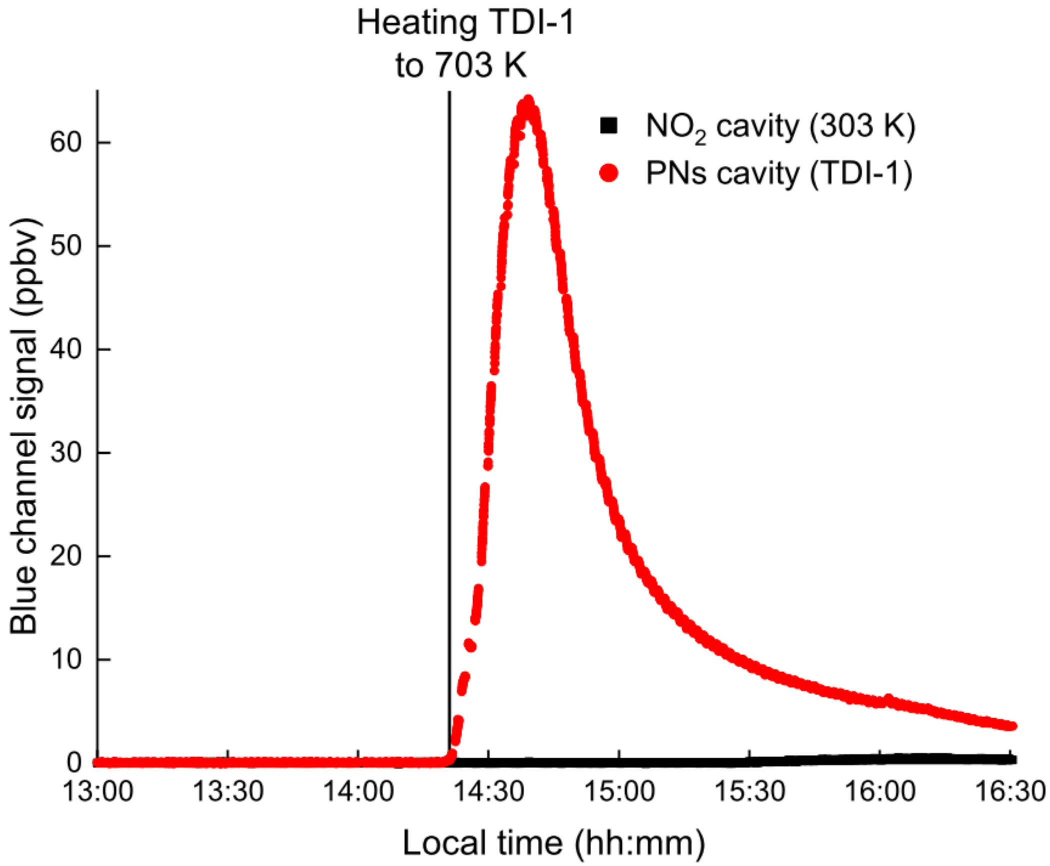

Figure S4: Unexpected detection of NO_2 in dry synthetic air when adding 120 ppbv O_3 to TDI-1. Initially, TDI-1 was at room temperature, with heating (to 703 K) of the TDI starting at ~14:20. When sampling via TDI-1 ~ 60 ppbv of NO_2 were observed, while no signal was registered when sampling into the NO_2 cavity through a cold inlet.

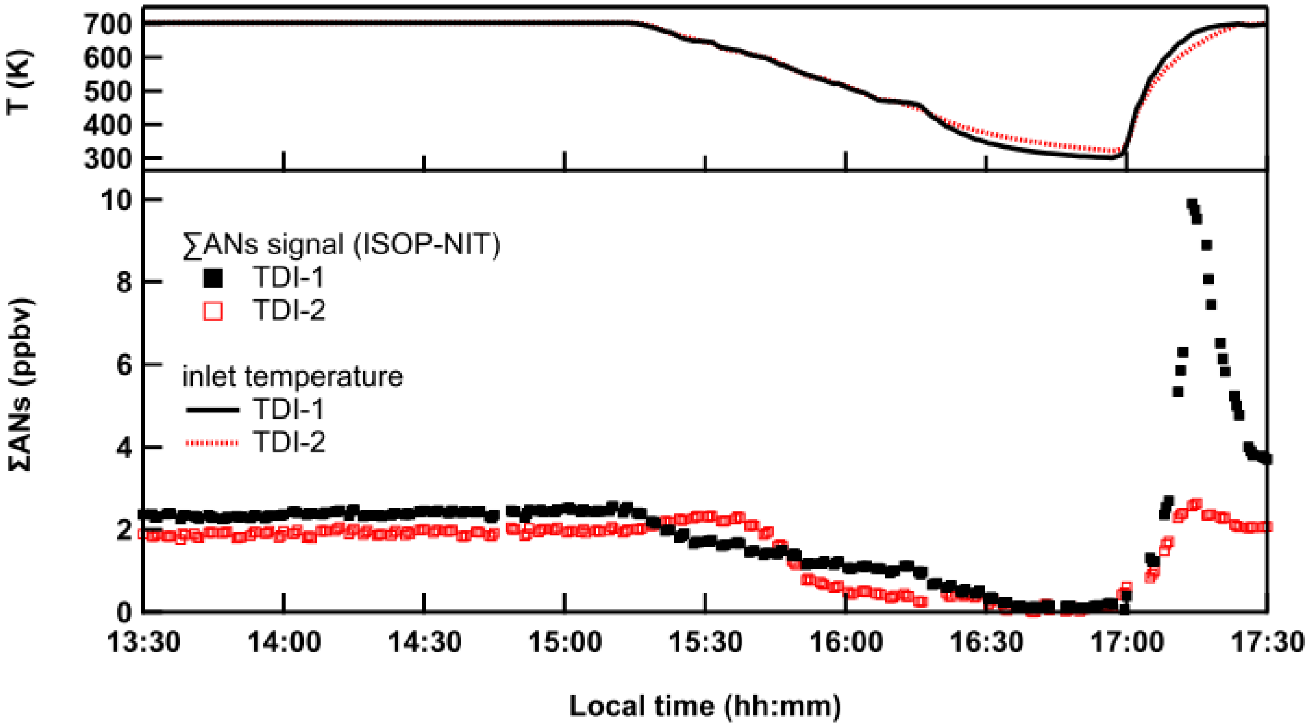

Figure S5: Mixing ratios of ISOP-NIT when sampling via TD-1 and TD-2 and different temperatures. ISOP-NIT was formed by flowing NO_2 (150 sccm of 1 ppmv) isoprene (9.8 sccm of 46.5 ppmv) and O_3 in 15 SLPM synthetic air into the SCHARK. The solid and dotted lines in the upper panel indicate the temperature of each TDI. At ~15:15 LT (when the signals were stable and the system in steady-state) the TDI temperatures were decreased to obtain a thermogram. For 30 min, starting at 16:30 LT both TDIs were kept close to room temperature before being re-heated to ~700 K at 17:00 LT. The strong increase in signal (above that observed at e.g. 15:00) observed when sampling via TD-1 indicates that ISOP-NIT can deposit on the glass beads and frit at lower temperatures. This effect is not observed for TDI-2 and is clearly related to the use of the glass-beads.

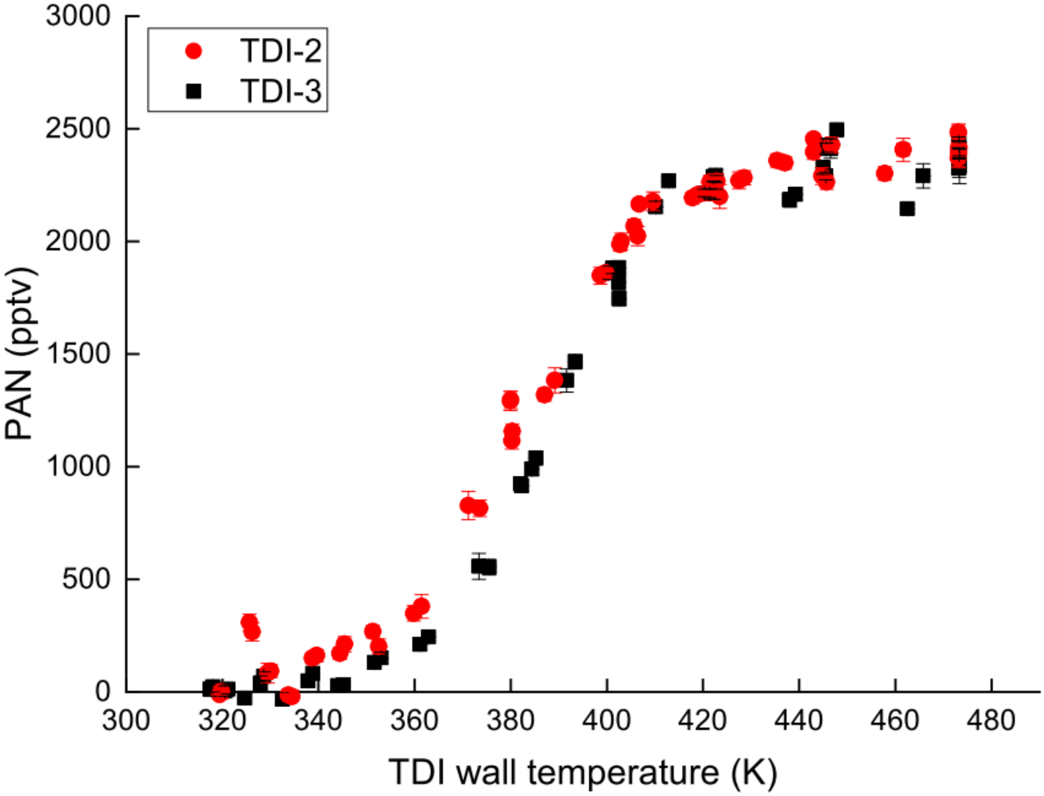

Figure S6: Thermograms of peroxy acetyl nitrate (PAN) obtained when sampling via TDI-2 and TDI-3. PAN (together with ~ 1.2 ppbv NO_2) was produced from a photochemical source as described recently (Eger et al., 2019) using the 285 nm photolysis of acetone in the presence of NO (Warneck and Zerbach, 1992; Flocke et al., 2005). The error bars represent standard deviation (1σ, 1 min) of the signal.

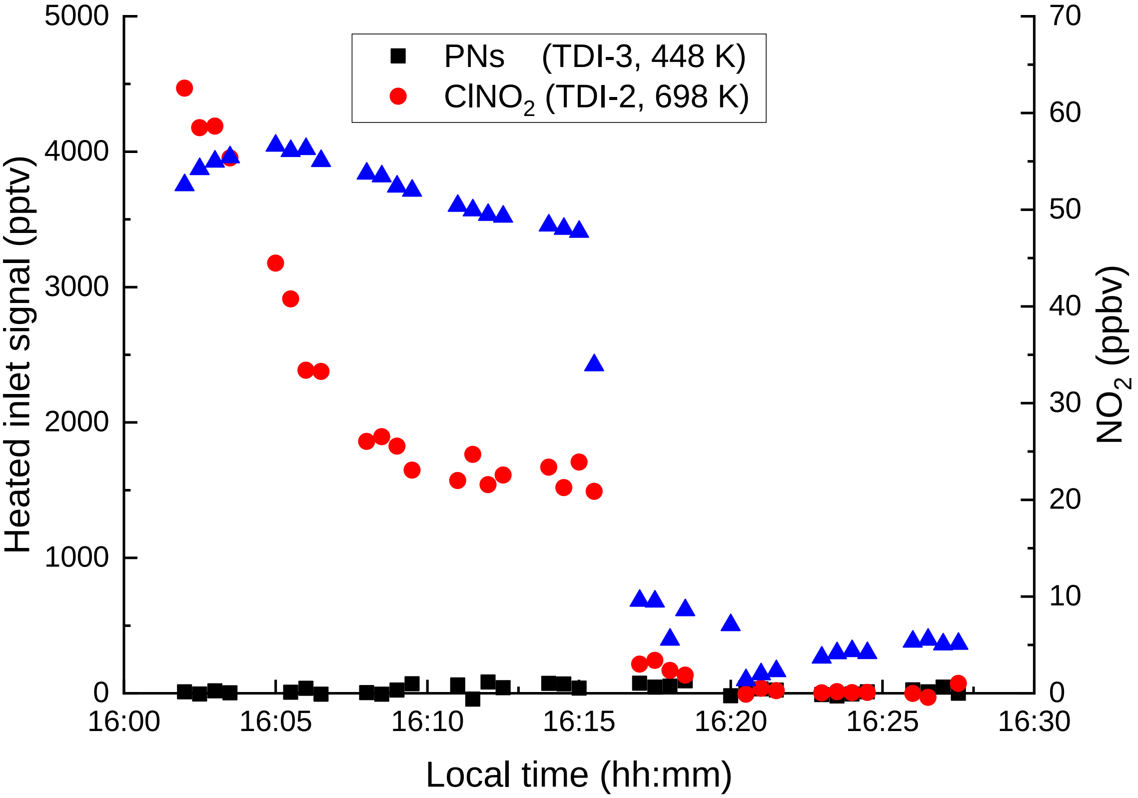

Figure S7: Mixing ratios of NO_2, PNs (measured with TDI-3 at 448 K) and $ClNO_2$ (measured with TDI-2 at 698 K) recorded with the TD-CRDS setup during an experiment in which Cl_2 (1-10 sccm of 50 ppmv in N_2) was passed through a glass bulb with sodium nitrate and diluted in 10 SLPM dry synthetic air. Variation of the amounts of $ClNO_2$ and NO_2 was achieved by changing the flow of Cl_2. The NO_2 signal measured with an unheated inlet was subtracted from the channels with TDIs. Note that, as expected, no signal additional to NO_2 was observed with TDI-3 at 448 K. Using TDI-2 at 698 K, $ClNO_2$ was detectable implying that it interferes detection of ANs.

S8 Detection of PAN, HONO and HNO_3 with I-CIMS

A chemical ionization mass spectrometer using iodide primary ions (I-CIMS) described recently (Dörich et al., 2021) was deployed to detect PAN, HONO and HNO_3. The I-CIMS was coupled to the SCHARK via ≈ 2m of ¼ inch PFA tubing heated to 40 °C. The flow rate through the PFA-tubing was ~2.1 SLM. Iodide anions were generated by passing 4 sccm of 400 ppmv methyl iodide (CH_3I in N_2) diluted in 750 sccm N_2 (Westfalen, 5.0) through a 370 MBq polonium (^{210}Po) source. PAN was thermally dissociated in an heated inlet (PFA tube at 170°C, residence time of 40 ms) to peroxy acetyl radicals which are detected as acetate ions $CH_3CO_2^-$ (*m/z* 59) after reaction with I^- (Phillips et al., 2013). Calibration was performed using a photochemical PAN source (Warneck and Zerbach, 1992). HNO_3 was detected as the $I^-(HNO_3)$ cluster ion at *m/z* 190 and calibrated using an HNO_3 permeation source characterised by optical absorption. HONO was detected as NO_2^- (*m/z* 46) using acetate anions (Veres et al., 2008) generated by adding a high concentration of PAN to the TD-inlet.

S9 Reaction scheme used for numerical simulations in inlets

```
*  Thermolysis of ozone and alkyl nitrates                ;

* ======================================================= ;
variable N2O5 NO3 NO OH HO2 HNO3 H2O2 HONO
HO2NO2 H2O ISOP O PROD PROD1 PROD2 ISOPNIT O3 NO2         ;
* ------------------------------------------------------- ;
* INITIAL CONCENTRATIONS                                  ;
* ------------------------------------------------------- ;
parameter O3i    3.53e12                                  ;
parameter NO2i   8.83e10                                 ;
parameter ISOPi  1.8e11                                  ;
parameter NO3i   8.82e7                                  ;
parameter N2O5i  8.82e8                                  ;
parameter NOi    0.0e10                                  ;
parameter O2                                             ;
parameter k1 k2 k2 k3 k4 k5 k6 k7 k8 k9 k10 k11 k12 k13 k14;
parameter k15 k16 k17 k18 k19 k20 k21 k22 k23 k24 k25 k26  ;
parameter k27 k28 k29 k30 k31 k32 k33 k34 k35              ;
parameter M                                                ;
parameter ISOPNITi 1.8E10                                  ;
parameter kWall 90                                         ;
* -------------------------------------------------------- ;
parameter P 543.478                                        ;
parameter T 298                                            ;
* --------------------------------------------------------;
*                                                         ;
COMPILE GENERAL                                           ;
M = P * 3.24E16 * 298/T                                   ;
O2 = 0.2*M                                                ;
**                                                        ;
COMPILE INITIAL                                           ;
N2O5  = N2O5i                                             ;
NO2 = NO2i                                                ;
O3 = O3i                                                  ;
O2 = O2i                                                  ;
NO = NOi                                                  ;
NO3 = NO3i                                                ;
ISOP = ISOPi                                              ;
ISOPNIT = ISOPNITi                                        ;
**                                                        ;
COMPILE EQUATIONS                                         ;
* --------------------------------------------------------;
* HOx and NOx chemistry                                   ;
*---------------------------------------------------------;
% k1                : N2O5 = NO3 + NO2                  ;
% k2                : NO2 + NO3 = N2O5                  ;
% k3                : NO + NO3 = NO2 + NO2              ;
% k4                : NO2 + O3 = NO3 + O2               ;
% k5                : NO + O3 = NO2 + O2                ;
% k6                : OH + O3 = HO2 + O2                ;
% k7                : HO2 + O3 = OH + O2 + O2           ;
% k8                : OH + HO2 = H2O + O2               ;
% k9                : OH + NO2 = HNO3                   ;
% k10               : OH + NO3 = HO2 + NO2              ;
% k11               : HO2 + NO3 = OH + NO2 + O2         ;
% k12               : OH + H2O2 = HO2 + H2O             ;
% k13               : HO2 + HO2 = H2O2 + O2             ;
% k14               : OH + NO = HONO                    ;
% k15               : HO2 + NO = OH + NO2               ;
% k16               : HO2 + NO2 = HO2NO2                ;
% k17               : HO2NO2 + OH = NO2 + H2O + O2      ;
% k18               : OH + HONO = NO2 + H2O             ;
% k19               : OH + HNO3 = NO3 + H2O             ;
% k20               : HO2NO2 = HO2 + NO2                ;
*-------------------------------------------------------;
* ISOPRENE oxidation                                    ;
*-------------------------------------------------------;
% k21*0.74          : ISOP + O3 = PROD                  ;
% k21*0.26          : ISOP + O3 = OH                    ; IUPAC recommended yield
% k22               : ISOP + NO3 = PROD                 ;
```

```
% k23               : ISOP + OH = PROD                  ;
*-------------------------------------------------------;
* Ox chemistry                                          ;
*-------------------------------------------------------;
% k24               : O3 = O + O2                         ; Peukert et al.
% k25               : O + O3 = O2 + O2                    ; IUPAC
% k26               : O + O2 = O3                         ; IUPAC
% k27               : O + H2O = OH + OH                 ;
% kWall             : O =                               ;
% k28               : NO2 + O = O2 + NO                 ; bimolecular
% k29               : NO2 + O = NO3                     ; termolecular
% k30               : NO3 + O = O2 + NO2                ;
% k31               : O + NO = NO2                      ;
*-------------------------------------------------------;
* Thermolysis of alkyl nitrates                         ;
*-------------------------------------------------------;
% k32             : ISOPNIT = NO2 + PROD1               ;
% k33             : ISOPNIT + O = NO2 + PROD2 + O2      ;
% k34             : ISOP + O = PROD                     ;
% k21             : ISOPNIT + O3 = NO2 + PROD2 + OH     ;
*-------------------------------------------------------;
*Rate equations                                         ;
k1 = ((1.3e-3*(T/300)@-3.5*exp(-11000/T))*M*
(9.7e14*(T/300)@0.1*exp(-11080/T)))/((1.3e-3*
(T/300)@-3.5*exp(-11000/T))*M+(9.7e14*(T/300)@0.1*
exp(-11080/T)))*10@(log10(0.35)/(1+(log10((1.3e-3*(T/300)@-3.5
*exp(-11000/T))*M/(9.7e14*(T/300)@0.1*exp(-11080/T)))
/(0.75-1.27*log10(0.35)))@2))                             ; N2O5 decomp IUPAC
k2 = ((3.6e-30*(T/300)@-4.1)*M*(1.9e-12*(T/300)@0.2))
/((3.6e-30*(T/300)@-4.1)*M+(1.9e-12*(T/300)@0.2))*
10@(log10(0.35)/(1+(log10((3.6e-30*(T/300)@-4.1)*
M/(1.9e-12*(T/300)@0.2))/(0.75-1.27*log10(0.35)))@2))     ; NO2 + NO3 IUPAC
k3 = 1.8E-11*exp(110/T)                                    ;IUPAC NO + NO3 (220-420)K
k4 = 1.4E-13 * exp (-2470/T)                               ;IUPAC NO2 + O3 (230-360)K
k5 = 2.07E-12 * exp (-1400/T)                              ;IUPAC NO + O3 (195-310)K
k6 = 1.70E-12*EXP(-940/T)                                  ;IUPAC OH + O3 (220-450)K
k7 = 2.03E-16*(T/300)@4.57*EXP(693/T)                      ;IUPAC HO2 + O3 (250-340)K
k8 = 4.8E-11*EXP(250/T)                                    ;IUPAC HO2 + OH (250-400)K
k9 = ((3.2e-30*(T/300)@-4.5)*M*(3.0e-11))/
((3.2e-30*(T/300)@-4.5)*M+(3.0e-11))*10@(log10(0.41)/
(1+(log10((3.2e-30*(T/300)@-4.5)*M/(3.0e-11))/
(0.75-1.27*log10(0.41)))@2))                              ; IUPAC HNO3 formation
k10 = 2E-11                                                ; IUPAC OH + NO3 (298K)
k11 = 4E-12                                                ; IUPAC HO2 + NO3 (298K)
k12 = 2.9E-12*exp(-160/T)                                  ; IUPAC OH + H2O2 (240-460)K
k13 = 2.20E-13*(1+(1.40E-21*EXP(2200/T)*H2O))*EXP(600/T)   ; IUPAC H2O2 formation (230-420)K
k14 = ((7.4e-31*(T/300)@-2.4)*M*(3.3e-11*(T/300)@-0.3))/
((7.4e-31*(T/300)@-2.4)*M+(3.3e-11*(T/300)@-0.3))*
10@(log10(0.81)/(1+(log10((7.4e-31*(T/300)@-2.4)*M/
(3.3e-11*(T/300)@-0.3))/(0.75-1.27*log10(0.81)))@2))      ; IUPAC HONO formation
k15 = 3.45E-12*exp(270/T)                                  ; IUPAC HO2 + NO (200-400)K
k16 = ((1.4e-31*(T/300)@-3.1)*M*(4.0e-12))/
((1.4e-31*(T/300)@-3.1)*M+(4.0e-12))*10@(log10(0.4)/
(1+(log10((1.4e-31*(T/300)@-3.1)*M/(4.0e-12))/
(0.75-1.27*log10(0.4)))@2))                               ; IUPAC HO2 + NO2
k17 = 3.2e-13*EXP(690/T)                                   ; IUPAC HO2NO2 + OH (210-300)K
k18 = 2.5e-12*EXP(260/T)                                   ; IUPAC HONO + OH (290-380)K
k19 = 2.40E-14*EXP(460/T) + ((6.50E-34*EXP(1335/T)*M)/
(1+(6.50E-34*EXP(1335/T)*M/2.70E-17*EXP(2199/T))))         ; IUPAC OH + HNO3
k20 = ((4.1e-5*exp(-10650/T))*M*(6.0e15*exp(-11170/T)))/
((4.1e-5*exp(-10650/T))*M+(6.0e15*exp(-11170/T)))*
10@(log10(0.4)/(1+(log10((4.1e-5*exp(-10650/T))*M/
(6.0e15*exp(-11170/T)))/(0.75-1.27*log10(0.4)))@2))       ; IUPAC HO2NO2 decomposition
k21 = 1.05E-14*exp(-2000/T)                                ; O3 + ISOP - IUPAC
k22 = 2.95E-12*exp(-450/T)                                 ; NO3 + ISOP - IUPAC
k23 = 2.1E-11*exp(465/T)                                   ; OH + ISOP - IUPAC
k24 = (37800*(T@-4.37)*EXP(-13738/T))*M*(1370000000000000*
(T@-0.67)*EXP(-13080/T))*10@(LOG10((1-0.647)*
EXP(-T/0.000391)+0.6417*EXP(-T/8680.74)+EXP(-6060.75/T))/
(1+(LOG10((37800*(T@-4.37)*EXP(-13738/T))*M/
(1370000000000000*(T@-0.67)*EXP(-13080/T)))/
(0.75-1.27*LOG10((1-0.647)*EXP(-T/0.000391)+0.6417*
EXP(-T/8680.74)+EXP(-6060.75/T))))@2))/
```

```
((37800*(T@-4.37)*EXP(-13738/T))*M+(1370000000000000*(T@-0.67)*
EXP(-13080/T)))                                            ; O3 thermolysis (T>700K), Peukert et al., 2013
k25 = 8E-12*exp(-2060/T)                                   ; IUPAC O + O3 (200-400)K
k26 = 6.0E-34*((T/300)@-2.6)*M                             ; IUPAC O + O2 (200-300)K
k27 = 8.44E-14*(T@0.946)*exp(-8571/T)                      ; O(3P) + H2O (250-2400)K Lifshitz et al., 1990
k28 = 5.1E-12*exp(198/T)                                   ; IUPAC NO2 + O (220-420)K
k29 = ((1.3e-31*(T/300)@-1.5)*M*(2.3e-11*(T/300)@0.24))/
((1.3e-31*(T/300)@-1.5)*M+(2.3e-11*(T/300)@0.24))*10@(log10(0.6)/
(1+(log10((1.3e-31*(T/300)@-1.5)*M/(2.3E-11*(T/300)@0.24))/
(0.75-1.27*log10(0.6)))@2))                                ; IUPAC termol NO2 + O
k30 = 1.7E-11                                              ; IUPAC NO3 + O (298K)
k31 = ((1.0e-31*(T/300)@-1.6)*M*(5e-11*(T/300)@-0.3))/
((1.0e-31*(T/300)@-1.6)*M+(5e-11*(T/300)@-0.3))*10@(log10(0.85)/
(1+(log10((1.0e-31*(T/300)@-1.6)*M/(5e-11*(T/300)@-0.3))/
(0.75-1.27*log10(0.85)))@2))                               ; IUPAC O + NO

k32 = 7.34E15*exp(-19676/T)                                ; thermolysis n-propylnitrate
k33 = 3.9E-12*exp(680/T)                                   ; 2-methyl-2-butene - Herron & Huie, 1973 (298-400K)
k34 = 3.5E-11                                              ; Paulson et al., 1995 (298K)
**                                                      ;
COMPILE INSTANT                                         ;
open 7   "thermo.sim" new                               ;
**                                                        ;
COMPILE BLOCK 3                                           ;
PSTREAM 3                                                 ;
**                                                        ;
COMPILE BLOCK 4                                           ;
T = 425                                                   ;
**                                                        ;
COMPILE BLOCK 5                                           ;
T = 298                                                   ;
**                                                        ;
COMPILE BLOCK 6                                           ;
T = 303                                                   ;
**                                                        ;
PSTREAM 3 7                                               ;
time O3 O NO2 M T PROD1 PROD2 ISOPNIT                     ;
**                                                        ;
when
1)  time = 0 + 0.01*128 call block 3                      ;
2)  time = 0.007 call block 4 restart                     ;
3)  time = 0.335 call block 5   restart                    ;
4)  time = 1.08 call block 6  restart                     ;
**                                                        ;
*hmax 0.01                                                ;
BEGIN                                                     ;
STOP                                                      ;
```

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