# Airborne measurements of nitrous acid (HONO), hydroxyl (OH), nitric oxide (NO), hydroperoxyl (HO<sub>2</sub>), and nitrogen dioxide (NO<sub>2</sub>) in the upper troposphere (UT): is peroxynitrous acid (HOONO) a source of HONO?



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### Measurements of excess HONO in the troposphere



Fig. 1: Altitude profiles of HONO volume mixing ratios from the EMeRGe-EU (2017), -Asia (2018), and CAFE-Africa (2018) campaigns. The high VMRs in the lower troposphere during EMeRGe and the upper troposphere during CAFE exceed predictions of the EMAC and MECO(n) models by a factor of 2-10.

- Excess HONO (relative to model predictions) is observed in the polluted air masses of the EMeRGe campaigns, above the boundary layer, and into the free troposphere.
- are several potential heterogeneous sources of HONO; most require NO<sub>2</sub> and aerosol or cloud particles.
- The correlation between reactants (or proxies thereof) and the HONO source depends on the chemical composition of the air masses.

## Photolysis of particulate nitrate in the low-NO, MBL









Fig. 2: Altitude profiles of nitrogen containing species and aerosol surface area in the MBL during CAFE-Africa. The black line in the fourth panel represents HONO formed by the known gas phase reaction OH + NO.

- - exceeds model predictions as well as gas phase formation according to measured OH and NO.
  - Under these low-NO<sub>x</sub> conditions, photolysis of pNO<sub>3</sub> may explain HONO in the observed tens of ppt range (Ye et al., 2016).

#### References

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According to the literature there

No.	Reactants		Products	Reference	Commen
		Gas phase reactions			
1	NO + OH + M	$\rightarrow$	HONO + M	Sander et al. [2011]	(i)
2	ortho-nitrophenols $+ h\nu$	$\rightarrow$	HONO + products	Bejan et al. [2006]	(ii)
3	$\mathrm{HO}_2 \cdot \mathrm{H}_2\mathrm{O} + \mathrm{NO}_2$	$\rightarrow$	$HONO + O_2 + H_2O$	Li et al. [2014] Ye et al. [2015]	(iii)
4	$NO_2 + h\nu$	$\rightarrow$	$NO_2^*$	Crowley and Carl [1997]	(iv)
	$NO_2^* + H_2O$	$\rightarrow$	HONO + OH	Amedro et al. [2011]	
		Reactions on surfaces			
5	$\rm NO_2$ + HC <sub>red</sub>	$\rightarrow$	$HONO + HC_{ox}$	Ammann et al. [1998] Kalberer et al. [1999] Monge et al. [2010]	(v)
6	$2NO_{2(q)}$	$\longleftrightarrow$	$N_2O_{4(q)}$	Goodman et al. [1999]	(vi)
	$N_2O_{4(q)}$	$\longleftrightarrow$	$N_2O_4(surface)$	Finlayson-Pitts et al. [2003]	
	N <sub>2</sub> O <sub>4(surface)</sub>	$\rightarrow$	ONONO <sub>2(surface)</sub>	Yabushita et al. [2009]	
	$ONONO_{2(surface)} + NO_{2(g)}$	$\rightarrow$	$N_2O_{4(surface)} + NO_{2(q)}$	Martins-Costa et al. [2020]	
	$ONONO_{2(surface)} + H_2O_{(surface)}$	$\rightarrow$	$HONO_{(g,surface)} + HNO_{3(surface)}$		
7	$Dust + h\nu$	$\rightarrow$	$h^{+} + e^{-}$	Ndour et al. [2008]	(vii)
	$e^{-} + O_{2}$		$O_2^-$	Dupart et al. [2014]	
	$NO_2 + O_2^-$ (or e <sup>-</sup> )	$\rightarrow$	$NO_2^- + O_2$	Dyson et al. [2021]	
8	$HNO_{3(ads)} + h\nu$	$\rightarrow$	$HONO + O(^{3}P)$	Zhou et al. [2003]	(viii)
				Ziemba et al. [2010]	1
				Laufs and Kleffmann [2016]	
		Reactions in the bulk			
9	$NO_{2(g)} + NO_{2(g)} + M$	$\rightarrow$	$N_2O_{4(g)} + M$	Sander et al. [2011]	(ix)
	$N_2O_{4(g)} + H_2O_{(l)}$	$\rightarrow$	$HONO + HNO_3$		20123
0	$NH_3 + ONONO_2 + nH_2O_{(1)}$	$\rightarrow$	$\mathrm{HONO} + \mathrm{HNO}_3 + \mathrm{NH}_3 + (\mathrm{n-1}) \mathrm{H}_2\mathrm{O}_{(\mathrm{l})}$	Li et al. [2018a] Xu et al. [2019]	(x)
1	$2 \operatorname{NO}_{2(a)} + \operatorname{HSO}_{3(a)} + \operatorname{H}_{2}O_{(l)}$	$\rightarrow$	$3 H_{(a)}^+ + 2 NO_2^-{}_{(a)} + SO_4^{2-}{}_{(a)}$	Cheng et al. [2016] Li et al. [2018b]	(xi)
12	$HA + h\nu$	$\rightarrow$	$A_{red} + X$	George et al. [2005]	(xii)
	$A_{red} + NO_2$	$\rightarrow$	A'' + HONO	Stemmler et al. [2006]	
13	$NO_3^- + h\nu$	$\rightarrow$	$NO_2 + O^-$	Warneck and Wurzinger [1988]	(xiii)
			$(\Phi = 0.01)$	Mark et al. [1996]	100.000
	$NO_3^- + h\nu$	$\rightarrow$	$NO_2^- + O$	Scharko et al. [2014]	
			$(\Phi = 0.011 \pm 0.002)$	Benedict et al. [2017]	

Table 1: Thirteen potential HONO sources according to previous studies. Most are mixed phase reactions. Some gas phase reactions have been discounted (ibid.).

Our measured HONO in the low-NO<sub>v</sub> marine boundary layer (MBL) is corroborated by those of Andersen et al. (2023). Here, measured HONO still

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### Why and how we measure HONO in the troposphere

OH, the most important oxidant in the atmosphere, is produced from HONO photolysis. In the troposphere, measured HONO often exceeds model predictions. There may also be an unaccounted  $NO_x$  reservoir in the upper troposphere (1). Onboard the HALO aircraft, HONO (and other gases) is measured in limb scattered UV/vis skylight using the mini-DOAS instrument. The DOAS inferred absorptions are interpreted by radiative transfer calculations and by applying the  $O_4$  scaling method (2).

## HOONO as a potential gas phase source of HONO

In the UT, upwards of 100 ppt HONO is measured during most flights (Fig. 1, right panel). This exceeds model predictions, and gas phase formation from OH + NO. Heterogeneous sources can be ruled out by the collision rate of air with measured aerosol surface area. Therefore, one may speculate on other gas-phase HONO formation. An explanation may be (exothermal) reactions of peroxynitrous acid (HOONO) with other oxidants ( $O_3$ , OH, NO, ...).

Gas phase formation of HOONO is known from the reaction OH + NO<sub>2</sub> (5), but controversial for HO<sub>2</sub> + NO (6). HOONO has not yet been measured in the atmosphere. The time for unimolecular decay at low temperatures

(~220 K) due to chemical equilibrium is ~ 14 days. Other losses such as photolysis or oxidation are not quantified.

The steady state production and destruction rates of HOONO necessary to explain our observations can be determined from the measured quantities OH, NO, NO<sub>2</sub>, HO<sub>2</sub>, O<sub>3</sub>, J<sub>HONO</sub> and HONO.

## Conclusions

the polluted boundary layer and free troposphere, HONO is produced heterogeneously; precise echanisms remain elusive.

the low-NO<sub>x</sub> MBL, HONO is chiefly produced by the photolysis of pNO<sub>3</sub> (Ye et al., 2016; Andersen et al., 23; and the present study).

the UT, heterogeneous sources of HONO at the required rate can be ruled out. We speculate that HONO produced from the oxidation of HOONO by OH, NO or O<sub>3</sub>, the former being produced by the reaction of ), and NO and surviving thermal decomposition at low temperatures. Reaction kinetics studies are derway to determine the feasibility of these results.

rther study requires measurements of HOONO in the atmosphere, as well as laboratory measurements its formation and destruction for relevant atmospheric temperatures and pressures.

#### Acknowledgements

ject is funded by the DFG-SPP 1294, grant numbers PF-384/17&PF-384/19, as well as by the BMBF ROMIC II SCI-HI 908D) project. We also thank our colleagues from the MPIC, FZJ, and KIT for the provision of their data.



#### Fig. 4: Reaction diagram of the formation of HOONO according to the recent literature.

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