Laboratory Generation of HO Radicals and Their Effects on Vehicle Emissions in a TiO_2 Coated Setting

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Abstract

This study focuses on the methodology of generating and measuring HONO to study its potential formation from self-cleaning surfaces such as TiO_2.

A HONO-generating system was built and optimized by reacting a humid nitrogen stream containing gaseous HCl with solid sodium nitrate and passing the flow through a set of denuders to remove HNO_3. The HONO produced was quantified by measuring its presence as NO_x using a TECO Model 42 chemiluminescence NO-NO_2-NO_x analyzer containing a molybdenum catalyst. NO and NO_2 are commonly classified as NO_x. However, the TECO measures NO_x as NO, NO_2, HONO and HNO_3. The optimum arrangement produced 84.7 ppb of NO_x of which 16.2 ppbv was HONO and 68.5 ppbv was HNO_3 in a 685 mL/min flow diluted to 5 L/min.

In a second set of experiments, a 150-L Teflon chamber was filled with HONO and also HONO and toluene and exposed to blacklight illumination. HONO photolyzed to produce the HO radical that oxidizes toluene. A proton-transfer-reactor mass spectrometer was used to measure the decay of toluene and generation of oxidation products. HONO generation from TiO_2 coated concrete was also measured.

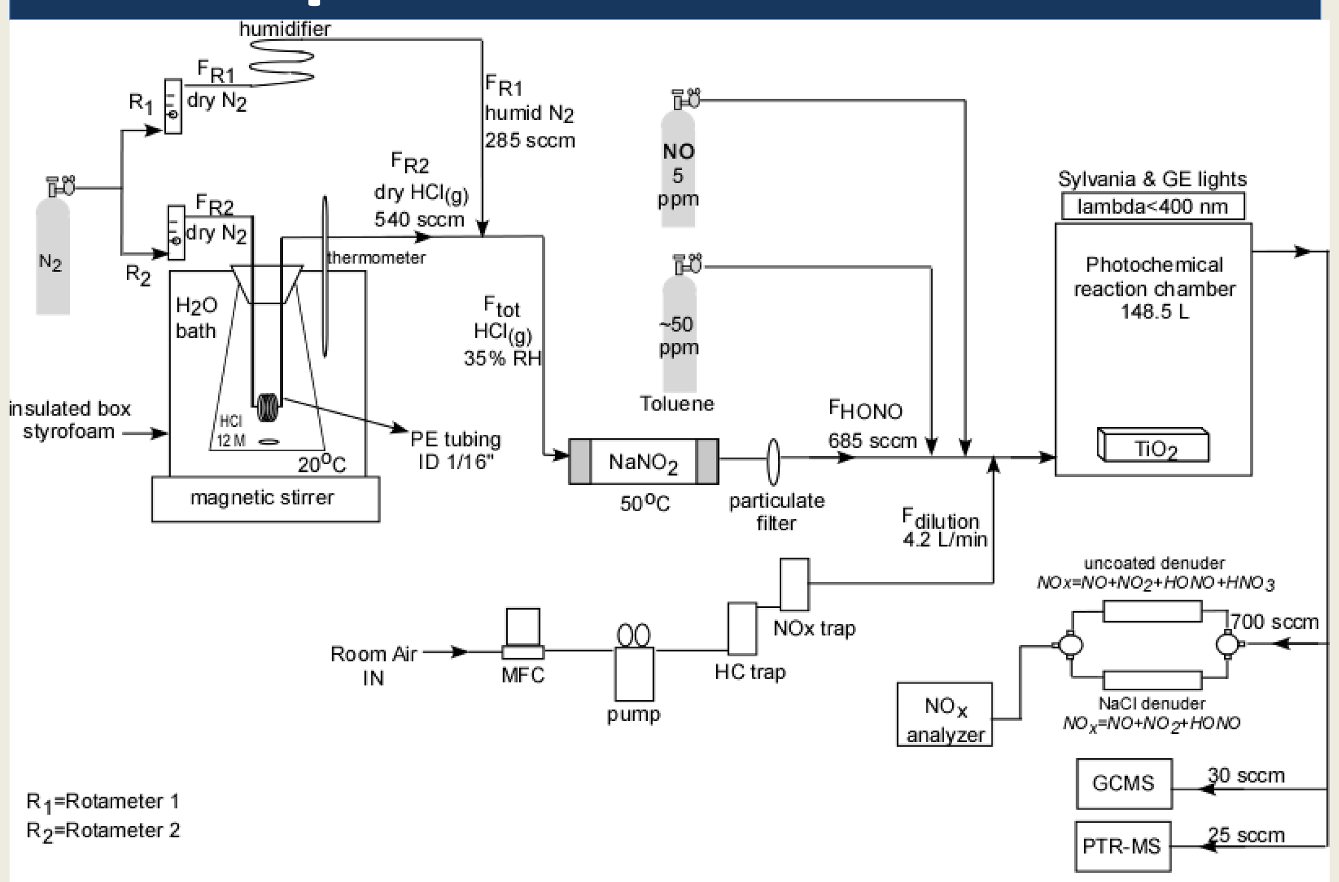
Background

Vehicle emissions, when oxidized in the presence of NO_x and sunlight, produce photochemical air pollution. A key step in these reactions is the creation of the hydroxyl (OH) radical which is a highly reactive molecule that catalytically oxidizes volatile organic compounds (VOCs). One way that HO is created is the photolysis of nitrous acid (HONO):

$$HONO + h\nu \rightarrow HO + NO$$

Self-cleaning surfaces contain TiO_2 that acts as a photocatalyst to oxidize surface absorbed compounds. It has been proposed that air pollution can be reduced by coating roads and roofs with TiO_2 to oxidize nitrogen oxides (NO_x) and organic compounds emitted from vehicles. NO_x oxidation on TiO_2 can yield HONO. Formation of HONO could increase photochemical ozone pollution by increasing the formation arte of HO radical. The oxidation of VOCs by TiO_2 can lead to compounds either more or less hazardous than the original VOCs.

Experimental Methods



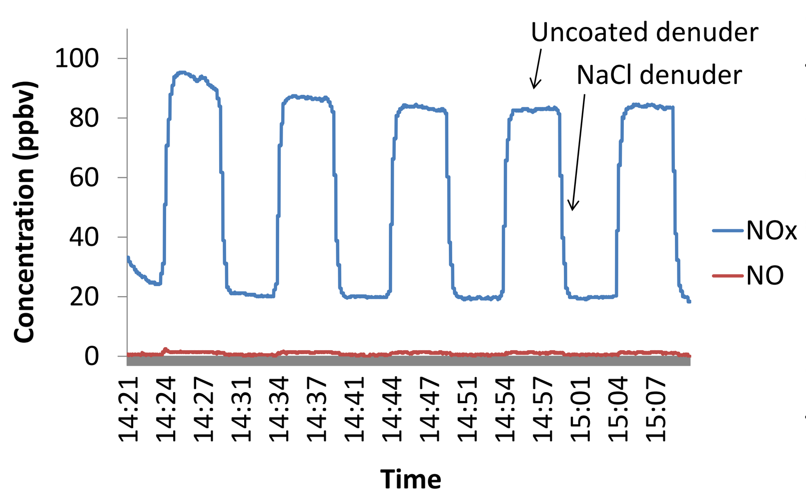
Optimized HONO Generating System

The HONO generation set-up is based on a well established procedure (Febo et al., EST, 1995). The system was optimized by adjusting humidities, low flow rates, and lengths and type of tubing in the HCl vessel. A NaCl coated denuder was used to remove HNO3 generated as a by-product in the HONO generation device.

Results & Discussion

1. HONO Generation Measurements

TECO 42 Results with Denuders



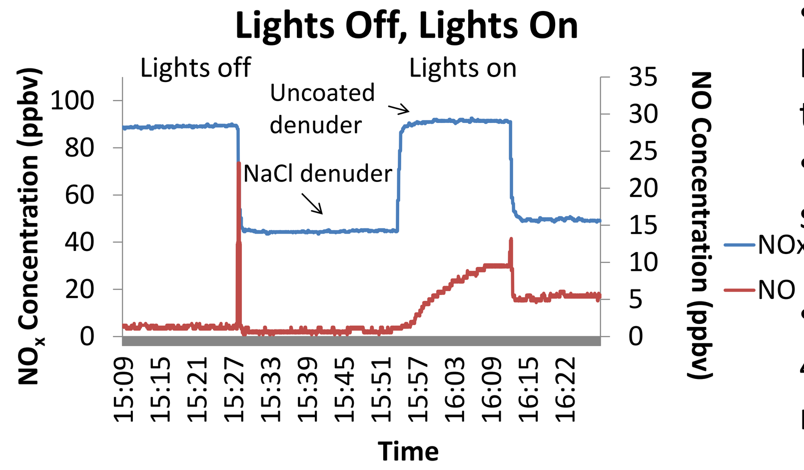
	Uncoated Denuder (ppbv)	St. Dev. (ppbv)	NaCl Denuder (ppbv)	St. Dev. (ppbv)	Δ Denuders (ppbv)
NO_x	83.1	0.62	20.4	0.60	62.7
NO_2	81.9	-	19.9	-	62.0
NO	1.2	0.24	0.5	0.190	0.7

- The NaCl denuder removed a total of 62.0 ppbv of HNO_3.
- With flows of 603 sccm, we calculated our 120cm long NaCl denuder absorbs 94.5% of HNO_3 in the system using the Gormley-Kennedy equation.
- If 62.0 ppbv is 94.5% of HNO_3, the 65.6 ppbv is 100% of HNO_3, leaving 16.3 ppbv of HONO.
- HNO_3 appears to be a major product of this source
  1. $HONO_{(g)} + HONO_{(ads)} \rightarrow NO + NO_2 + H_2O$
  2. $HONO + NO_2 \rightarrow HNO_3 + NO$

  however, NO was not observed.

2. HONO Photolysis in Photochemical Reaction Chamber

TECO 42 Measurements: Lights Off, Lights On

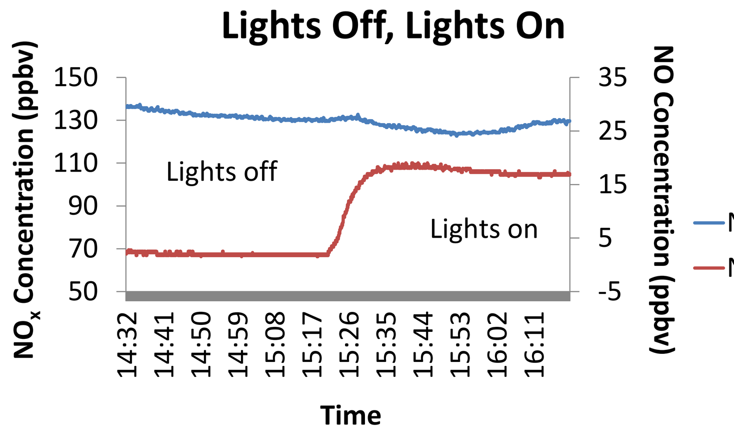


- The increase in NO when UV lights were turned on, is evidence that HONO was present.
- An increased NO reading signifies we have made HONO: $HONO + h\nu \rightarrow HO + NO$
- NO concentration increased by 4.7 ppbv, but the chamber had not reached steady state yet.

	No Photolysis (Average)					Photolysis (Average)					Δ	
	Uncoated Denuder (ppbv)	St. Dev. (ppbv)	NaCl Denuder (ppbv)	St. Dev. (ppbv)	Δ Denuders (ppbv)	Uncoated Denuder (ppbv)	St. Dev. (ppbv)	NaCl Denuder (ppbv)	St. Dev. (ppbv)	Δ Denuders (ppbv)	Uncoated Denuder (ppbv)	NaCl Denuder (ppbv)
NO_x	89.0	0.39	44.5	0.36	44.5	91.2	0.50	49.4	0.44	41.8	2.2	4.9
NO_2	87.7	-	43.8	-	43.9	84.2	-	44.0	-	40.2	-3.5	0.2
NO	1.3	0.23	0.7	0.25	0.6	7.0	2.41	5.4	0.30	1.6	5.7	4.7

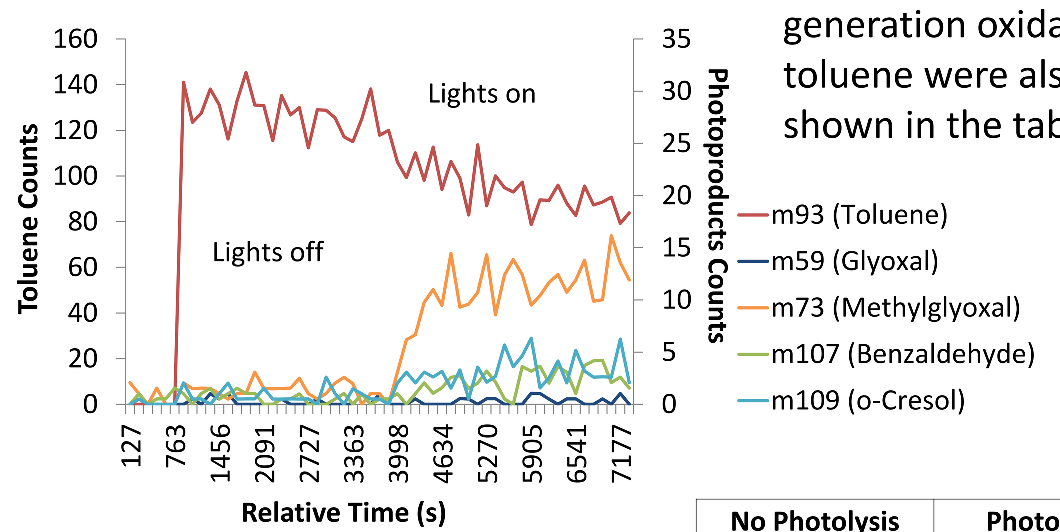
3. HONO and Toluene in Photoreaction Chamber

TECO 42 Results: Lights Off, Lights On



	No Photolysis		Photolysis		
	Avg. (ppbv)	St. Dev. (ppbv)	Avg. (ppbv)	St. Dev. (ppbv)	Δ Avg. (ppbv)
NO_x	132.4	1.98	126.1	1.94	-6.30
NO_2	130.4	-	108.6	-	-21.8
NO	2.0	0.25	17.5	0.65	15.50

PTR-MS Measurements of Toluene and Photoproducts



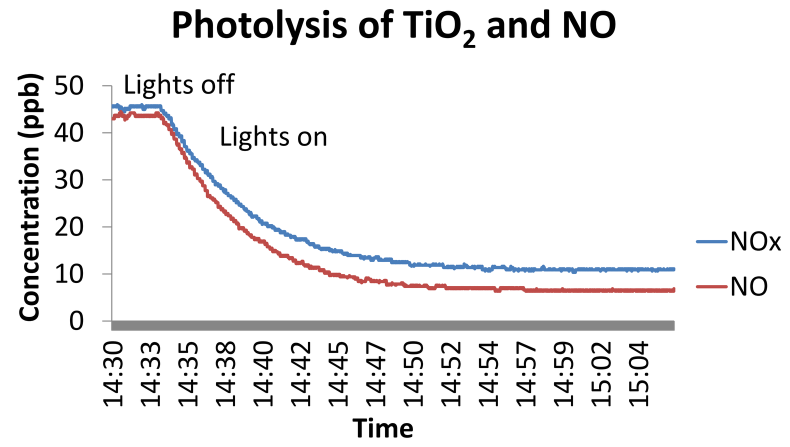
- Since there is a decrease in the NO_2 signal and an increase in the NO signal, we have evidence we made HONO.
- The 15.5 ppbv is the results of HONO photolysis.
- This is consistent with the 16.3 ppbv calculated from the denuder measurements in section 1.
- Photolysis of HONO creates HO radical that can oxidize toluene.
- Toluene counts decrease in the chamber as expected, evidence that HO radicals were produced.
- From the change in toluene concentration, we estimated the HO radical concentration was 3.2×10^7 molecules/cm^3.
- Homogeneous gas phase first generation oxidation products of toluene were also identified as shown in the table below.

	No Photolysis		Photolysis		
	Avg. (counts)	St. Dev. (counts)	Avg. (counts)	St. Dev. (counts)	Δ Avg. (counts)
Glyoxal (m59)	7.2	4.76	25.5	4.54	18.3
Methylglyoxal (m73)	1.4	0.76	12.0	1.88	10.6
Toluene (m93)	127.2	8.86	88.6	5.87	-38.7
Benzaldehyde (m107)	0.6	0.51	2.8	1.26	2.2
o-Cresol (m109)	0.8	0.69	3.5	1.56	2.7

Results & Discussion

NO_x Removal Using Self-Cleaning TiO_2 Coated Concrete

TECO 42 Results: Photolysis of TiO_2 and NO



- The TiO_2 catalytically removed 85% of the NO flowing through the chamber.
- An increase in NO_2 was observed and this is attributed to the formation of HONO.
- The HONO yield from NO destruction by TiO_2 was measured as 7%.

	No Photolysis		Photolysis			
	Avg. (ppbv)	St. Dev. (ppbv)	Avg. (ppbv)	St. Dev. (ppbv)	Δ Avg. (counts)	% Change
NO_x	45.5	0.32	10.9	0.14	-34.6	-76.04
NO_2	1.8	-	4.4	-	2.6	142.92
NO	43.7	0.36	6.5	0.13	-37.2	-85.11

Conclusion

We have developed HONO generator, proved that HONO was produced, and measured HONO photolysis. In addition we discovered that the TiO2 coated concrete produced HONO as a by-product of NO oxidation.

References

Febo, A.; Perrino, C.; Gherardi, M.; Sparapani, R., *Environ. Sci. Technol.* **1995**, *29*, 2390-2395.

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Acknowledgements

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