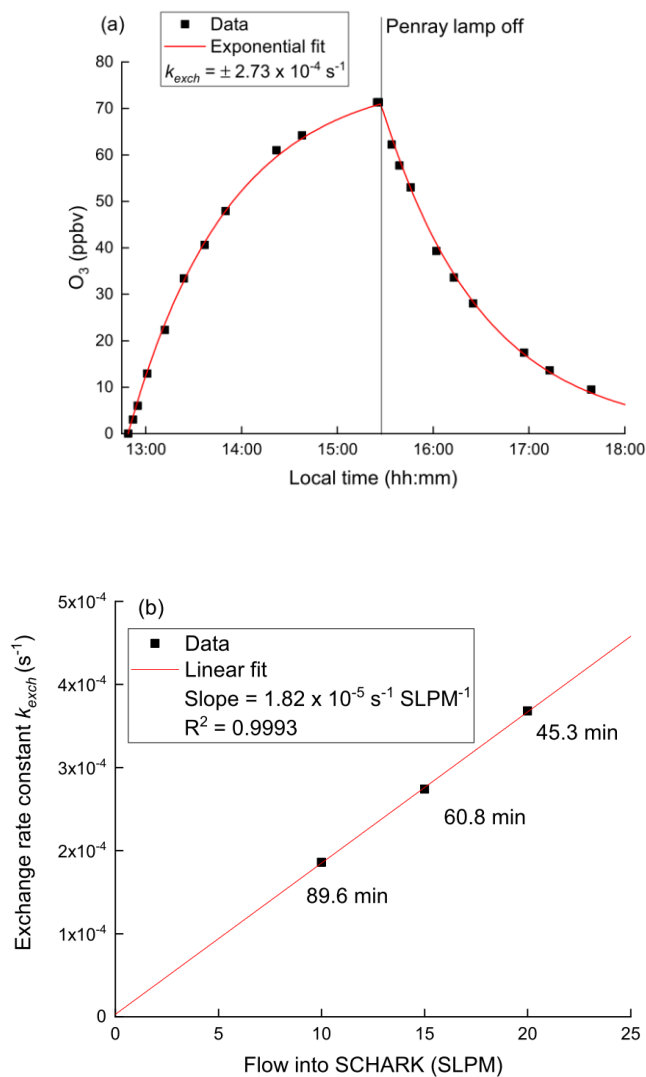
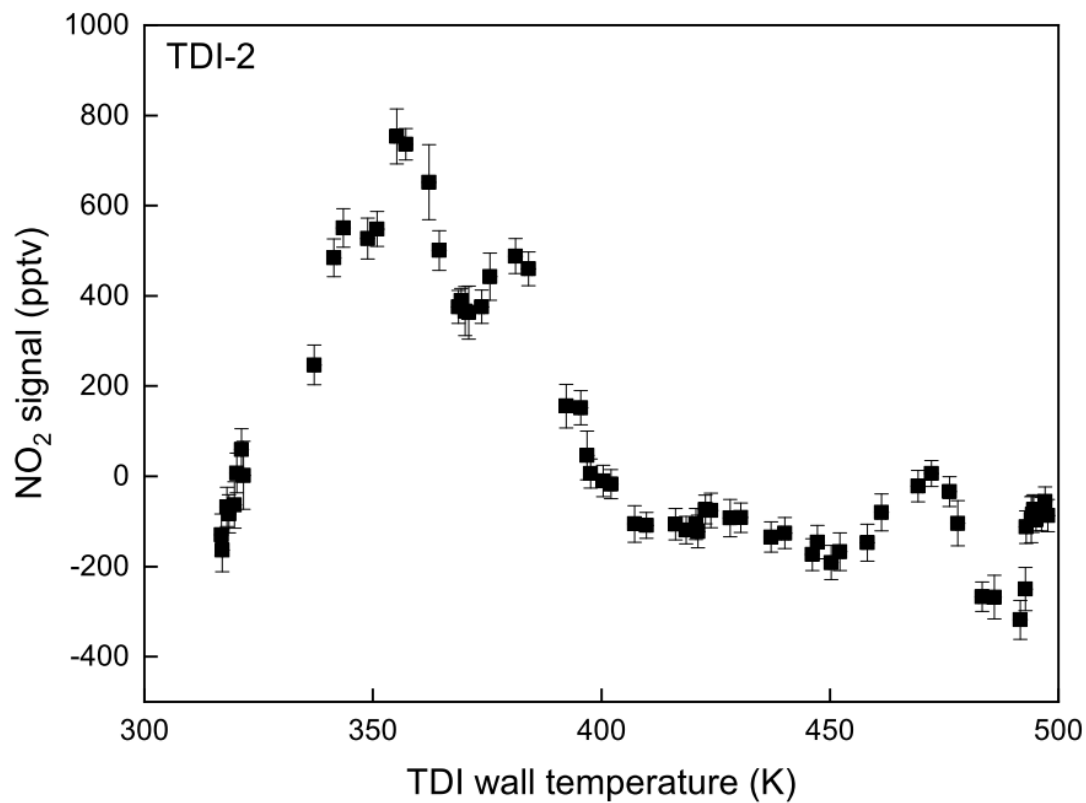


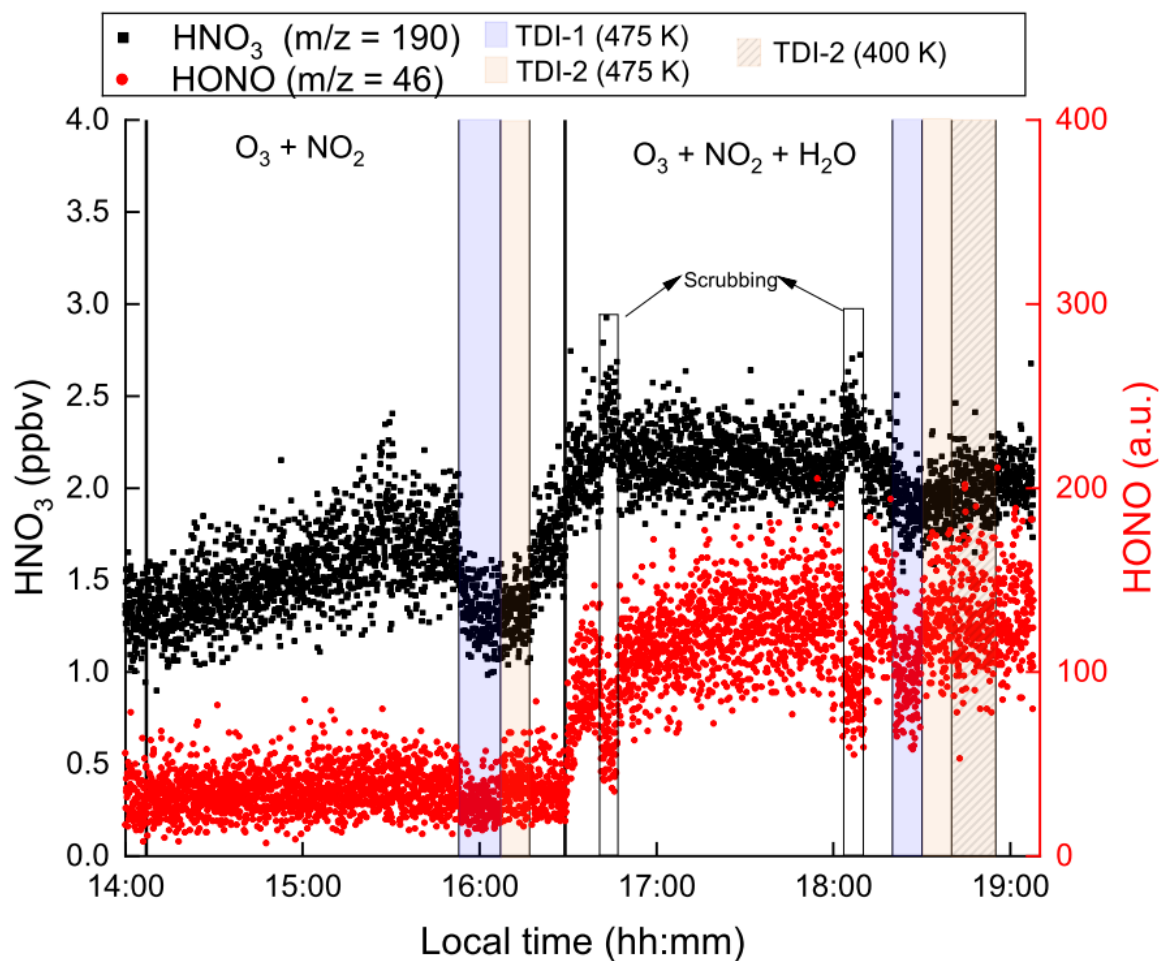
## Supplement



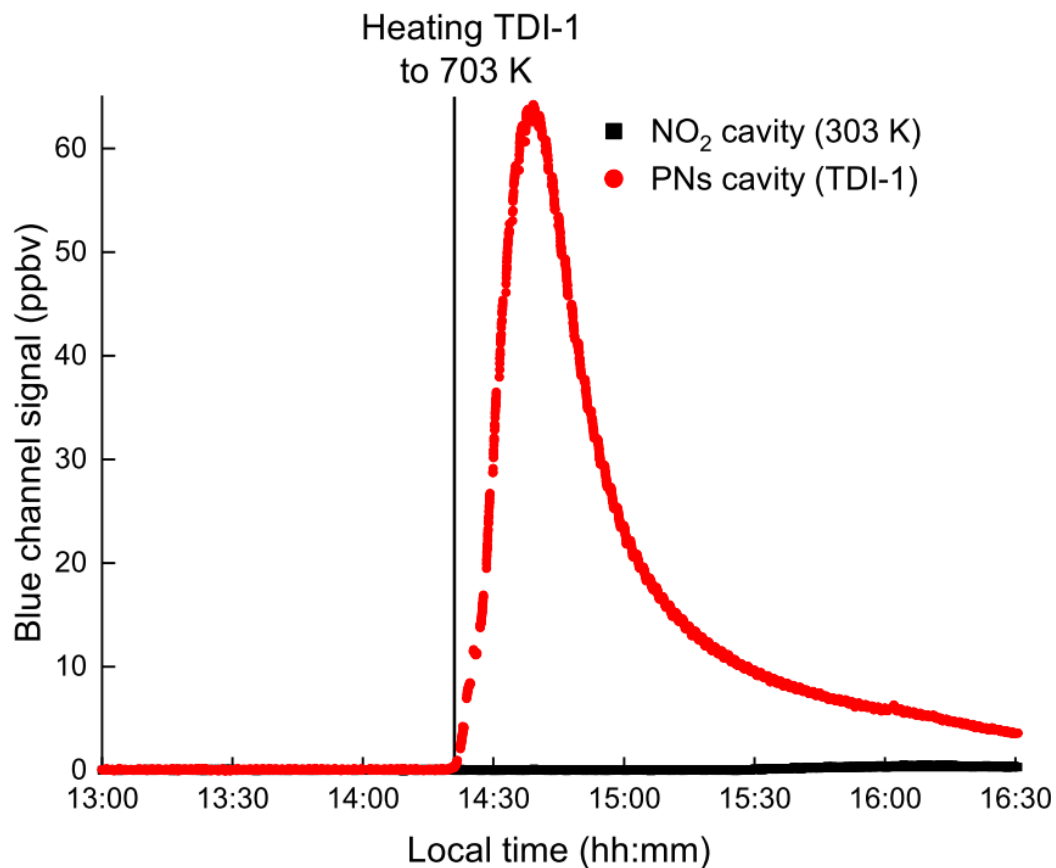
**Figure S1:** (a) Time-series of  $O_3$  in the SCHARK at a flow rate of 15 SLPM dry zero-air. The Penray lamp used to generate  $O_3$  was switched on at ~12:50 LT and switched off at 13:28 LT. The growth and depletion of the  $O_3$  signal are reproduced by exponential expressions to derive the exchange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



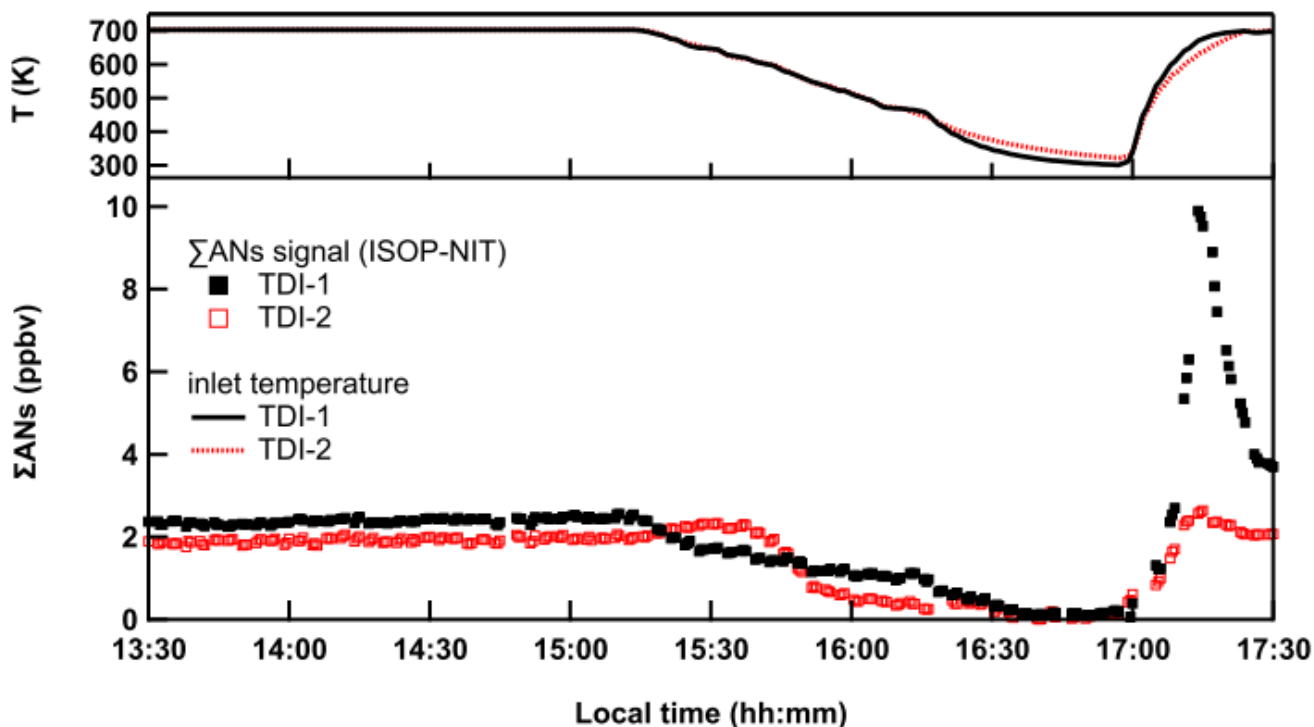
**Figure S2:** Dependence of NO<sub>2</sub> detection on TD temperature when sampling a mixture of 10.8 ppbv NO<sub>2</sub> in 15 SLPM humidified synthetic air (RH = 40%, 23°C) through TDI- 2. The NO<sub>2</sub> signal measured in the NO<sub>2</sub> cavity (unheated inlet) has been subtracted. The error bars represent standard deviation (1 $\sigma$ , 1 min) of the signal.



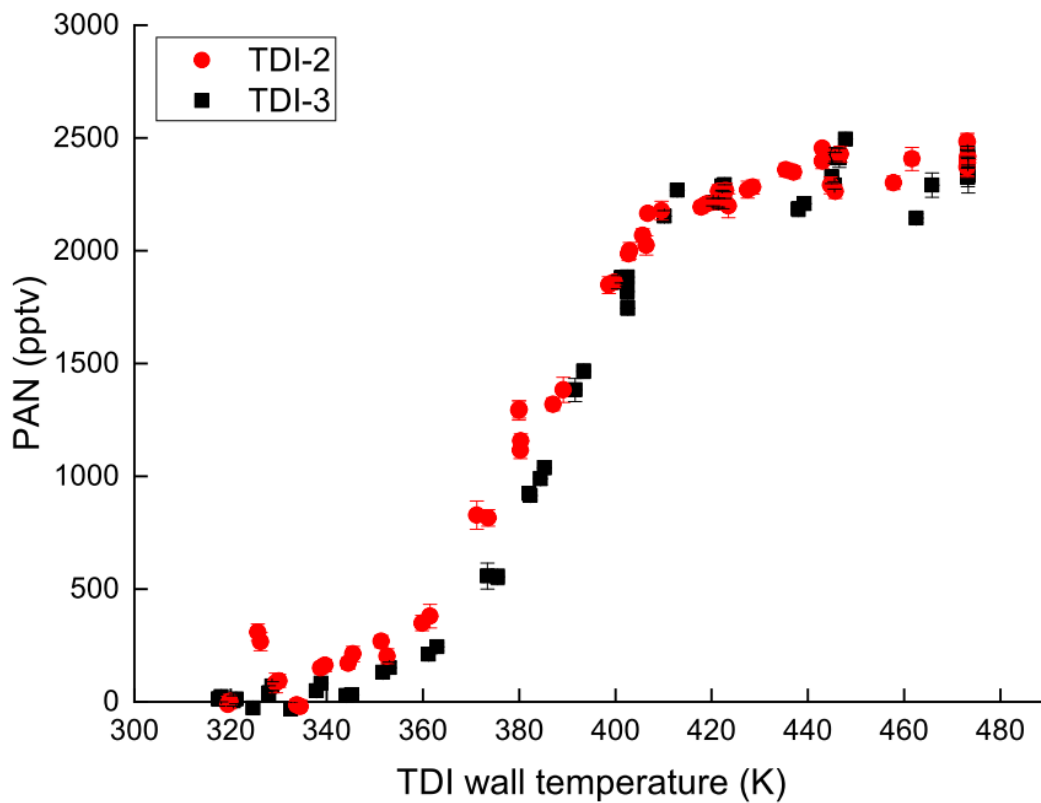
**Figure S3:** CIMS measurement of HNO<sub>3</sub> and HONO during an experiment in which NO<sub>2</sub> (10.8 ppbv) and O<sub>3</sub> (150 ppbv) were mixed in the SCHARK. At 16:30 LT the zero-air was humidified (RH = 23%, 23°C). Periods during which air from the SCHARK was first passed through TDI-1 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<sub>2</sub> in dry synthetic air when adding 120 ppbv O<sub>3</sub> 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<sub>2</sub> were observed, while no signal was registered when sampling into the NO<sub>2</sub> 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  $\text{NO}_2$  (150 sccm of 1 ppmv) isoprene (9.8 sccm of 46.5 ppmv) and  $\text{O}_3$  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  $\sim 1.2$  ppbv  $\text{NO}_2$ ) 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 ( $1\sigma$ , 1 min) of the signal.



```

% 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*(13700000000000000*
(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/
(13700000000000000*(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
;

```

## References

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Warneck, P., and Zerbach, T.: Synthesis of peroxyacetyl nitrate in air by acetone photolysis, *Environmental Science & Technology*, 26, 74-79, 1992.