Influence of ambient NO and NO_2 on the quantification of total peroxy nitrates (∑PNs) and total alkyl nitrates (∑ANs) by thermal dissociation cavity ring-down spectroscopy (TD-CRDS)

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Supplement

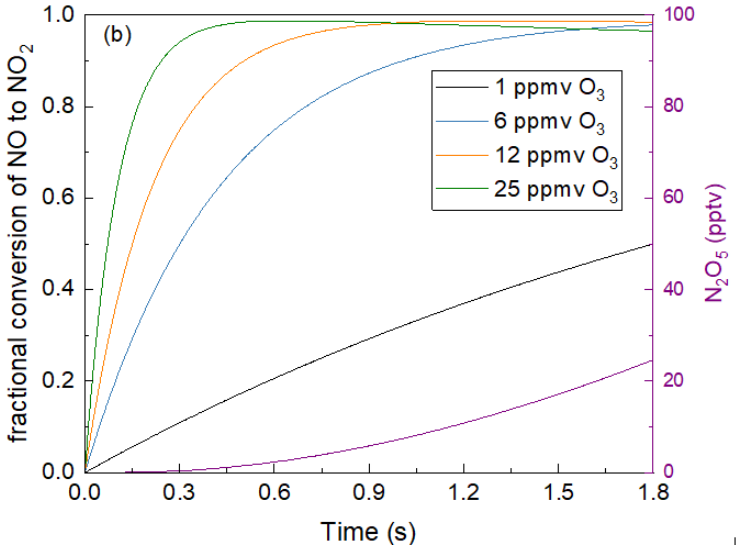

Figure S1: Numerical simulation of the conversion of NO to NO_2 in the presence of O_3. The reaction scheme used is given below, the rate coefficients are those preferred by IUPAC (IUPAC, 2024).

$NO + O_3 \rightarrow NO_2 + O_2$	k = 2.07e-12*exp(-1400/T)
$NO_2 + O_3 \rightarrow NO_3 + O_2$	k =1.4e-13*exp(-2470/T)
$NO + NO_3 \rightarrow 2\ NO_2$	k =1.8e-11*exp(110/T)
$NO_3 + NO_2 \rightarrow N_2O_5$	k_0 = 3.6e-30*(T/300)$^{-4.1}$
	k_∞ = 1.9e-12*(T/300)$^{0.2}$
	Fc = 0.35
$N_2O_5 \rightarrow NO_2 + NO_3$	k_0 = 1.3e-3*(T/300)$^{-3.5}$*exp(-11000/T)
	k_∞ = 9.7e14*(T/300)$^{0.1}$*exp(-11080/T)
	Fc = 0.35

Rate coefficients for termolecular reactions were calculated using the parameters k_0, k_∞ and Fc and the "Troe expression" as defined by IUPAC (IUPAC, 2024).

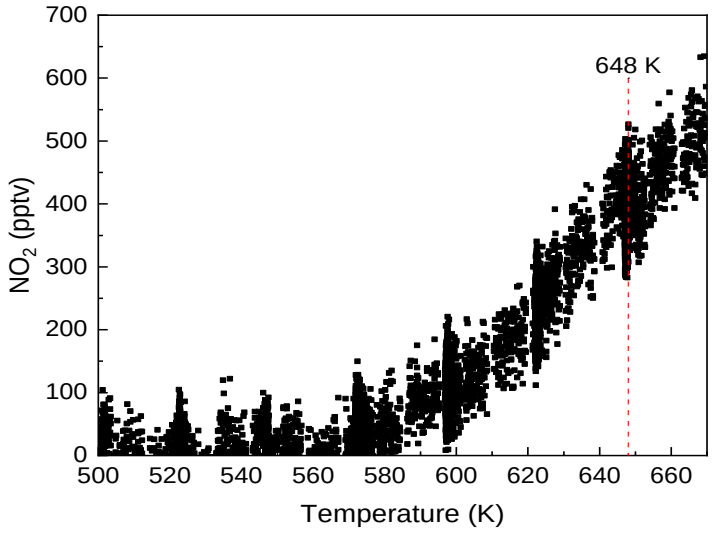

Figure S2: Effect of adding acetone (43 ppmv) to the TD-inlet associated with the ΣANs cavity in the presence of 16 ppbv NO. The vertical red line indicates the normal operating temperature of the inlet at which ~ 400 pptv NO_2 are observed.

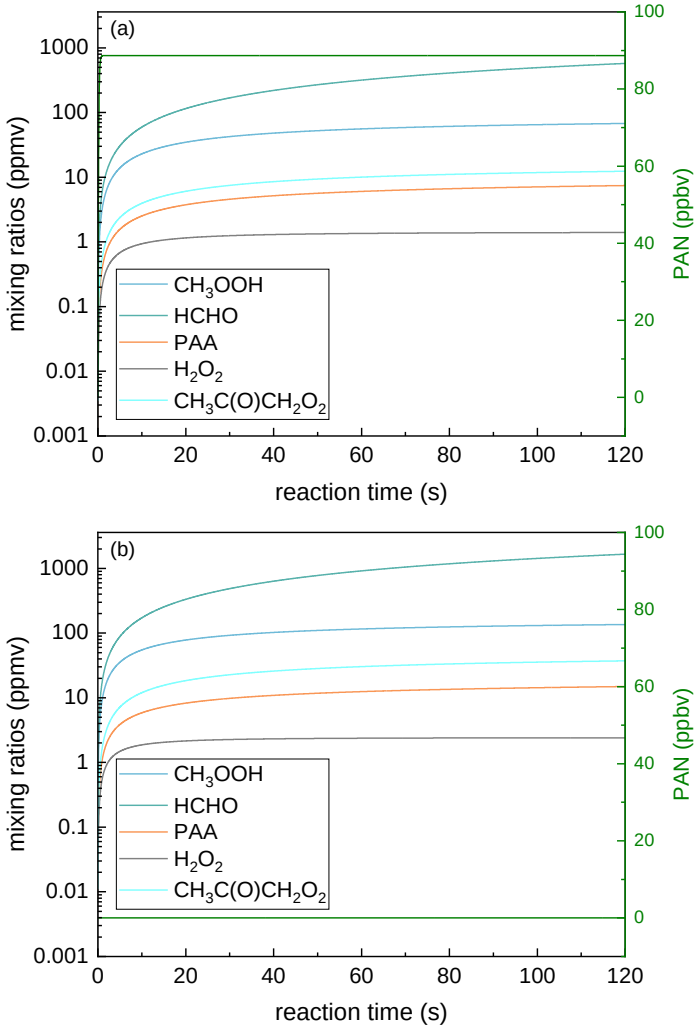

Figure S3: (a) Numerical simulation of the photochemical PAN reactor: 89 ppbv NO and 0.2 % acetone lead to the production of 88 ppbv PAN (right y-axis). **(b)** Same simulation but without NO (and therefore no PAN production). The reaction scheme used is listed in Table S1.

35

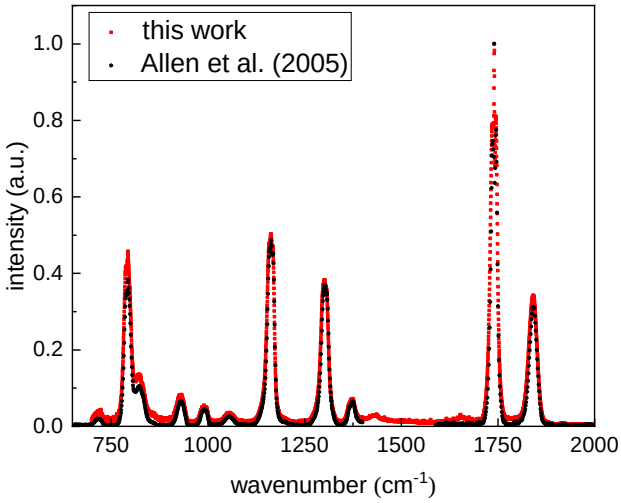

Figure S4: Intensity-normalised, averaged FTIR spectrum of PAN in air (red symbols) recorded at a resolution of 0.5 cm^{-1}. Good agreement to values from Allen et al. (2005) (black symbols).

Table S1: Reactions considered in the numerical simulation of the PAN photochemical source.

Reaction	Rate coefficient
$CH_3C(O)CH_3$ (+ O_2) → $CH_3C(O)O_2$ + CH_3O_2	[a]2.94e-3
HO_2 + NO → OH + NO_2	3.45e-12*exp(270/T)
OH + CO → HO_2	1.44e-13* (1+M/4.2e19)
OH + O_3 → HO_2	1.7e-12*exp(-940/T)
HO_2 + O_3 → OH + 2 O_2	2.03e-16*(T/300)$^{4.57}$*exp(693/T)
OH + HCHO → HO_2	5.4e-12*exp(135/T)
CH_3O_2 + NO (+ O_2) → NO_2 + HO_2 + HCHO	2.3e-12*exp(360/T)
CH_3O_2 + HO_2 → CH_3OOH + O_2	3.8e-13*exp(780/T)
CH_3OOH + OH → CH_3O_2 + H_2O	5.3e-12*exp(190/T)*0.6
CH_3OOH + OH (+ O_2) → OH + HO_2 + HCHO	5.3e-12*exp(190/T)*0.4
$CH_3C(O)O_2$ + NO_2 + M → PAN + M	k_0 = 2.7e-28*(T/300)$^{-7.1}$ k_∞ = 1.2E-11*(T/300)$^{-0.9}$ Fc = 0.3
PAN → $CH_3C(O)O_2$ + NO_2	k_0 = 4.9e-3*exp(-12100/T) k_∞ = 7.5e16*exp(-13830/T) Fc = 0.3
$CH_3C(O)O_2$ + HO_2 → $CH_3C(O)OOH$ + O_2	1.5e-12*exp(480/T)
$CH_3C(O)O_2$ + HO_2 → $CH_3C(O)OH$ + O_3	4.4e-15*exp(1910/T)
$CH_3C(O)O_2$ + HO_2 → OH + CH_3O_2 + CO_2	4.66e-12*exp(235/T)
$CH_3C(O)O_2$ + NO (+O_2) → NO_2 + CH_3O_2 + CO_2	7.5e-12*exp(290/T)
OH + PAA → $CH_3C(O)O_2$ + H_2O	3.0e-14
$CH_3C(O)O_2$ + CH_3O_2 → $CH_3C(O)OH$ + HCHO	2.0e-12*exp(500/T)*0.1
$CH_3C(O)O_2$ + CH_3O_2 → HO_2 + CH_3O_2 + HCHO	2.0e-12*exp(500/T)*0.9
CH_3O_2 + CH_3O_2 → 2 HCHO + 2 HO_2	1.03e-13*exp(365/T)*0.63
CH_3O_2 + CH_3O_2 → HCHO + CH_3OH + O_2	1.03e-13*exp(365/T)*0.37
HO_2 + HCHO → $HOCH_2OO$	9.7e-15*exp(625/T)
$HOCH_2OO$ + NO → NO_2 + HO_2 + HCOOH	5.6e-12
$HOCH_2OO$ + HO_2 → $HOCH_2OOH$ + O_2	0.5*1.2e-11
$HOCH_2OO$ + HO_2 → HCOOH + O_2	0.3*1.2e-11
$HOCH_2OO$ + HO_2 → HO_2 + OH + HCHO	0.2*1.2e-11
$HOCH_2OOH$ + OH → $HOCH_2OO$ +H_2O	1e-11
$CH_3C(O)OH$ + OH (+ O_2) → CH_3O_2 + CO_2 + H_2O	4.0e-14*exp(850/T)
CH_3OH + OH (+O_2) → HCHO + HO_2 + H_2O	2.85e-12*exp(-345/T)
$CH_3C(O)CH_3$ + OH → $CH_3COCH_2O_2$ + H_2O	8.8e-12*exp(-1320/T) + 1.7e-14*exp(423/T)
$CH_3COCH_2O_2$ + NO → NO_2 + $CH_3C(O)O_2$ + HCHO	8e-12
NO + O_3 → NO_2	3.0e-12*exp(-1500/T)
OH + NO_2 → HNO_3 + NO_2	k_0 = 3.2e-30*(T/300)$^{-4.5}$ k_∞ = 3.0x 10^{-11} Fc = 0.41
HO_2 + HO_2 → H_2O_2	2e-12
H_2O_2 + OH → HO_2	2.9e-12*exp(-160/T)
OH + NO → HONO	k_0 = 7.4e-31*(T/300)$^{-2.4}$ k_∞ = 3.3e-11*(T/300)$^{-0.3}$ Fc = 0.81
OH + HONO → NO_2	2.5e-12*exp(260/T)

Notes: [a]Calculated from measured photolysis rate of O_3 combined with acetone and O_3 cross sections and quantum yields at 280 nm. M = molecular density in molecule cm^{-3} and T is the temperature in K. Rate coefficients for termolecular reactions were calculated using the parameters k_0, k_∞ and Fc and the "Troe expression" as defined by IUPAC (IUPAC, 2024).

References

Allen, G., et al.: Improved mid-infrared cross-sections for peroxyacetyl nitrate (PAN) vapour, Atmos. Chem. Phys., 5, 47-56, 2005.

IUPAC: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.). Last access Sept. 2024, https://iupac.aeris-data.fr/, 2024.