

Electrical Discharges Produce Prodigious Amounts of Hydroxyl and Hydroperoxyl Radicals

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Key Points:

- Abundant hydroxyl and hydroperoxyl radicals generated by electric discharges were measured in the laboratory for the first time
- Measured hydroxyl and hydroperoxyl radical mixing ratios showed small to no dependence on pressure and water vapor mixing ratio
- The laboratory results are consistent with the extreme amounts of hydroxyl and hydroperoxyl radicals observed in thunderstorm anvils

Abstract

Reaction with the hydroxyl radical (OH) is often the first step in the removal of many atmospheric pollutants. The nitrogen oxides (NO_x) generated by lightning can increase the amount of HO_x (HO_x = OH + HO₂) present in the atmosphere, but direct HO_x production from lightning has never been quantitatively investigated in the laboratory. In this laboratory study, prodigious amounts of HO_x were generated by both visible and subvisible electrical discharges over ranges of pressure and water vapor mixing ratios relevant to the troposphere. Also measured were NO, total nitrogen oxides (NO_x), ozone (O₃), and OH exposure, which is the integral of the hydroxyl radical concentration over time since the discharge. HO_x and OH exposure were approximately independent of pressure from 360 to 970 hPa and only slightly increased as water vapor increased from 1000 to 8000 parts per million volume (ppmv), while NO_x was approximately independent of both pressure and water vapor over the same ranges. These laboratory measurements of excessive HO_x and OH exposure are similar to measurements of electrically-generated HO_x discovered in electrified anvil clouds during a 2012 airborne study, thus demonstrating the relevance of these laboratory results to the atmosphere and the importance of understanding the electrically-generated HO_x contribution to atmospheric oxidation.

Plain Language Summary

Lightning is known to generate nitrogen oxides and ozone, which indirectly create the hydroxyl radical (OH), the atmosphere's primary oxidant. This laboratory study proves that the weak visible electrical discharges associated with lightning flashes generate extreme amounts of OH and the hydroperoxyl radical (HO₂) directly, and, surprisingly, so do weak electrical subvisible discharges. Further, the abundant OH is generated in similar amounts for all tropospheric pressures, varies little over a wide range of water vapor, exists much longer than expected, and is comparable to amounts seen in electrified thunderstorms during a 2012 airborne study. Thus, atmospheric electrical discharges are likely an important source of oxidation throughout the lower atmosphere.

1 Introduction

Hydroxyl (OH) and hydroperoxyl (HO₂) dominate the oxidative capacity of the Earth's troposphere. In particular, the hydroxyl radical (OH) reacts with many atmospheric pollutants, oxidizing them into water soluble molecules that are removed from the atmosphere through rain or gas-phase and particle deposition. Atmospheric OH comes primarily from reactions involving ozone (O₃) photolysis by UV radiation to produce an excited-state O atom followed by reaction of the excited O atom with water vapor (H₂O). The hydroperoxyl radical (HO₂) comes from formaldehyde photolysis or reactions of OH with many atmospheric trace constituents. Additionally, HO₂ can be converted back to OH by reaction with nitric oxide (NO), so that OH and HO₂ are rapidly exchanged. Together, OH and HO₂ are called HO_x.

Lightning is calculated to generate 10-15% of the total global amount of NO and nitrogen dioxide (NO₂), together called NO_x (Nault et al., 2017; Schumann & Huntrieser, 2007).

However, in the upper troposphere near the tops of deep convective clouds, lightning-generated NO_x (LNO_x) is a major NO source that reacts with HO₂, increasing the amounts of OH and O₃

(Zhang et al., 2003). This increased O₃ alters the radiative balance in this climate-sensitive upper troposphere / lower stratosphere region (Denman et al., 2007).

LNO_x has been extensively studied in the atmosphere and laboratory, demonstrating that LNO_x is generated over a the wide range of currents that occur in atmospheric corona, streamers, and lightning flashes (Bierle et al., 2010; Bond et al., 2001; Chameides et al., 1977; Cooray et al., 2009; Hill et al., 1988; Levine et al., 1981; Nault et al., 2017; Peyrous & Lapeyre, 1982; Pollack et al., 2016; Rahman et al., 2011; Rehbein & Cooray, 2001; Schumann & Huntrieser, 2007; Stark et al., 1996; Stockwell et al., 1999; Tie et al., 2002; Wang et al., 1998; Zhang et al., 2003). These studies focused on quantifying LNO_x as a function of observable quantities, such as lightning flash rates, so that LNO_x can be included in global chemical transport and climate models. Thus, laboratory studies have quantified LNO_x as a function of factors such as pressure, water vapor, peak current, energy, corona vs. spark discharge, and polarity of the discharge (Chameides et al., 1977; Hill et al., 1988; Levine et al., 1981; Peyrous & Lapeyre, 1982; Rahman et al., 2011; Rehbein & Cooray, 2001; Stark et al., 1996; Wang et al., 1998).

Ozone is known to be produced directly by electrical discharges, implying that lightning produces it as well. Lightning-generated O₃ will be called LO₃. Laboratory studies have shown that sparks generate no detectable O₃ (Levine et al., 1981; Peyrous & Lapeyre, 1982), but corona discharges generate more O₃ than NO_x (Hill et al., 1988). There is some evidence that electrical activity in thunderstorms produces O₃ (Bozem et al., 2014; Orville, 1967), but ozone-rich stratospheric air wraps down around thunderstorms and their anvils (Pan et al., 2016), so that it is difficult to assign enhanced ozone to electrical discharges themselves.

Lightning-generated HO_x (LHO_x) has been studied in corona discharges in previous laboratory studies as a potential way to lower industrial pollution emissions, with only estimates of the OH concentration (Hibert et al., 1999; Nakagawa et al., 2011; Ono & Oda, 2002). Attempts to quantify LHO_x in more depth have been done only as part of two lightning flash chemistry modeling studies (Bhetanabhotla et al., 1985; Hill et al., 1981). Both studies concluded that, although LHO_x was generated, its lifetime was too short for it to have any significant atmospheric impact. However, HO_x can be short lived but still influential because the loss of an OH reactant depends not on the OH concentration or OH lifetime alone, but on the integral of the product, which is called the OH exposure:

$$OH_{exp} = \int [OH] dt, \quad (1)$$

where the time interval integrated over can be any time interval of interest, and in the case of an electric discharge is the time since the discharge occurred. Therefore, LHO_x could still contribute to global atmospheric oxidation if the total OH exposure generated by all lightning is a significant fraction of the OH produced by O₃ photolysis in the rest of the atmosphere.

Evidence that LHO_x is being produced in the atmosphere was discovered during the Deep Convective Clouds and Chemistry (DC3) field campaign, which occurred over the central United States in 2012 (Barth et al., 2015). During DC3, the NASA DC-8 aircraft, outfitted to measure many chemical constituents including HO_x, NO_x, and O₃, flew through thunderstorm outflow anvils, some of which were electrified according to measurements by lightning mapping arrays (Brune et al., 2021). Within these electrified regions, OH and HO₂ were often several hundred parts per trillion (pptv), orders of magnitude larger than typical background values of a few tens of pptv for HO₂ and tenths of pptv for OH.

During DC3, all enhanced HO_x was measured in electrified thunderstorm clouds, but only a few times was a visible flash observed in front of the aircraft shortly before enhanced HO_x was observed (Brune et al., 2021). Most enhanced LHO_x was detected in regions where NO was at most a few ppbv and no lightning flashes were detected by the ground-based lightning mapping array. Research into lightning initiation in the last decade has shown that high-current visible lightning flashes are the culmination of much smaller and weaker electrical events occurring in thunderstorms; however, most of these weak electrical do not result in lightning flashes (Kostinskiy et al., 2020; Petersen et al., 2008; Rison et al., 2016). It is likely that the observed LHO_x was a result of subvisible electrical discharges too weak for the lightning mapping array to detect. Thus, these weak electrical discharges are as atmospherically relevant for LHO_x as high-current lightning flashes and possibly even more so because the weaker discharges occur more frequently and over a larger volume in electrified thunderstorms than the high-current lightning flashes do.

To further investigate the LHO_x detected during the field campaign, we conducted a series of laboratory studies to measure electrically-generated OH and HO_2 for different atmospherically relevant environmental and electrical conditions. Our laboratory setup, in which the time between the spark and the detection of HO_x , NO_x , and O_3 can be varied, also allowed us to calculate the corresponding OH exposures. NO , total NO_x , and O_3 were simultaneously measured with OH and HO_2 so that relationships among LHO_x , LO_3 , and LNO_x can be determined. This laboratory study relates previously unknown LHO_x to known LNO_x and discovers the dependence of LHO_x on ranges of pressure, water vapor, and electrical discharge characteristics that are relevant to the troposphere.

2 Materials and Methods

2.1 Laboratory Setup

The laboratory set-up consists of a vacuum-tight flow tube, an electrical discharge source, a moveable spark gap, and instruments to measure the chemical species OH , HO_2 , NO , total NO_x , and O_3 and the flow tube pressure, temperature, and humidity (Figure 1a).

Two types of electrical discharges were used in these experiments: discharges that emit visible radiation and sound, called sparks, and weak, low-charge discharges that emit no visible radiation (Petersen et al., 2008), called subvisible discharges. Both discharges types were generated by a solid-state Tesla coil (Eastern Voltage Research, Plasmasonic® 1.3). Tesla coils produce rapid alternating current (AC) electrical pulses and have been used in some previous LNO_x and LO_3 studies (Donohoe et al., 1977; Hill et al., 1988), but their pulses are different from the direct current (DC) pulses produced by the Marx generators and high-voltage capacitor discharges used in most previous LNO_x studies (Rahman et al., 2011; Rehbein & Cooray, 2001; Stark et al., 1996; Wang et al., 1998). Neither device can reproduce all aspects of a lightning flash, from initiation through the leader, return stroke, and subsequent leaders and return strokes.

However, previous studies have shown that the differences in LNO_x production between different discharges types is mostly due to differences in current and how long the discharge lasts (Cooray et al., 2009; Rahman et al., 2011), and information on both of those variables has been provided in this work. Additionally, both AC and DC pulses can interact with atmospheric gases in the same way (Raizer, 1997), making the AC discharges used in this study suitable for reproducing the discharges encountered during the DC3 field campaign, which were typically the

weaker anvil discharges and not the strong high-current lightning (Brune et al., 2021). As a test, we used DC pulses from a Marx generator to also make sparks and found that comparable values for LNO_x and LHO_x were produced for weak currents from both devices.

The discharges were generated between two metal electrodes inside a borosilicate glass flow tube (5.1 cm OD x 4.7 cm ID x 105 cm long, Corning PYREX®). Pointed wire electrodes made of tungsten (0.10 cm diameter) were used to generate visible spark discharges, and rounded copper electrodes (diameter 2.5, 3.3 cm radius of curvature) on tungsten wire posts were used to generate all subvisible and some visible discharges. The gap length for either type of electrode could be adjusted, up to 1.20 cm for the pointed tungsten electrodes and up to 1.00 cm for the rounded copper-style.

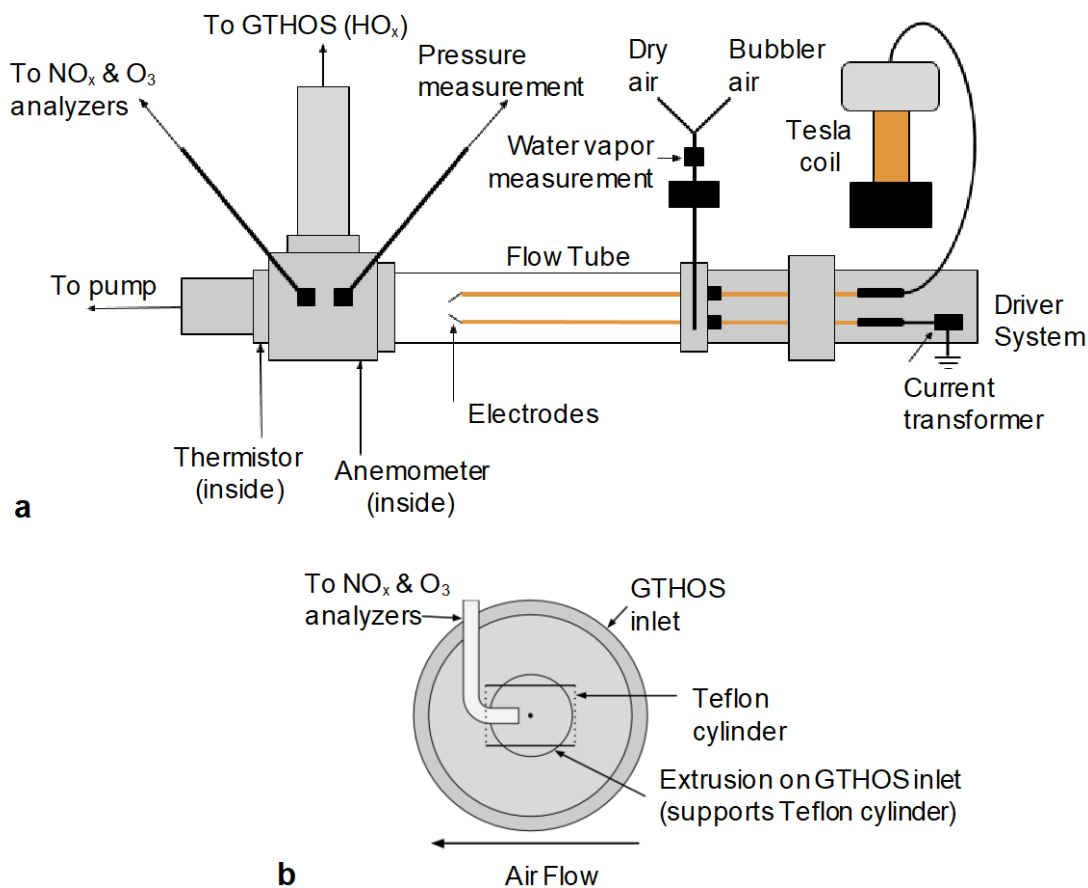


Figure 1. (a) Top-down schematic view of the laboratory setup used to measure LHO_x , LNO_x , and LO_3 . Diagram is not to scale with the actual setup. (b) Close up diagram view of the GTHOS inlet with NO_x and O_3 sample line and Teflon cylinder. Sampling for GTHOS occurs through the small black dot in the center of the inlet.

Each electrode is attached to a copper rod (0.635 cm diameter, 140 cm long, 99.99% pure). Outside the flow tube, one copper rod is connected to the Tesla coil toroid thru an 8-gauge copper cable while the other is connected to a laboratory ground. The two copper rods were

attached to a driver system which guided the rods forward and backward in the flow tube, changing the position of the electrodes (and therefore discharges) in the flow tube. As a result, the time it took air exposed to the discharge to reach the analyzer inlets was changed as well. A current transformer (Eastern Voltage Research) with oscilloscope (Siglent, SDS-1202X-E) was placed on the grounded side of the setup to capture the current waveforms of the visible sparks. The current from the subvisible discharges was too low to be observed with the current monitor setup that was used for these experiments, but they were observed by an RF antenna placed on top of the flow tube. To find the breakdown voltage of the discharges, a 10,000:1 voltage divider (Bertran Associates, Inc., HVD-60) connected to a separate oscilloscope (Tektronix, TDS-3032) was attached across the two copper rods in between experiments.

Compressed air that had been dried and purified was added to the setup via four ports equally spaced around the upstream end of the flow tube. A portion of the air was passed through a bubbler filled with water (spectroscopic grade) and then added to the main flow to produce different amounts of water vapor in the air flow. The final water vapor mixing ratio of the air was measured as it entered the flow tube (Vaisala HMT310). The dry air was produced by an air compressor (Beko XCp 100), which dried the air to a dewpoint of -40°C . This air was further purified in the laboratory by passing it through Carulite® 300 (Carus® Corporation, LLC) to remove any remaining carbon monoxide in the air and Molculite (Molecular Products, 814 Mesh) to remove any other hydrocarbon contaminants. After filtration, the compressed air had a final carbon monoxide mixing ratio less than a few ppbv and final carbon dioxide mixing ratio of 2-3 ppmv (Picarro, Inc., G2302). To check the air for hydrocarbons, the OH reactivity was measured (Mao et al., 2009) and found to be $\sim 1\text{ s}^{-1}$, similar to the OH reactivity in the clean middle-to-upper troposphere (Thames et al., 2020).

Connected to the back of the flow tube is a hollow aluminum detection block. A large vacuum pump (Edwards XDS35) attached to the back of the detection block was used to adjust the pressure and/or air velocity in the flow tube. The pressure in the setup was measured via a pressure transducer (MKS Instruments Baratron® Type 222) connected to the system by an FEP line on top of the detection block. A hot wire anemometer (TSI Inc., 8455-09) and a thermistor inside the detection block measured the velocity and temperature, respectively, of the air leaving the flow tube. After setting up the experiment, but before generating any sparks, anemometer measurements were made at the center of the flow and then the anemometer was moved out of the flow path.

Attached to one side of the detection block is the inlet for the Ground-based Tropospheric Hydrogen Oxide Sensor (GTHOS), which detects OH and HO₂ using laser-induced fluorescence (Faloona et al., 2004) and is set at right angles to the airflow. A small FEP cylinder (1.5 cm dia., 3 cm long) aligned with the flow is attached to the GTHOS inlet fixture. NO_x and O₃ were sampled through an FEP Teflon ¼" line, the end of which is pointed into the flow inside the back of the small cylinder (Figure 1b). The ¼" line is attached to a ½" Teflon line leading to a NO-NO_x-NO₂ analyzer (ECO PHYSICS nCLD 855Y, with custom hard sealing) and a fast O₃ analyzer (Kalnajs & Avallone, 2010) by a vacuum pump (Edwards XDS10). This arrangement ensures that NO_x and O₃ were sampled from the same air mass that HO_x was.

The absolute uncertainties of the chemical species measurements for short-lived sparks or subvisible discharges are the same as for typical atmospheric measurements, but the limits-of-detection (LOD) are higher because the integration time is 0.2 s instead of the usual 20 s. The absolute uncertainty and LOD at the 68% confidence level for the different chemical species are

the following: OH and HO₂, $\pm 20\%$ and ~ 1 pptv; NO and NO_x, $\pm 10\%$ and ~ 1 -3 ppbv; and O₃, $\pm 5\%$ and ~ 10 -20 ppbv. Ranges are given for the LODs because, for all chemical species, they depend on the measurement conditions.

The GTHOS electronics and data collection system controlled all experiments and collected all the data. The data collection frequency is 5 Hz.

2.2 Experiment Procedure

The short HO_x lifetime required three key changes to our flow tube system relative to the setups used to previously study LNO_x in the laboratory (Chameides et al., 1977; Donohoe et al., 1977; Hill et al., 1988; Rahman et al., 2011; Rehbein & Cooray, 2001; Stark et al., 1996; Wang et al., 1998). First, to minimize the loss of HO_x prior to measurements, our setup used faster flow rates in the flow tube (30-70 standard liters per minute (slpm) here versus less than 1 to 20.5 slpm in previous studies (Chameides et al., 1977; Hill et al., 1988; Rahman et al., 2011)). The Reynolds number for the flow was typically 1700, but the velocity profile was flatter than parabolic because the fully developed laminar flow requires 4 times the length of our flow tube (Figure S1). Second, pulses of rapidly firing discharges (referred to as “discharge packets”) were used in place of individual discharges. Using discharge packets created broader, more consistent chemical signals that could be more reliably detected by the NO_x and O₃ instruments in the fast flows. The final change to the setup was the ability to move the discharge location in the flow tube relative to the HO_x, NO_x, and O₃ detection.

Experimental data were collected using automated sequences and the following process. Values were selected for each of the different variables such as pressure, total flow rate, bubbler flow rate, electrode gap length, and the discharge packet parameters. The discharge packet parameters that were adjusted include the pulse width, which controls the energy discharged by the Tesla coil; the pulse interval, which controls the spacing between discharges in a packet; and the number of discharges in the packet. The pointed tungsten electrodes were used in all experiments except the subvisible discharge experiments. The driver system moved the electrodes to five different positions in the flow tube, and four discharge packets, which had five-second spacing between each packet, were generated in each of the five positions.

The first position for the discharge is as close as the discharge can get to the GTHOS inlet without sparks striking the inlet or the metal detection block instead of between the electrodes, about 5.5 cm for the pointed electrodes and about 7.8 cm for the rounded electrodes (the equivalent of 0.025-0.056 seconds of reaction time). The next position for the discharge is 5 cm (0.052-0.13 seconds reaction time) back from the first position, and the spacing between each of the remaining positions is 7.5 cm (0.094-0.23 seconds, 0.14-0.34 seconds, and 0.18-0.44 seconds reaction time for each subsequent position). Once data were collected in each position, new values were chosen for the variables and the process was repeated. Details on the exact procedures and conditions used to conduct each set of experiments presented in the results section can be found in the Supporting Information.

2.3 Tests of experimental factors

Three tests were performed to check that the OH and HO₂ signals were due to real LHO_x and were neither due to electrical noise nor an interference made within the GTHOS instrument. In the first test, the GTHOS laser wavelength was set off the OH absorption wavelength for one of

the four discharge packets at each position, and, for this setting, the OH and HO₂ signals were at background levels. In the second test, the OH and HO₂ signals, which are counted in 50-ns bins, decayed as expected based on the known OH excited state quenching and lifetime. Lastly, we added perfluoropropylene (C₃F₆) to the flow tube, a chemical which rapidly reacts with OH. Anywhere from 90-99% of the OH was removed by the C₃F₆, whereas, if the OH was generated internally, the C₃F₆ would remove at most 3% of the OH. These three tests prove that LHO_x is real.

Additionally, two experimental factors, the pulse interval and number of discharges per packet have no atmospheric equivalent, but were also tested. A pulse interval of 25,000 μ s was chosen for most experiments, and a broad range of pulse intervals were tested to determine whether the laboratory results were sensitive to this value. The pulse interval only appears to impact LHO_x and the OH exposure at 970 hPa, while LHO_x and the OH exposure at 360 hPa and LNO_x at either pressure were independent of the pulse interval (Figure S2). The reason for this impact occurring only under some conditions is likely because the increase in spacing decreases the chance for the LHO_x produced from one spark to overlap with the LNO_x from the next spark. For the number of discharges per packet, tests were performed using different numbers of discharges per packet to determine how to scale the results from the 5 or 10 discharges per packet used in most experiments down to a single discharge. Increasing the number of sparks in a packet led to linear increases in LHO_x, LNO_x, and the OH exposure (Figure S3).

Additional details on all these tests can be found in the Supporting Information.

2.4 Data Analysis

The data analysis process has been summarized below; further details can be found in the Supporting Information.

2.4.1 Procedure for converting mixing ratios to molecules

To make comparisons between our results, which are in terms of mixing ratio, and those from previous studies, which were in terms of molecules, we converted our results to molecules. This conversion was accomplished by first converting the measured mixing ratios to molecules cm⁻³, and then calculating the total volume those molecules occupied to remove the volume dependence (Equation S1).

2.4.2 Diffusion and Sampling corrections

The LHO_x data were corrected for diffusion by using the measured average LNO_x diffusion for the same conditions (Figure S4a). Additionally, the LHO_x, LNO_x, and LO₃ data were all corrected by 15% to account for the fraction of each of these chemicals that were not sampled by our analyzers and instead by-passed the sampling tube and were exhausted out of the flow tube setup (Figure S4b).

2.4.3 Method for calculating initial OH, initial HO₂, and the OH exposure

The initial OH or HO₂ formed by the spark is determined by first calculating the time it took the HO_x to reach the GTHOS inlet from each stage position, using the distance from the inlet to each position and the anemometer velocities. Then an equation was developed to model the OH and HO₂ decays, assuming first-order, constant losses of HO_x. The reported initial amount of OH or HO₂ generated in the spark came from extrapolating this equation back to time zero. The

extrapolated fits of the OH decays were also integrated from time zero out to the time corresponding to the last stage position to determine the OH exposures.

2.4.4 Scaling

After applying the diffusion and sampling corrections, and performing the OH and HO₂ extrapolations, the data collected at multiple discharges per packet were scaled down to a single discharge, based on the linearity with discharge number shown in Figure S2, before reporting them in Figures 2-6, S2, and S4-S8.

3 Results from laboratory simulations of lightning

Table 1. Typical ranges of conditions for the atmosphere and this laboratory study

Influential factor	Troposphere	Current lab studies
Environmental Factors:		
Pressure (hPa)	100 – 1000	360 – 970
Concentration (10 ¹⁹ cm ⁻³)	0.3 – 2.5	0.88 – 2.4
In-cloud Water vapor (%)	0.002 – 3.0	0.01 – 0.8
Air velocity (m s ⁻¹)	0 – 20	1.22 – 2.85
Temperature (K)	200 – 320	293-297
In a cloud?	Both in and out	No clouds
Main trace gases	CO ₂ , CH ₄ , CO	negligible
Electrical Factors:		
Peak current (A)	sub-A up to 30 kA in large flash channels ^a	1.5 A for visible discharges
Charge transfer (C)	sub-C up to ~20 C in negative flashes ^b	Up to 9×10 ⁻⁵ C
Energy (J)	sub-J up to 6.7 × 10 ⁹ for cloud-ground flashes ^{c,d}	0.060-0.630
Visible/subvisible	both	both
Discharge (gap) length	meters to kilometers ^e	0.40 – 1.20 cm
Polarity/Type	± DC discharges with AC components	AC discharges

^aWacker and Orville (1999). ^bRakov (2002). ^cPrice et al. (1997). ^dCooray (1997). ^eKostinskiy et al. (2020).

The evolution of LHO_x and LNO_x was followed for times between about 0.025 and 0.44 seconds after the discharge, with the exact range of observed evolution depending upon the velocity in the flow tube during the experiment. Table 1 shows that these laboratory studies cover a substantial range of most atmospherically relevant factors, although the laboratory sparks were much smaller than typical main lightning channels and had much lower peak current, charge

transferred, and energy. Temperature was not varied in this study, but a follow-on laboratory study will be conducted at lower temperatures, possibly with laboratory-generated clouds.

These laboratory results confirm the DC3 measurements of extreme amounts of OH and HO₂ generated by electrical discharges. In the atmosphere and the laboratory, enhanced HO_x was detected at times between hundredths to tenths of seconds after visible electrical discharges. This result stands in stark contrast to the modeling studies, for which OH and HO₂ decrease to ambient amounts within milliseconds (Bhettanabhotla et al., 1985). The following sections describe the behavior of the electrical discharge generated LHO_x, LNO_x, and LO₃ mixing ratios, scaled to individual sparks, as a function of pressure, water vapor concentration, gap length, and spark charge. A final section discusses the LNO_x, LO₃, and LHO_x that are generated by individual weak subvisible discharges.

We report our LHO_x, LNO_x, and LO₃ results in terms of mixing ratios. Many previous studies of LNO_x reported their results in terms of molecules (Chameides et al., 1977; Hill et al., 1988; Levine et al., 1981; Rahman et al., 2011; Rehbein & Cooray, 2001; Stark et al., 1996; Wang et al., 1998), which is more absolute but loses some ease of interpretation. In the laboratory, we have determined the volume sampled to be in the range of ~180-540 cm³ depending on the experimental conditions and so can convert from mixing ratio to molecules. For completeness, we have provided alternate versions of Figure 1 and Figure 2 in the Supporting Information (Figure S5 and Figure S6, respectively) where the HO_x and NO_x results are reported as molecules instead of mixing ratios. Because the experiments for all variables other than pressure and water vapor were at constant pressure, the LHO_x, LO₃, and LNO_x trends are the same for these variables whether they are reported in terms of mixing ratios or molecules.

3.1 Pressure

Lightning can occur at any altitude in the atmosphere, and therefore at any pressure as well. In the laboratory setup, the pressure in the flow tube was changed through two different methods: keeping a constant velocity and changing the standard mass flow rate, or vice versa. For each method, the water concentration was kept constant as the pressure was varied. The results for both cases are shown in Figure 2.

Mixing ratios for LHO_x, LOH, LHO₂, LNO_x, and LNO, and the OH exposure are largely independent of pressure for both methods (Figure 2a, 2b, 2c). Applying linear fits to each set of data yielded slopes that were either zero within error or very small (Table S1). NO_x consists of ~95% NO and ~5% NO₂, although most of the NO₂ was likely O₃ generated in the spark that reacted with NO to form NO₂ in the 2 seconds before the O₃ could be detected.

That the mixing ratios for each chemical species and the OH exposure were constant or nearly constant over the entire pressure range suggests that approximately the same fractions of H₂O, N₂, and O₂ are converted by electrical discharges to HO_x and NO_x regardless of pressure. The

mixing ratios for both LHO_x and LNO_x were also similar across the two approaches, with the error bars ($\pm 1\sigma$, standard deviation) from each data set often overlapping.

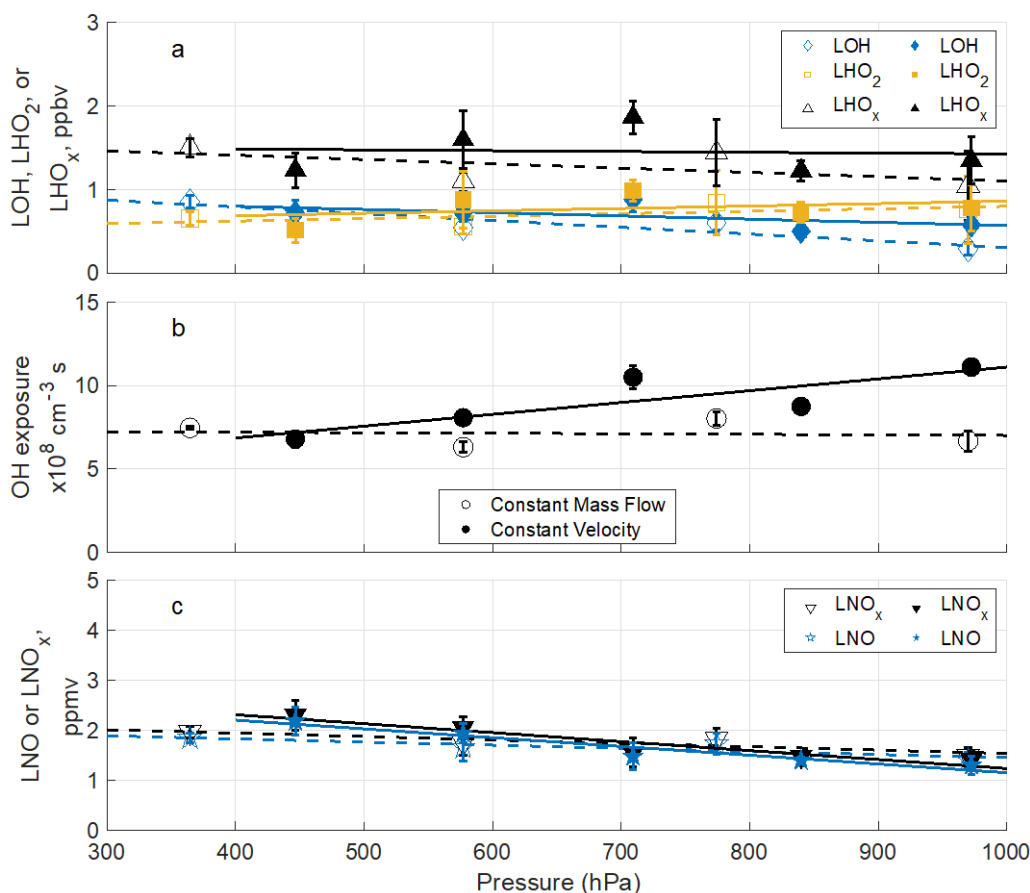


Figure 2. Electrical discharge generated quantities as a function of pressure: (a) LOH (diamonds), LHO_2 (squares), total LHO_x (upward triangles); (b) OH exposure (circles); (c) LNO (stars) and total LNO_x (downward triangles). The filled symbols and fitted solid lines indicate data collected with a constant velocity, while the open symbols and fitted dashed lines indicate data collected with a constant mass flow rate. Different water concentrations were used in the two methods, but all other variables were kept the same between the two experiments. Linear fits were applied to each chemical species and the OH exposure for both methods of changing the pressure, and the slopes, intercepts, and standard errors for each fit are shown in Table S1. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

3.2 Water Vapor Concentration

Water vapor is a key ingredient in producing HO_x in the background atmosphere and in discharges (Bhettanabhotla et al., 1985; Hill & Rinker, 1981). In the atmosphere, the water vapor mixing ratio varies over wide ranges from a few hundred to thousands of parts per million volume (ppmv) for pressures between 200 to 1000 hPa. Thus, the water dependence of LHO_x

and LNO_x was examined as a function of both water vapor and pressure in a set of experiments different from those done for the pressure dependence. For these experiments, pressure was changed using the constant mass flow method, but the electrical discharge characteristics were held constant. The results are shown in Figure 3.

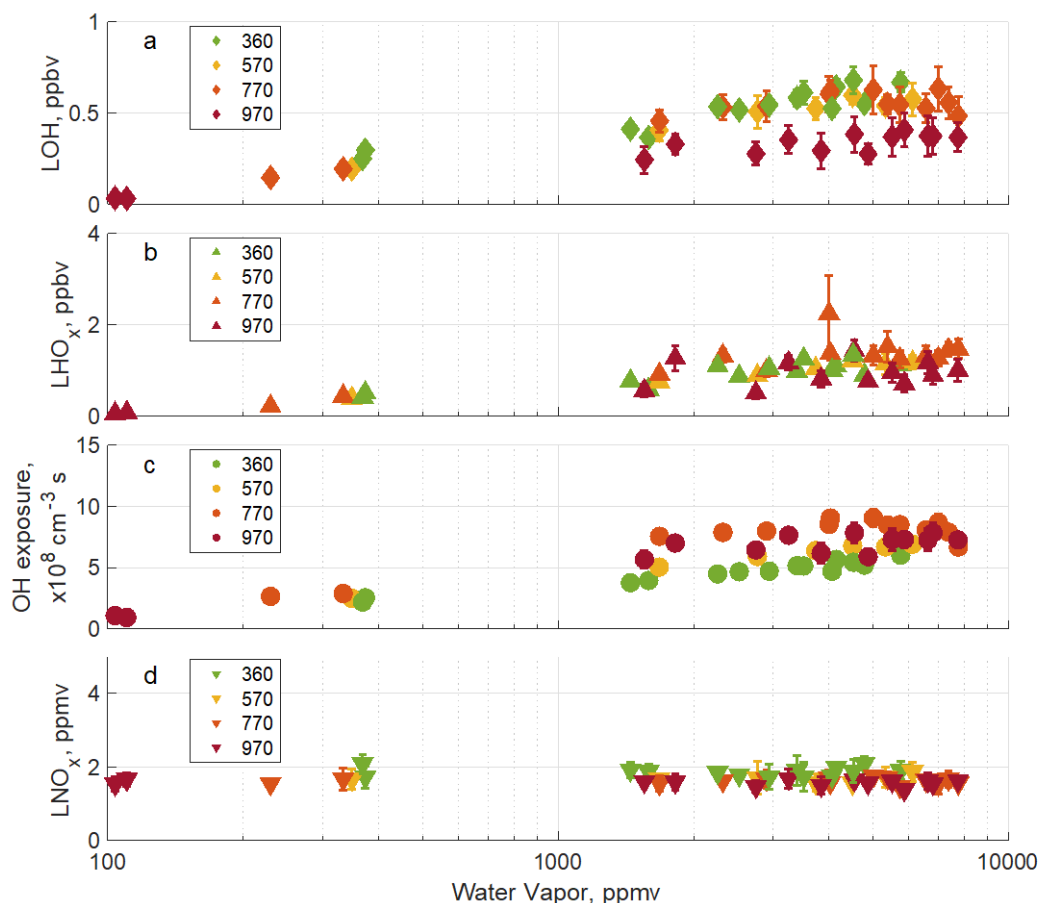


Figure 3. Electrical discharge generated quantities as a function of water and pressure: (a) LOH; (b) total LHO_x ; (c) OH exposure; (d) total LNO_x . The color of the data points goes from cooler to warmer colors from low to high pressure. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

LOH and LHO_x are lowest at the lowest water vapor concentrations, then increase slightly with increasing water vapor, changing less than a factor of two between water vapor mixing ratios of 1000 and 8000 ppmv (Figure 3a, 3b). The OH exposure follows the same basic trend as LOH and LHO_x (Figure 3c). It is not surprising that LOH and LHO_x increase with increasing water vapor, but this slow, seemingly logarithmic dependence is unusual in atmospheric-temperature chemical kinetics and will require a modeling study that incorporates the spark chemistry and dynamics as well as the subsequent atmospheric-temperature gas phase kinetics.

LNO_x was unaffected by water vapor concentration (Figure 3d). This outcome is consistent with the theory for LNO_x formation (Zel'dovich & Raizer, 1966), which also does not require water

molecules to generate LNO_x. The data points at each pressure are in line with the observations from the previous section that LNO_x is generally pressure-independent within measurement uncertainty across the pressures. NO_x again consisted of ~95% NO and ~5% NO₂.

3.3 Gap Length

Increasing the gap length can impact the breakdown voltage of the spark under certain conditions (Paschen, 1889), but, in this study, the breakdown voltage did not change significantly as the gap length was increased from 0.4 to 1.2 cm at two different pressures, 970 hPa and 360 hPa. However, LHO_x, LNO_x, and the OH exposure all increased with increasing gap length (Figure S7), directly due to the longer spark contacting more N₂, O₂, and H₂O compared to a shorter spark and producing more LHO_x and LNO_x as a result. These increases were not proportional to those of gap length, that is, as the gap length triples, LHO_x increased a factor of 1.7 at 970 hPa and a factor of 4.7 at 360 hPa.

The reason for these different LHO_x increases between the two pressures is likely due to chemistry. It is not due to spark energy changes with gap length because the breakdown voltage and the spark charge did not change by more than 10% for either pressure. However, HO_x is readily lost to NO_x by the reactions $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$, $\text{OH} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M}$, and $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$, and the LNO_x concentration at 970 hPa is about twice the concentration at 360 hPa. Furthermore, the air velocity for the experiments at 970 hPa was 60% of that for the experiments at 360 hPa. Thus, between the spark and the first sampling position, there was more NO_x that reacted for a longer time with OH and HO₂ before they are first detected at 970 hPa compared to 360 hPa. Based on this information, the increase in LHO_x with spark gap should be less for 970 hPa than for 360 hPa.

3.4 Spark Charge

The charge transferred by the spark is a good indicator of the amount of energy available to generate HO_x and NO_x because the breakdown voltages were measured to be roughly constant at ~7000 V for the two pressures used in these experiments. The spark charge was varied between 8.4×10^{-6} and 8.7×10^{-5} coulombs for a single spark by varying the discharge pulse width, although there was a point at which the pulse width was increased further but the spark charge remained constant, likely due to some electrical limitations of the Tesla coil. The discharge energies calculated from the charge and the voltage ranged from approximately 60 to 630 mJ for the spark charges shown in Figure 4.

LHO_x initially decreases as charge increases at both pressures, mostly due to decreases in the number of LHO₂ molecules (Figure 4a, 4b). These decreases probably do not reflect an actual change in HO_x production, but instead increased HO_x loss due increases in the number of NO_x molecules through the reactions described in the previous section. For repeated measurements at a constant spark charge of $\sim 8.7 \times 10^{-5}$ coulombs, LHO_x showed a range of values at both pressures.

When the mixing ratios are plotted as a function of pulse width (Figure S8), starting at a pulse width of 150 μs , LHO_x increases with increasing pulse width for a pressure of 970 hPa but does not change as much at 360 hPa. Despite these differences in LHO_x between the two pressures,

the OH exposure trend with increasing pulse width is similar at each pressure (Figure 4b, 4e), and matched the trend with LHO_x and pulse width at 970 hPa.

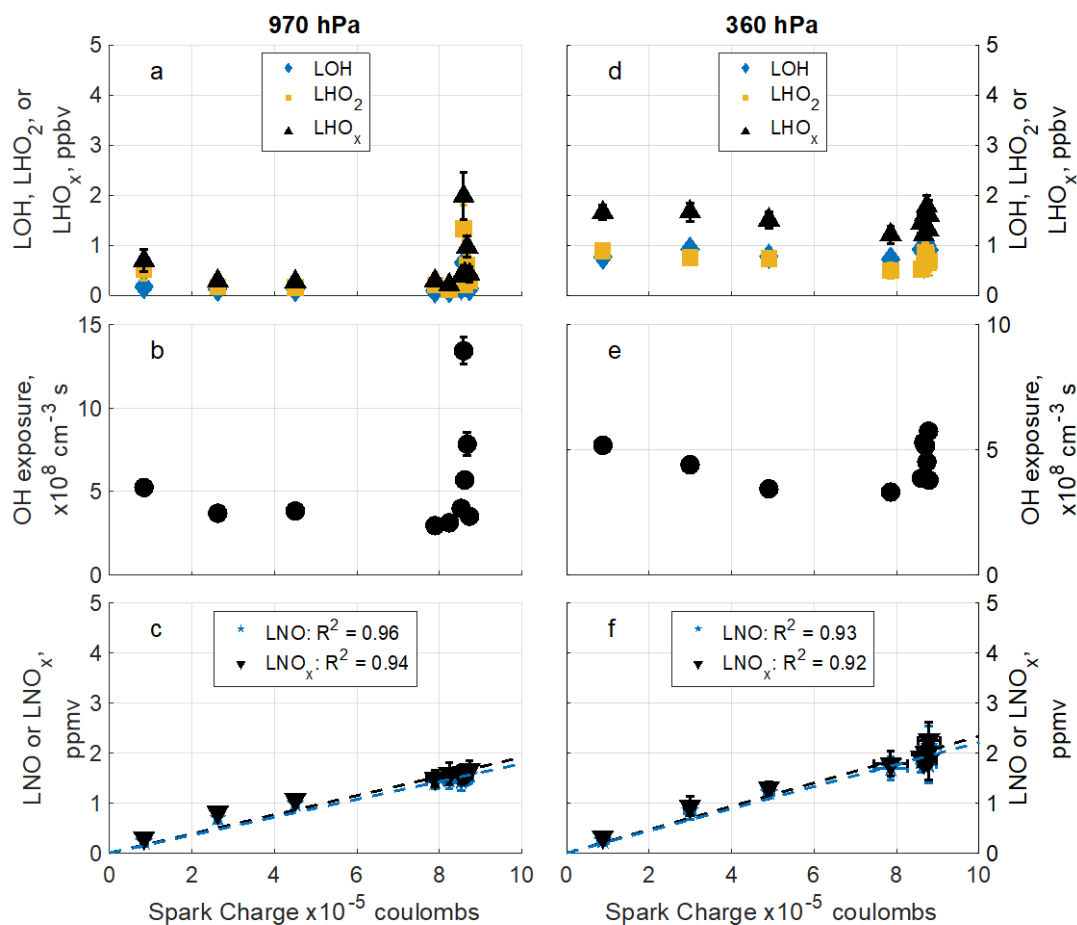


Figure 4. Electrical discharge generated quantities as a function of spark charge: (a) & (d) LOH (diamonds), LHO₂ (squares), total HO_x (upward triangles); (b) & (e) OH exposure (circles); (c) & (f) LNO (stars) and total LNO_x (downward triangles). Data in plots (a)-(c) were collected at 970 hPa, and the data in plots (d)-(f) were collected at 360 hPa. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

The changes in LHO_x for constant charge but increasing pulse width appear to be related to an increase in spacing between sparks within a discharge packet. As the pulse width was increased above 150 μs at both pressures, the spark duration stayed the same (Figure S9), but the Tesla coil waited the full pulse width before discharging again. For example, at a pulse width of 1500 μs , the spark duration was 150 μs , leaving a gap of 1350 μs (plus the pulse interval) prior to another spark discharge. For a pulse width of 100,000 μs the spark duration was still 150 μs , leading to 99,850 μs (plus the pulse interval) before the next discharge. Possibly, this increased spacing between sparks decreases the loss of HO_x to NO_x from the next spark in the discharge packet, leading to the observed increase in LHO_x with increasing pulse width. Because the air velocity

was higher for the experiments at 360 hPa compared to 970 hPa, the additional spacing between sparks affected the results obtained at 970 hPa but not 360 hPa.

At both pressures, LNO_x linearly increases as the spark charge is increased up to $\sim 8.7 \times 10^{-5}$ coulombs by increasing the discharge pulse width (Figure 4c, 4f). As the pulse width is increased more, the spark charge remains constant, as does the LNO_x , creating the mass of data points at the same spark charge and mixing ratio.

In general, LO_3 could not be detected above the O_3 instrument limit-of-detection of ~ 20 ppbv and it is assumed that the NO_2 that was observed came from spark-generated O_3 that reacted with NO to form NO_2 . However, for only the lowest charge at 970 hPa, approximately 100 ppbv of O_3 was detected. The sum of the O_3 and NO_2 mixing ratios makes up $\sim 30\%$ of total NO_x at the lowest charge, and decreased down to $\sim 5\%$ of NO_x as LNO_x increased, which provides evidence that much of the observed NO_2 was initially generated in the spark as O_3 and that LO_3 does not increase as much as LNO with increasing charge.

3.5 Subvisible electrical discharges

Subvisible electrical discharges expend much less charge than either sparks or corona. Because it was hard to produce subvisible discharges with the pointed electrodes, rounded electrodes with more uniform electric field gradients were used to obtain higher voltages before breakdown in order to examine the effects of subvisible discharges. Using the pulse width as the surrogate for energy, the pulse width was increased over the range from no electrical discharge, to subvisible discharge, to sparks. In Figure 5, LHO_x , the OH exposure, LO_3 , the sum of LO_3 and LNO_2 , and LNO_x are shown for one of these experiments as a function of increasing discharge charge. The sum of LO_3 and LNO_2 is included as any NO_2 likely originated from the reaction of O_3 with NO , and therefore the total amount of O_3 generated by the discharge would be the sum of LO_3 and LNO_2 . Although we have shown the results for one set of experimental conditions, keep in mind that changing these conditions, such as pressure, water vapor, gap length, and the electrodes, can vary these numbers by a factor of 2 or more, as has been demonstrated in the previous sections. However, the basic trends shown in Figure 5 hold regardless of the experimental conditions.

At the lowest pulse widths, no visible discharge, corona, HO_x , NO_x , or O_3 were detected. As the pulse width was increased, increasing the energy discharged by the Tesla coil, only OH and HO_2 were detected. At greater pulse widths, O_3 was measured. Only when visible sparks were triggered at the electrodes was NO_x detected. Prior to spark onset, LHO_x and the OH exposure had been steadily increasing with the pulse width, but both the LHO_x mixing ratios and the OH exposure reached their maximum values at pulse widths near the transition to sparks, then decreased slightly for increasing pulse width after the transition to sparks. LO_3 increased slightly with pulse width up to the spark transition, then after the transition decreased as NO_x converted most of the LO_3 to LNO_2 . LNO_x continued to increase with increasing pulse width, consistent with the observations from the pointed electrodes (Figure S7).

During the DC3 field campaign, enhanced HO_x was measured, usually with little corresponding enhanced LNO_x or electrical activity detected in the volume of air that the aircraft flew through (Brune et al., 2021). These experiments confirm the observation that LHO_x can be generated in weak, subvisible discharges, without little to no detectable NO_x present. The behavior of LHO_x ,

LO_3 , and LNO_x shown in Figure 5 can be explained by noting that the discharge generation of OH, HO_2 , and O_3 requires only the dissociation of H_2O and O_2 , with subsequent reactions of H and O with O_2 , while the discharge generation of NO requires not only the dissociation of N_2 , which has a dissociation energy roughly twice that of H_2O or O_2 , but also high-temperature chemistry (Brune et al., 2021).

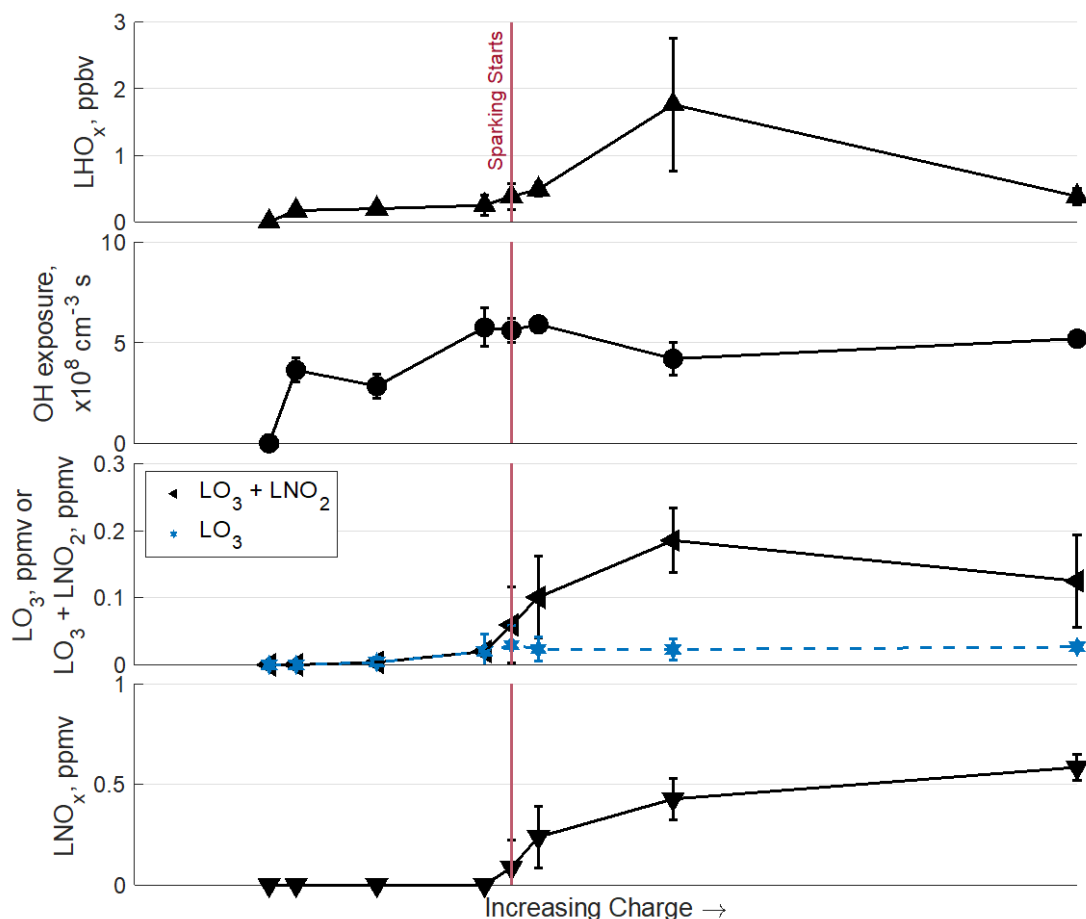


Figure 5. Electrical discharge generated quantities as a function of individual discharge charge: (a) total LHO_x , (b) OH exposure, (c) LO_3 (orange) and $\text{LO}_3 + \text{LNO}_2$ (green), and (d) total LNO_x . The red vertical line indicates the charge at which sparking started. Left of the red line on each plot, the discharges are subvisible, and, on the right side of the line, the discharges are visible sparks. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

4 Discussion

Most previous laboratory work was conducted at atmospheric pressure near 1000 hPa and therefore has been compared to the present laboratory results from 970 hPa, while the DC3 data was collected near 260 hPa and will be compared to the laboratory results from 360 hPa. It

should be noted that the molecule number concentration for 360 hPa at laboratory temperatures is equivalent to that for 290 hPa in the colder upper atmosphere.

4.1 Comparison to other laboratory studies

4.1.1 NO_x

The increases in LNO_x with increasing pressure (in terms of number of molecules generated), increasing gap length, and increasing peak current/energy were similar to those seen in previous studies (Rahman et al., 2011; Stark et al., 1996; Wang et al., 1998). Some previous work has found no connection between the water content of the air and LNO_x (Chameides et al., 1977; Rehbein & Cooray, 2001), which is consistent with our results, while other studies have found water dependence on either total LNO_x formed or on the fraction of LNO_x that forms NO₂ (Peyroux & Lapeyre, 1982; Stark et al., 1996). The Peyroux & Lapeyre (1982) study used discharges in static cells with long residence times, which could allow heterogeneous reactions affecting NO_x to occur on the humidified walls (Spataro & Ianniello, 2014). The residence time is not explicitly stated in the Stark et al. (1996) study, so similar heterogeneous reactions cannot be ruled out as an explanation of the water dependence in that study as well. With high flow rates and short residence times, this study is free from heterogeneous wall effects and demonstrates that water vapor has no influence on LNO_x.

We have reported our LNO_x results in terms of mixing ratio, but previous studies found that the number of molecules per length of discharge was in the range of 1×10^{19} to 1×10^{22} NO_x or NO molecules m⁻¹ (Rahman et al., 2011; Wang et al., 1998). The range from this study is $(2.3 \pm 0.5) \times 10^{18}$ to $(1.3 \pm 0.2) \times 10^{19}$ NO_x molecules m⁻¹, overlapping with the lower end of the previous range. This study used currents less than 2 A, at the low end of the range from A to kA used in previous studies. This study also shows a strong dependence of discharge-generated NO_x on charge, and charge increased with increasing current. Additionally, previous studies have also found that LNO_x increased with increasing peak current (Rahman et al., 2011; Wang et al., 1998). Therefore, we would expect that using currents closer to those used in previous studies would increase the number of NO_x molecules generated and bring our results into even better agreement with previous work.

When scaling the number of molecules per spark by energy instead, the previously reported range for LNO_x is from 2.74×10^{16} to 3.75×10^{17} molecules J⁻¹ of NO or NO_x (Chameides et al., 1977; Levine et al., 1981; Rahman et al., 2011; Rehbein & Cooray, 2001; Stark et al., 1996; Wang et al., 1998). Our results overlapped with this range, varying from $(1.1 \pm 0.4) \times 10^{16}$ to $(2.8 \pm 0.6) \times 10^{17}$ NO_x molecules J⁻¹.

4.1.2 O₃

Total O₃ generated from the discharges, determined from the sum of LNO₂ and LO₃, ranged from $(3-8) \times 10^{15}$ O₃ molecules for experiments using pointed electrodes. Previous studies have found either no LO₃ was made in visible sparks (Levine et al., 1981; Peyroux & Lapeyre, 1982;) or LO₃ was as much as half of total NO_x based on the amount of NO₂ measured (Stark et al., 1996). In this study, NO₂ + O₃ was typically 5-30% of total NO_x, with higher percentages at lower NO_x amounts. These percentages are within the previous ranges for visible spark

discharges. In the subvisible discharges, LO_3 was as much as $(5.2 \pm 0.8) \times 10^{13}$ molecules. Similar to previous work (Peyroux & Lapeyre, 1982), maximum LO_3 occurred for electrical charges near the transition from subvisible to visible discharge. However, if, for our laboratory setup, the LNO_2 measured after a two-second transit time to the NO_x -measuring instrument originated as LO_3 immediately after the spark, then LO_3 could actually be much larger with higher electrical charge.

4.1.3 HO_x

These are the first LHO_x laboratory measurements, but comparisons are possible with previous spark modeling work (Bhettanabhotla et al., 1985; Hill et al., 1981). The modelling studies calculate that initially as much as $(3.4\text{--}5) \times 10^{-8}$ moles cm^{-3} of OH and 9.0×10^{-11} moles cm^{-3} of HO_2 are produced in spark discharges at 2800–3000K. As the air cools down in the model, both the OH and HO_2 concentrations decrease to negligible values in less than 0.01 seconds, with the HO_2 concentration increasing later due to mixing with HO_2 -rich ambient air. In this study, the maximum OH and HO_2 measured was $(2.9 \pm 0.7) \times 10^{-14}$ mole cm^{-3} and $(6 \pm 2) \times 10^{-14}$ mole cm^{-3} respectively, well below the initial amounts calculated by the model, but they were measured at least 0.025 s after the flash. According to the model calculations, little LHO_x should remain when the air reaches ambient temperatures, and therefore, we should have measured no LHO_x in the laboratory at all. Possible reasons for this discrepancy are discussed in Section 4.3 Comparisons to a photochemical box model.

4.2 Comparison to DC3

4.2.1 NO_x and O_3

In the DC3 campaign, the measured peak LNO_x enhancements were often a few ppbv and occasionally ~ 10 ppbv (Brune et al., 2021). This laboratory study found that peak LNO_x was frequently 100–200 ppbv, although in some weaker spark discharges peak LNO_x was 5–20 ppbv. There are two potential explanations for the laboratory results often being higher than the DC3 results. First, in the DC3 campaign, the DC-8 aircraft flew only in thunderstorm anvils or on edges of convective cores, where the lightning and other subvisible discharges were generally weaker compared to the core itself. The air was sampled in the proximity of three lightning flashes, but unfortunately, the NO_x and O_3 instruments suffered electrical interference and no values were reported for those times. Thus, the LNO_x that was sampled in the anvil was either transported and diluted from the convective core or made by weak electrical discharges in the anvil itself. Because the few ppbv of NO observed in DC3 is near the limit of detection for our laboratory instrument as it was used in these experiments, it may be that either ppbv amounts of NO were being produced in the laboratory by charges near the spark transition or we have not yet simulated the exact electrical discharges that occurred in the cloud anvil to produce such low LNO_x . Additionally, we do not know the atmospheric volume into which LNO_x was mixed, further complicating comparison of the laboratory and atmosphere mixing ratios, which depend on volume.

Enhancements of O_3 were also detected from discharges in the DC3 study, with peak O_3 in the 10s of ppbv range. The laboratory results were similar to the DC3 results, with peak O_3 often in

the 10s of ppbv range and a few measurements of O₃ as high as 300 ppbv in weak visible spark discharges.

4.2.2 HO_x and OH exposure

Results from the DC3 flight report peak HO_x values in the range of 130 – 2000 pptv for both visible and subvisible discharges. In this study, peak HO_x mixing ratios fell in this range for lower water concentrations or weak subvisible discharges, while the visible sparks discharges exceeded 3000 pptv, at least when measured in the first stage position. With increasing distance from the GTHOS inlet, the peak OH fell more into the range measured in the DC3 study. As pointed out in the DC3 paper, likely some fractions of seconds to seconds elapsed between the visible and subvisible electrical discharges and the sampling by the HO_x-measuring instrument. In addition, the DC-8 HO_x-measuring instrument primarily sampled LHO_x from the weaker subvisible electrical discharges in the anvil or the edge of the convective core.

Furthermore, while we know the volumes into which the HO_x mixed for the laboratory discharges, there is again no way of determining this volume for the measurements made in the atmosphere. This volume question also applies to the OH exposures as well, because the OH exposure is calculated based on the number concentration of OH and is therefore also volume based. Finally, even if we knew the volume into which the HO_x mixed for the DC3 measurements, we still have no knowledge of the number or structure of the subvisible atmospheric discharges (Rison, 2016). If we assume that the volumes and subvisible discharges were comparable between the atmosphere and laboratory, then, for the weaker discharges or longer times in between generation and measurement of HO_x, the laboratory LHO_x and DC3 LHO_x agree.

The OH exposures measured in this study were in the range of $(1.1 \pm 0.1) \times 10^8$ to $(1.34 \pm 0.8) \times 10^9$ molecules cm⁻³ s in individual sparks and up to $(1.5 \pm 1) \times 10^9$ molecules cm⁻³ s in individual subvisible discharges. These values slightly overlap the modelled OH exposure range for the DC3 study, which was 1.2 to 11.8×10^9 molecules cm⁻³ s for both visible and subvisible discharges (Brune et al., 2021). As has been mentioned elsewhere in this paper, reactions with NO_x can be a large sink for HO_x, so the discrepancy between the laboratory and DC3 results for sparks likely comes in part from the larger amounts of NO_x detected in the laboratory relative to the amount detected in the DC3 study. For the subvisible results, the same considerations that complicate comparing the laboratory and atmosphere HO_x measurements also complicate comparing the laboratory and atmosphere OH exposures: the lack of more electrical information on these types of discharges, the inability to determine the volume into which LHO_x was mixed for the atmosphere, and, to a lesser extent, the actual initial values of OH and HO₂ just after the discharge.

4.3 Comparison to a photochemical box model

It is puzzling that the OH and HO₂ decays with time are not faster when the NO mixing ratio is in the ppmv range. The OH lifetime due to HONO formation alone should be a few milliseconds, but the observed decay gives an OH lifetime of hundreds of milliseconds. Using the same Framework for 0-D Atmospheric Modelling with the Master Chemical Mechanism, v3.3.1 used by Brune et al. (2021) for analysis of the DC3 observations, we modelled the OH decay

measured in these experiments. The model was initialized multiple ways, with the same amount of initial HO_x and NO_x as observed in the experiments, the same HO_x but less NO_x , and the same HO_x and no NO_x . HO_x decays in a few milliseconds for the first case, and much slower than observed for the third case (Figure 6). For the second case, the modelled OH decay was comparable to the observed decay for NO_x amounts that were 0.5% of the observed NO_x .

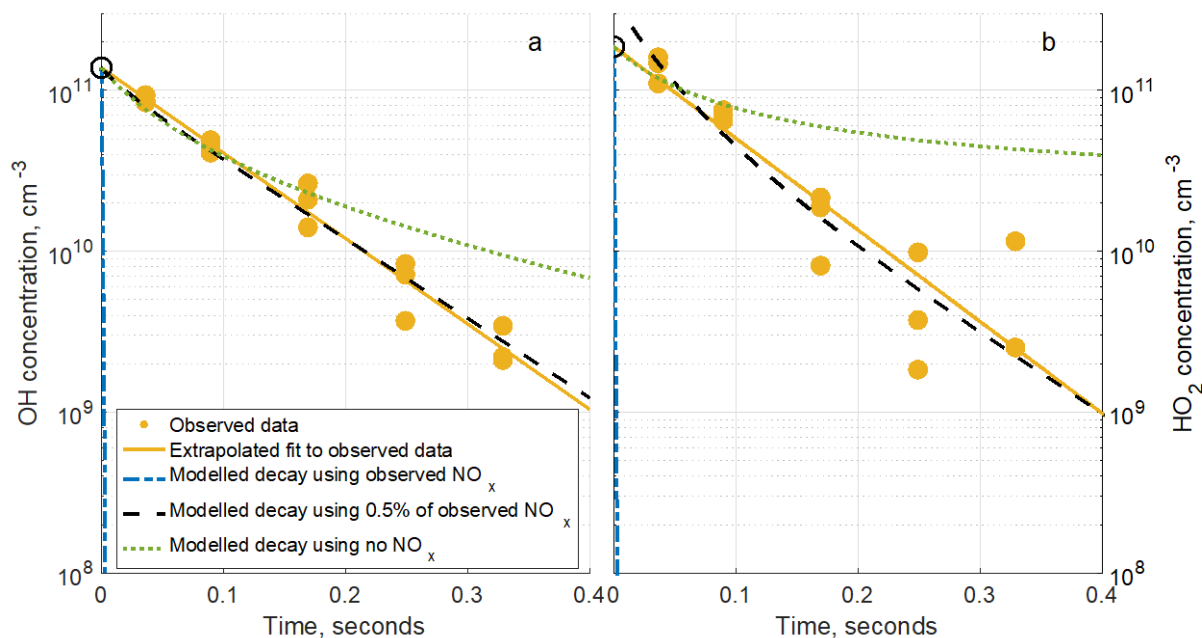


Figure 6. Observed and modelled (a) OH and (b) HO₂ decays. The observed data (yellow circles) are from a typical OH or HO₂ concentration decay from a visible spark across five times (positions). The fit applied to the extrapolated data (solid yellow line) is based on Equation S2, with R^2 values of 0.97 for OH and 0.81 for HO₂. When the OH or HO₂ concentrations are low or inconsistent, such as at low water vapor concentrations or in weak subvisible discharges, the decays are noisier with smaller R^2 values. The modelled decays include model results using the same HO_x and NO_x mixing ratios as we observed in the solid yellow line data (blue dash-dot line), using 0.5% of the observed NO_x (black dashed line), and using no NO_x (green dotted line). The observed and modelled OH and HO₂ concentrations used the integrated OH and HO₂ concentrations based on 10 discharges per packet in the experiments. The black circle at the intercept of the extrapolated fit with the y-axis is the initial OH or HO₂ formed in the spark.

There are three possibilities for the drastic differences between the observed OH and HO₂ decays and the decay modeled using the observed HO_x and NO_x . First, the HO_x - NO_x chemistry has unknown reactions that could recycle HO_x (Brune et al., 2016; Baier et al., 2017). The unidentified regeneration has been seen for decades in HO₂ measurements for higher amounts of ambient NO by essentially every research group that has the ability to measure ambient HO₂ (Emmerson et al., 2005; Kanaya et al., 2007; Ren et al., 2003; Ren et al., 2013). Brune et al. (2016) speculated that the reaction $\text{OH} + \text{NO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{NO}_2$ was the cause, but subsequent laboratory and theoretical work has shown that energy barrier prevents this reaction even though it is exothermic (Fittschen et al., 2017). Clearly, if such a reaction involves only reactions between HO_x and NO_x , it would occur during atmospheric electrical discharges.

Second, NO_x is generated in the spark while O_3 and HO_x are also generated in a much larger region around the spark, effectively partially segregating them in space. Finally, HO_x and NO_x are produced at different times in the discharge process, segregating them in time and thus space. If the chemistry is assumed to be well known, then the slower-than-expected OH decay would be due to the separation of HO_x and NO_x generation either spatially or temporally.

4.4 Relationship between LHO_x and LNO_x

Any attempt to develop a simple relationship between LHO_x and LNO_x that could be applied to global chemical models with LNO_x quickly leads to caveats. For visible spark discharges in environments with water vapor concentrations above ~ 1000 ppmv and spark charges of $\sim 8.7 \times 10^{-5}$ coulombs, the ratio of LHO_x to LNO_x is typically $\sim 7 \times 10^{-4}$ across all the tested pressures. However, the ratio decreases for decreasing water vapor and increases for decreasing spark charge, sometimes by orders of magnitude. In subvisible discharges where there was no measurable LNO_x , the ratio is much greater than 1. Therefore, there is no simple way to relate LHO_x and LNO_x without knowing much more about the distribution of sparks and subvisible electrical discharges in thunderstorms.

5 Conclusions

Substantial LHO_x is generated by both subvisible and visible discharges (sparks) and lasts longer than predicted by previous modelling studies. In terms of mixing ratio, this LHO_x was found to be roughly independent of all tested pressures and increases only slowly with increasing water vapor mixing ratios. LHO_x appears to decrease slightly with increasing spark charge, likely due to increasing LNO_x .

There are some challenges to relating the laboratory results and DC3 results for LHO_x , LNO_x , LO_3 , and the OH exposure, most notably the inability to determine the volume into which the discharge-generated chemical species are mixed for the atmospheric measurements and the lack of information on the atmospheric subvisible discharges. Despite these challenges, the laboratory results and DC3 results do show some agreement and are still close even when they do not overlap. Furthermore, the measurement of LHO_x from even subvisible discharges in the laboratory supports the observation in the DC3 study that HO_x is produced by low-energy subvisible discharges that were likely occurring in the anvils of thunderstorm clouds. Since subvisible discharges can occur throughout the anvil and core of thunderstorms, and possibly even around high-voltage power transmission lines, the impact of LHO_x on the atmosphere may be widespread.

To assess this impact, the results from these laboratory studies and the DC3 field experiment may be sufficient for devising simplistic and highly uncertain LHO_x parameterizations in models of lightning discharge, chemical transport, and climate. However, to reduce model uncertainty, more LHO_x studies are necessary. Additional laboratory work should measure LHO_x under even more realistic atmospheric conditions, such as lower temperatures and in clouds. To connect laboratory studies to the atmosphere, future field studies are needed to simultaneously measure atmospheric electrical discharge properties, HO_x , NO_x , and O_3 near lightning flashes and especially in subvisible electrical discharge regions. These future efforts outlined here will be

necessary to build a more confident understanding of the LHO_x contribution to global atmospheric oxidation.

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Data Availability Statement

All data used in the figures is publicly available at <https://doi.org/10.26208/1f6w-3n24>.

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Electrical discharges produce prodigious amounts of hydroxyl and hydroperoxyl radicals

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Introduction

Additional information regarding the experimental procedures, tests, and data processing are presented below, followed by supporting figures and table.

Text S1. Experimental Procedures

S1.1 Pressure

The pressure was changed by two methods in our laboratory setup. In the first method, the air flow in the flow tube was maintained at a constant velocity of $94 \pm 2 \text{ cm sec}^{-1}$, and the pressure was increased by increasing the standard mass flow rate from 30 to 70 slpm (standard liters per minute) in 10 slpm increments. In the second approach, a constant standard mass flow of 50 slpm was maintained in the flow tube, and the pressure was changed by changing the velocity using a valve on the vacuum pump. For the experiments looking at the pressure dependence of LHO_x and LNO_x , the water vapor concentrations were different for the two methods ($(1.14 \pm 0.04) \times 10^{16} \text{ cm}^{-3}$ for constant velocity and $(4.5 \pm 0.1) \times 10^{15} \text{ cm}^{-3}$ for constant mass flow), but all other variables were kept constant, including the pulse width (50,000 μs), pulse interval (25,000 μs), number of sparks (10 per packet), gap length (0.7 cm), and charge $((9.6 \pm 0.1) \times 10^{-6} \text{ coulombs})$.

S1.2 Water

The water vapor mixing ratio was changed by changing the portion of the total flow that passed through the bubbler in increments of 5 slpm from 0 slpm to 30 slpm (the maximum flow the bubbler could support). For experiments examining the water vapor dependence, the pressure was changed by keeping the standard mass flow constant (50 slpm) and changing the velocity. All other variables were kept constant, including the pulse width (50,000 μs), pulse interval (25,000 μs), number of sparks (10 per packet), gap length (0.7 cm), and charge $((9.5 \pm 0.3) \times 10^{-6}$ coulombs).

S1.3 Pulse Width

The pulse width is the amount of time that the Tesla coil is allowed to build up energy before it is discharged. Because the charge accumulated in the capacitor increases with time, shorter pulse widths lead to less accumulated charge. Thus, increasing the pulse width led to higher currents passing through the sparks and longer spark durations, up to a limit (Figures S7, S8). For pulse widths greater than $\sim 150 \mu\text{s}$, the current and duration of the sparks remained constant. This levelling off is likely due to some electrical limitation in the Tesla coil electronics.

The charge of the sparks was calculated by integrating the absolute value of the current waveforms over the duration of the waveform. The absolute value of the waveform was used because the Tesla coil produces alternating current discharges, so the sign of current of the discharges oscillated between positive and negative. However, both positive and negative current contribute to LHO_x , LNO_x , or LO_3 . Because the spark charge is calculated from the waveforms, and the waveforms become constant above the critical pulse width, the charge also becomes constant above the critical pulse width.

Different water vapor concentrations were used at 360 hPa $((5.6 \pm 0.1) \times 10^{15} \text{ cm}^{-3})$ and 970 hPa $((1.51 \pm 0.03) \times 10^{16} \text{ cm}^{-3})$, but all other factors were kept constant, including the mass flow (50 slpm) pulse interval (25,000 μs), number of sparks (10 per packet), and gap length (0.7 cm).

S1.4 Gap Length

The gap length experiments were also conducted at 970 hPa and 360 hPa, with the water vapor concentrations of $(1.46 \pm 0.02) \times 10^{16} \text{ cm}^{-3}$ and $(4.36 \pm 0.09) \times 10^{15} \text{ cm}^{-3}$, respectively, and spark charges of $(9.2 \pm 0.3) \times 10^{-6}$ coulombs and $(9.5 \pm 0.1) \times 10^{-6}$ coulombs, respectively. The mass flow (50 slpm), pulse width (50,000 μs) pulse interval (25,000 μs), number of sparks (10 per packet), were also kept constant.

S1.5 Subvisible Discharge

All of the data in Figure 5 are based on data generated using rounded copper electrodes. Starting at a pulse width where no visible discharge was present and neither HO_x , NO_x , nor O_3 were detected, the pulse width was increased in small steps (1-5 μs) to just past the point where sparks were triggered at the electrodes, then increased in larger steps (5-15 μs) up to 50 μs . These experiments were conducted at pressures of 970 hPa and 360 hPa, with respective water concentrations of $1.5 \times 10^{16} \text{ cm}^{-3}$ and $4.25 \times 10^{15} \text{ cm}^{-3}$. At 970 hPa, gaps lengths of 0.40 and 0.64 cm

were used, and, at 360 hPa, gap lengths of 0.79 and 0.95 cm were used. The mass flow (50 slpm), pulse interval (25,000 μ s), and number of discharges (5 per packet) were kept constant. Only 5 discharges per packet were used in these experiments with subvisible discharges, compared to 10 discharges per packet in the experiments with the pointed electrodes, to help reduce the sparking at the electrodes and ensure measurements were made with purely subvisible discharges. The results in Figure 5 are from experiments conducted at 970 hPa, with gap length of 0.64 cm and water concentration of $1.5 \times 10^{16} \text{ cm}^{-3}$.

Text S2. Tests of experimental factors

S2.1 OH and HO₂ signals due to LHO_x

Three tests were used to determine that the OH and HO₂ signals were due to LHO_x and not artifacts generated by electrical noise in the GTHOS electronics or to OH made within the GTHOS instrument.

First, during each experiment, the GTHOS laser wavelength was set off the OH absorption wavelength during one of the four discharge packets. In all cases, the OH or HO₂ signals were at the small background levels. Second, the GTHOS detection system uses a signal counter card that sorts counts into 50-ns bins following each of the 3000 30-ns laser pulses per second. The OH signals are largest for the bins nearest the laser pulse and then decay for later bins due to lifetime and the quenching of the OH molecule excited state. The signal decays observed for the large OH and HO₂ signals following the sparks agree with the decays expected from the known OH excited state quenching and lifetime. Thus, these signals are due to LHO_x. Third, a chemical species that reacts with OH, perfluoropropylene (C₃F₆), was added to the flow tube either downstream of the discharge through a Teflon tube attached to the same platform that held the electrodes, or upstream of the discharge by adding it to entire flow tube. When the C₃F₆ was added downstream, 98-99% of OH was removed across all stage positions compared to when no C₃F₆ was added, and for the upstream case at least 90-96% of OH was removed. For the amount of C₃F₆ added, at most 3% of OH is removed inside the GTHOS instrument, indicating that the OH is removed in the flow tube, not the GTHOS instrument.

These three tests prove that LHO_x is real.

S2.2 Variation of electronic discharge parameters

Two experimental variables, the pulse interval and the number of sparks in a packet, may not have equivalents in the real atmosphere, but were tested to assess their impact on the laboratory results. For both of these variables, these tests used the same mass flow (50 slpm), pulse width (50,000 μ s), and gap length (0.7 cm).

The pulse interval did not appear to affect LHO_x or the OH exposure at 360 hPa, nor LNO_x at either pressure (Figure S1). At 970 hPa, LHO_x and the OH exposure are initially flat, but, at a pulse interval of $\sim 10,000 \mu$ s, both started to increase. This increase likely occurs for the same reasons that an increase in LHO_x was observed for pulse widths above $\sim 150 \mu$ s at 970 hPa, wherein the increased spacing between sparks is decreasing losses of HO_x only at 970 hPa because the air velocity was slower at 970 hPa relative to 360 hPa.

At 360 hPa, the water concentration and spark charge were $(4.28 \pm 0.08) \times 10^{15} \text{ cm}^{-3}$ and $(9.56 \pm 0.05) \times 10^{-6}$ coulombs, respectively, while at 970 hPa, the water vapor concentration and charge were $(1.52 \pm 0.02) \times 10^{16} \text{ cm}^{-3}$ and $(9.14 \pm 0.08) \times 10^{-6}$ coulombs, respectively. The pressure was changed by keeping a constant mass flow rate (50 slpm) and changing the velocity, and 10 sparks per packet was used in all the experiments.

At both pressures, LNO_x scales directly with the number of sparks, approximately doubling and tripling as the number of sparks is increased from 5 to 10 to 15 sparks (Figure S2). The OH exposure and LHO_x both show strongly linear increases with increasing number of sparks, though neither scales as well as LNO_x , likely due to reactions of OH and HO_2 with the increasing NO and NO_2 .

At 360 hPa, the water concentration and spark charge were $(4.42 \pm 0.02) \times 10^{15} \text{ cm}^{-3}$ and $(9.51 \pm 0.02) \times 10^{-6}$ coulombs, respectively, while at 970 hPa, the water vapor concentration and charge were $(1.59 \pm 0.03) \times 10^{16} \text{ cm}^{-3}$ and $(9.138 \pm 0.006) \times 10^{-6}$ coulombs, respectively. The pressure was changed by keeping a constant mass flow rate (50 slpm) and changing the velocity, and a pulse interval of 25000 μs was used in all the experiments.

Text S3. Data analysis

S3.1 Procedure for converting mixing ratios to molecules

The equation for converting the measured mixing ratio to total molecules, X_{total} is

$$X_{total} = \frac{P}{k_b T} \times \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \times \int \chi_x dt \times (10^{-12} \text{ or } 10^{-9}) \times (Total \text{ Sample Flow}) \times \frac{1000 \text{ mL}}{L} \times \frac{1 \text{ cm}^3}{1 \text{ mL}} \times \frac{1 \text{ min}}{60 \text{ seconds}} \times Peak \text{ Time} \quad (S1)$$

where P is pressure in Pa, k_b is Boltzmann's constant, T is temperature in Kelvin, and χ_x is the mixing ratio of X per fifth of a second. The HO_x , NO_x , and O_3 data are reported as mixing ratios peaks by their respective analyzers, and each peak is integrated over time to determine the net chemical mixing ratio from the spark. These integrated mixing ratios are converted to fractions by multiplying by 10^{-12} for pptv or 10^{-9} for ppbv. The total sample flow, in units of standard liters per minute (slpm), is the sum of the flow into the GTHOS inlet and the flow through the sample lines that bring air over to the NO_x and O_3 analyzers. The peak time has units of seconds and is the length of time over which the measured HO_x , NO_x , and O_3 mixing ratio peaks were detected.

Physically, the first part of this equation uses the ideal gas law to convert the integrated mixing ratios to number concentrations, while the second part further converts the concentration to the total number of molecules by the determining the volume those molecules occupied.

S3.2 Diffusion and Sampling Corrections

S3.2.1 Diffusion

The measured LNO_x decreased at stage positions farther from the NO_x sampling point (Figure S3a). Because the NO_x lifetime is much longer than the 0.25 seconds in the flow tube, this

decrease in the measured LNO_x as the electrodes were moved further back from the sample inlets was likely due to diffusion that spread LNO_x radially outward and away from NO_x sampling port in the middle of the flow tube. Prior to any further processing, the LHO_x data were corrected for diffusion losses by using the average LNO_x diffusion for the same conditions.

S3.2.2 Sampling Correction

Only part of the total flow in the flow tube was captured for analysis through the cylinder attached to the GTHOS detection inlet, while the rest of the air that flowed around this cylinder was exhausted out of the flow tube through the large pump connected to the back of the detection block. To account for any HO_x, NO_x, or O₃ that was generated by the spark but not measured, a series of paired experiments were performed at 30, 50, and 70 slpm. In one experiment in each pair, the NO_x analyzer sampled the air stream normally captured by the sample line, and in the other experiment the NO_x analyzer sampled the air stream normally missing the sample line. Approximately 27 slpm is normally pulled through the main sample line while the NO_x analyzer pulls around 1 slpm, so switching the NO_x analyzer between the two lines decreases the total sample flow only around 4% between the two cases. The entire assessment was performed twice, both times at 970 hPa, with a pulse width of 50,000 μs, pulse interval of 25,000 μs, 10 sparks per packet, gap length of 0.7 cm, and a water concentration of $(1.55 \pm 0.02) \times 10^{16} \text{ cm}^{-3}$ for the first assessment and $(1.76 \pm 0.05) \times 10^{16} \text{ cm}^{-3}$ for the second assessment. The assessment was also repeated at gap lengths of 0.40 cm and 1.2 cm.

For each flow rate, 80-85% of the LNO_x generated in the discharge is normally captured in the first stage position for a gap length of 0.7 cm (Figure S3b). The results from running the assessment at 0.4 cm and 1.2 cm are not shown but were the same as for 0.7 cm. Based on this percentage, all the LNO_x data at all stage positions was corrected up 15% to account for the NO_x that misses detection due to sampling effects. Since it was not possible to switch the sampling for LHO_x or LO₃, we assumed that the same percentage of LO₃ and LHO_x is captured as of LNO_x and corrected those data up 15% for all stage positions as well.

After correcting for sampling, the average values of LNO_x or LO₃ from when the spark was in the first driver position are reported as the initial LNO_x or LO₃ values, since those values were the least affected by diffusion.

S3.3 Method for calculating initial OH, initial HO₂, and the OH exposure

To determine the initial amount of HO_x formed in the spark, the 5 stage positions were converted to 5 time intervals using the distance from the GTHOS inlet to the spark and the anemometer velocity. Using these times and the total OH or HO₂ concentration at each of the positions, an equation was developed to model to OH or HO₂ decay:

$$\ln([OH]) = \ln([OH]_i) + kt \quad (\text{S2})$$

$[OH]$ is the integrated OH concentration in cm^{-3} , $[OH]_i$ is the initial OH number concentration formed in the spark in cm^{-3} , k is the rate coefficient of any loss of OH in units of $\ln(\text{cm}^{-3}) \text{ s}^{-1}$, and t is time in seconds. Note that this equation assumes that any processes contributing to the loss of OH are unchanging or the concentration of any chemical reacting with OH can be treated as

constant. The same equation is used for HO_2 , though, of course, using HO_2 concentrations instead. The extrapolated fits for OH were also used to determine the OH exposure for each run by integrating the above equation from zero seconds out to the last time that data was collected at (the last stage position). The error bars for the OH exposures were determined from running Monte Carlo simulations on the slope, slope standard error, intercept, and intercept standard error from the extrapolated fits. An example of the OH decay and extrapolated fit can be seen in Figure 6.

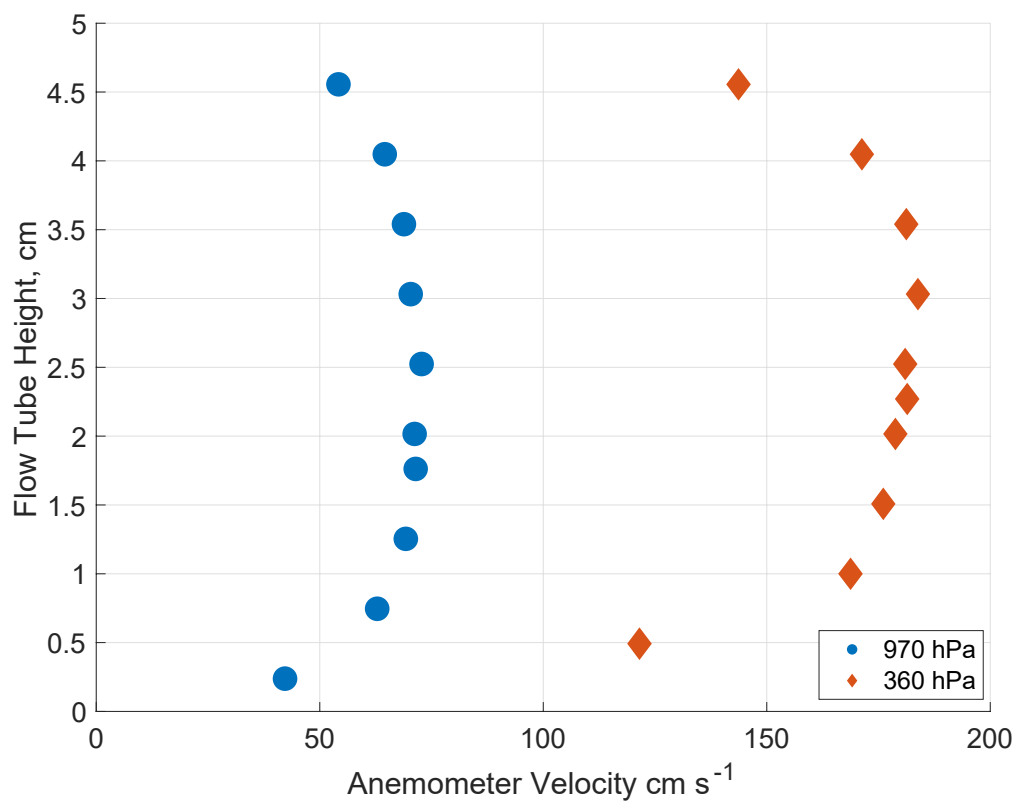


Figure S1. Vertical flow profiles measured at the end of the flow tube, for two flow conditions covering the range of conditions used in most of the experiments: 970 hPa, 50 slpm (circles) and 360 hPa, 50 slpm (diamonds).

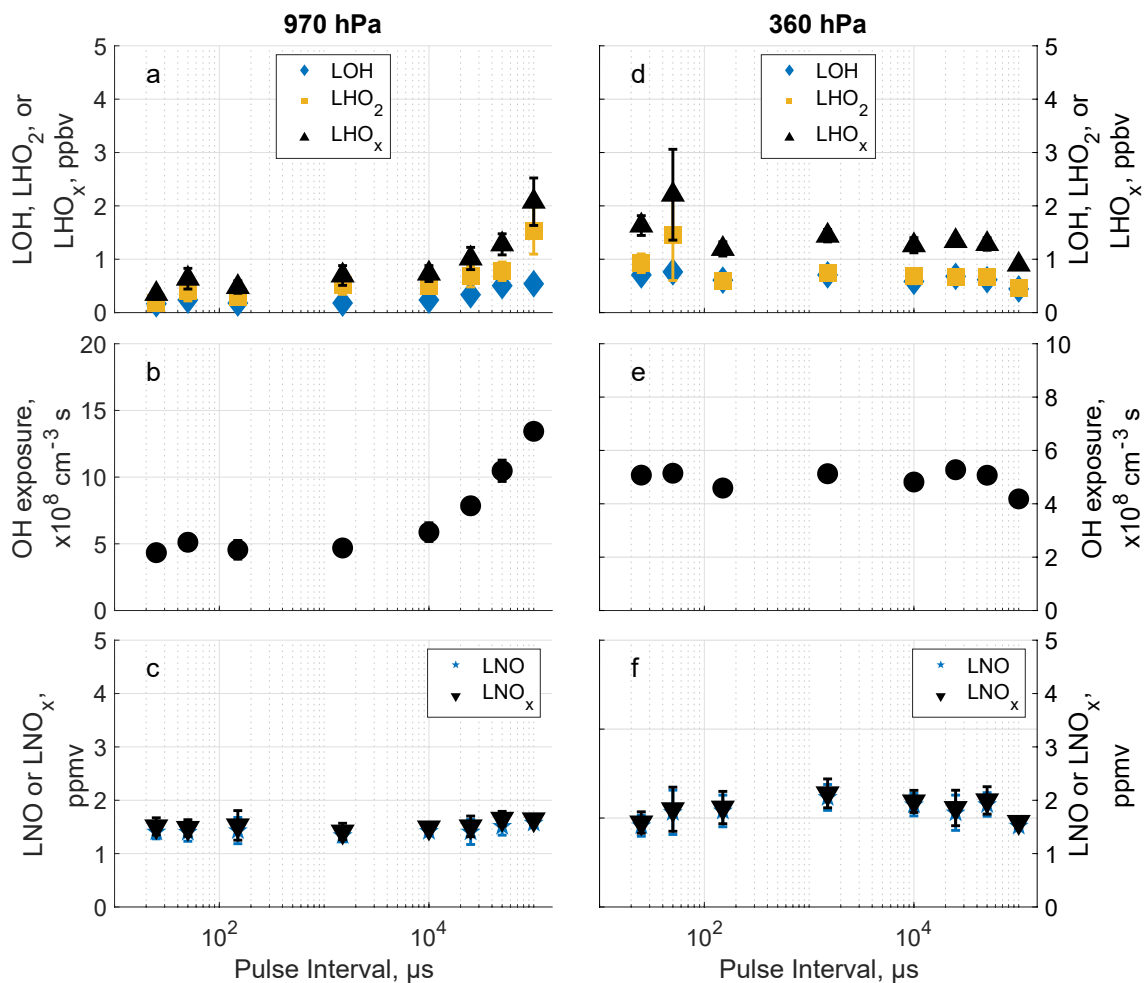


Figure S2. Electrical discharge generated quantities as a function of pulse interval: (a) & (d) LOH (diamonds), LHO_2 (squares), total LHO_x (upward triangles); (b) & (e) OH exposure (circles); (c) & (f) LNO (stars) and total LNO_x (downward triangles). Data in plots (a)-(c) were collected at 970 hPa, and the data in plots (d)-(f) were collected at 360 hPa. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

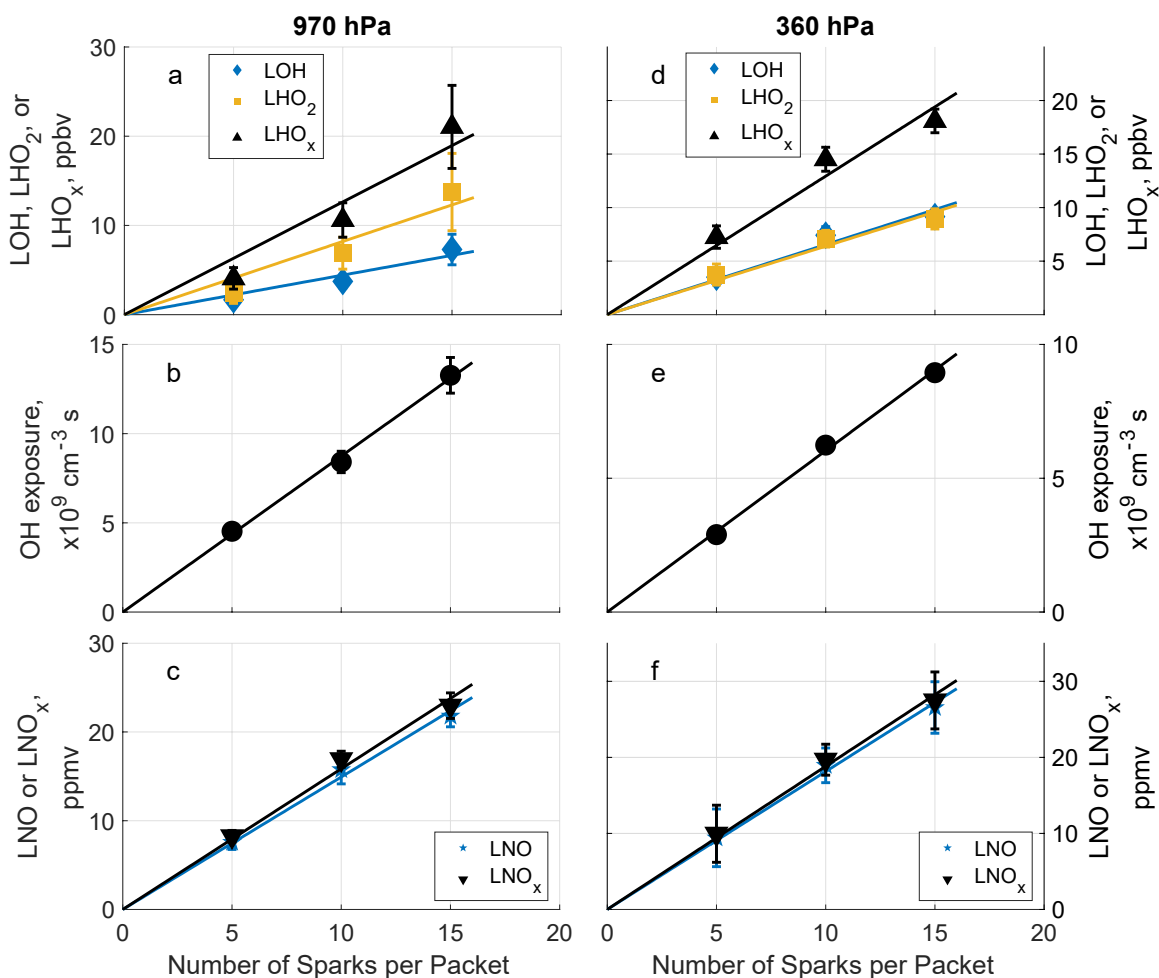


Figure S3. Electrical discharge generated quantities as a function of number of sparks per packet: (a) & (d) LOH (diamonds), LHO₂ (squares), total LHO_x (upward triangles); (b) & (e) OH exposure (circles); (c) & (f) LNO (stars) and total LNO_x (downward triangles). Data in plots (a)-(c) were collected at 970 hPa, and the data in plots (d)-(f) were collected at 360 hPa. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

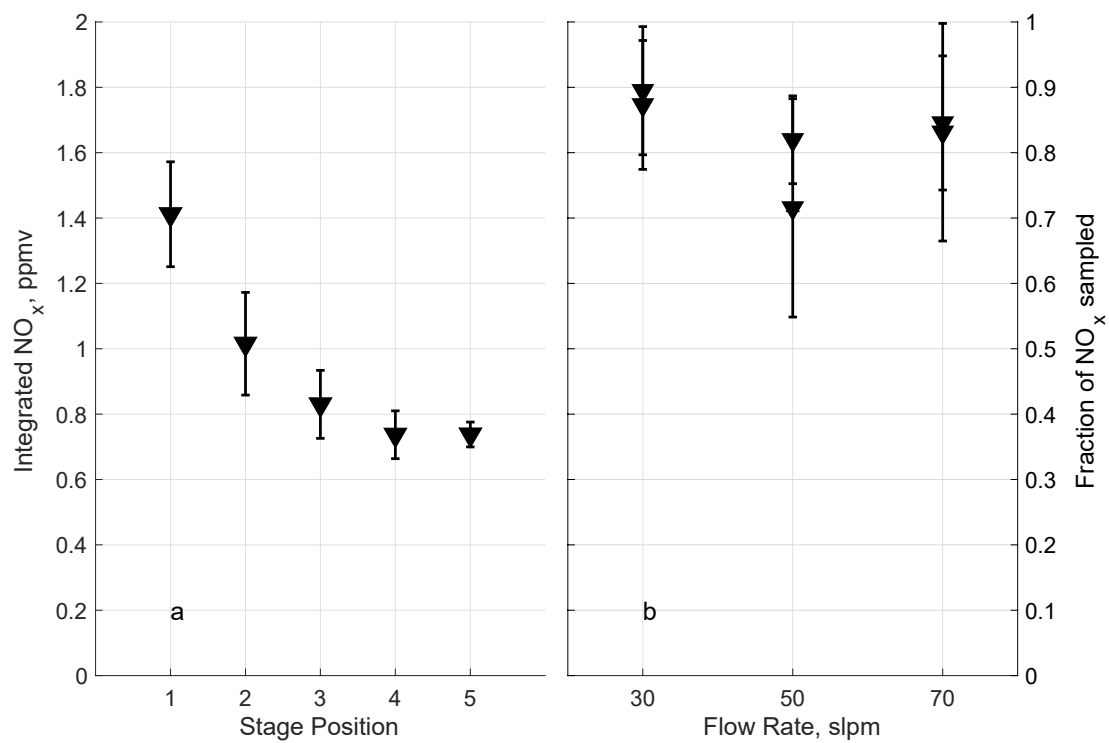


Figure S4. (a) Decay of NO_x with stage position in the flow tube. (b) Fraction of NO_x that is sampled out of the total NO_x generated in discharges at three different flow rates.

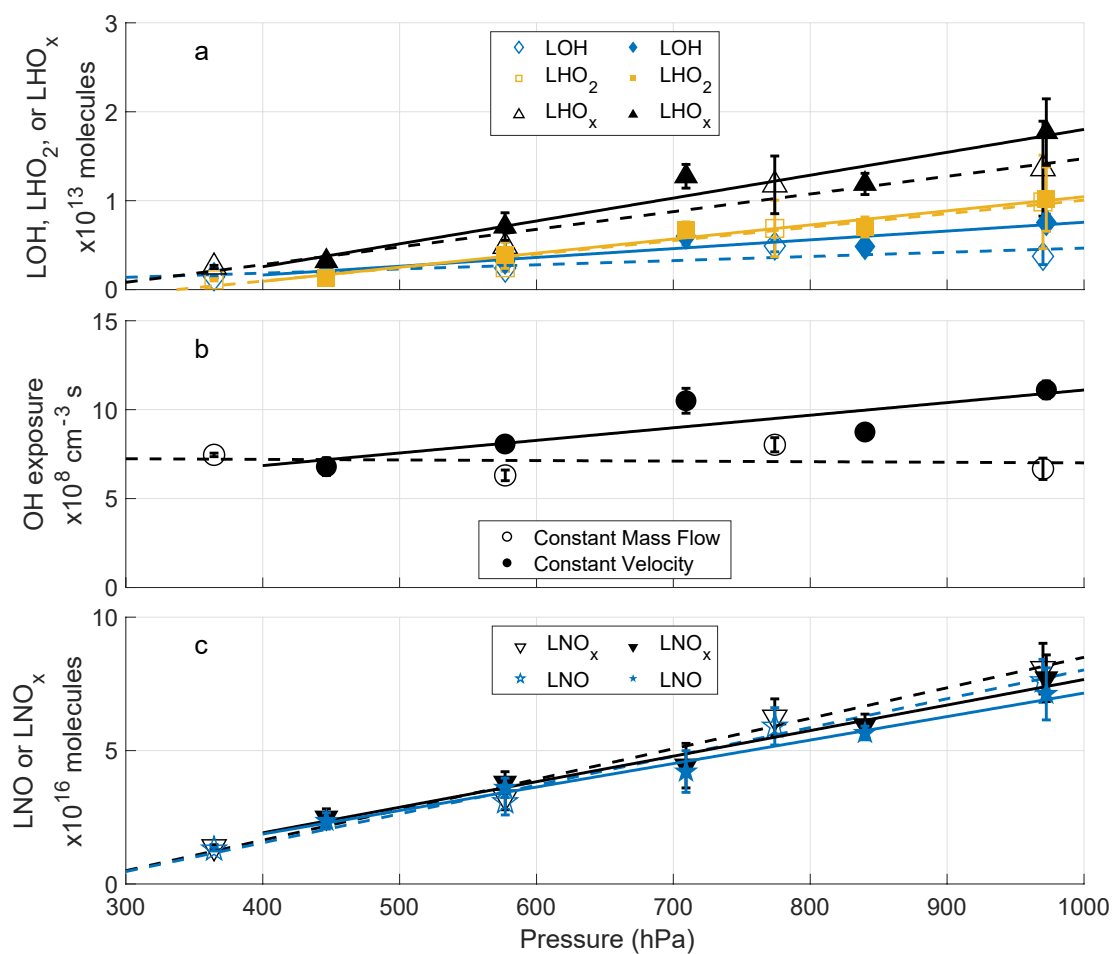


Figure S5. Molecules and OH exposure generated from individual sparks as a function of pressure: (a) LOH (diamonds), LHO₂ (squares), total LHO_x (upward triangles); (b) OH exposure (circles); (c) LNO (stars) and total LNO_x (downward triangles). The filled symbols indicate data that were collected with a constant velocity, while the open symbols indicate data that were collected with a constant mass flow rate. Different water concentrations were used in the two methods, but all other variables were kept the same between the two experiments. Linear fits were applied to each chemical species and the OH exposure for both methods of changing the pressure, and the R^2 for the linear fits are displayed in the legends on each plot. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

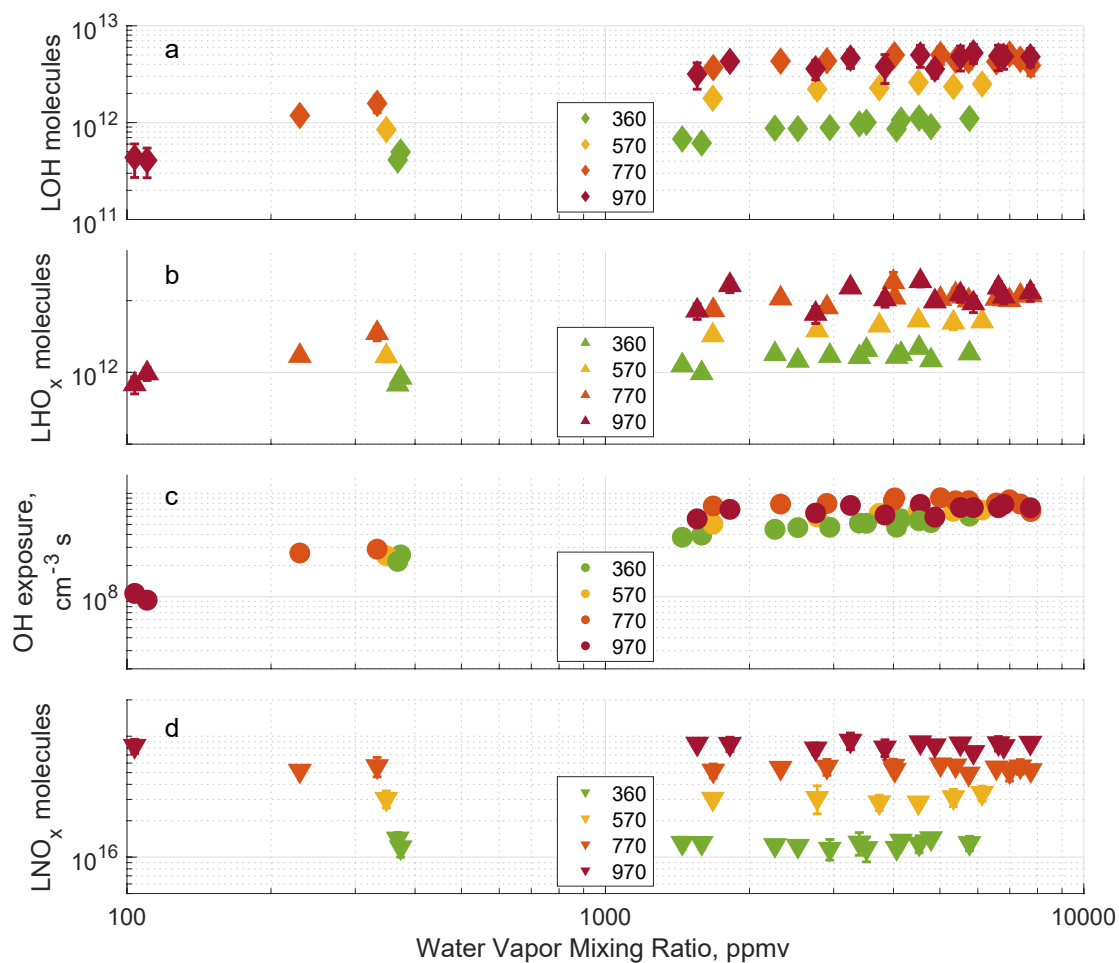


Figure S6. Molecules and OH exposure generated from individual sparks as a function of water and pressure: (a) LOH; (b) total LHO_x; (c) OH exposure; (d) total LNO_x. The color of the data points goes from cooler to warmer colors from low to high pressure. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

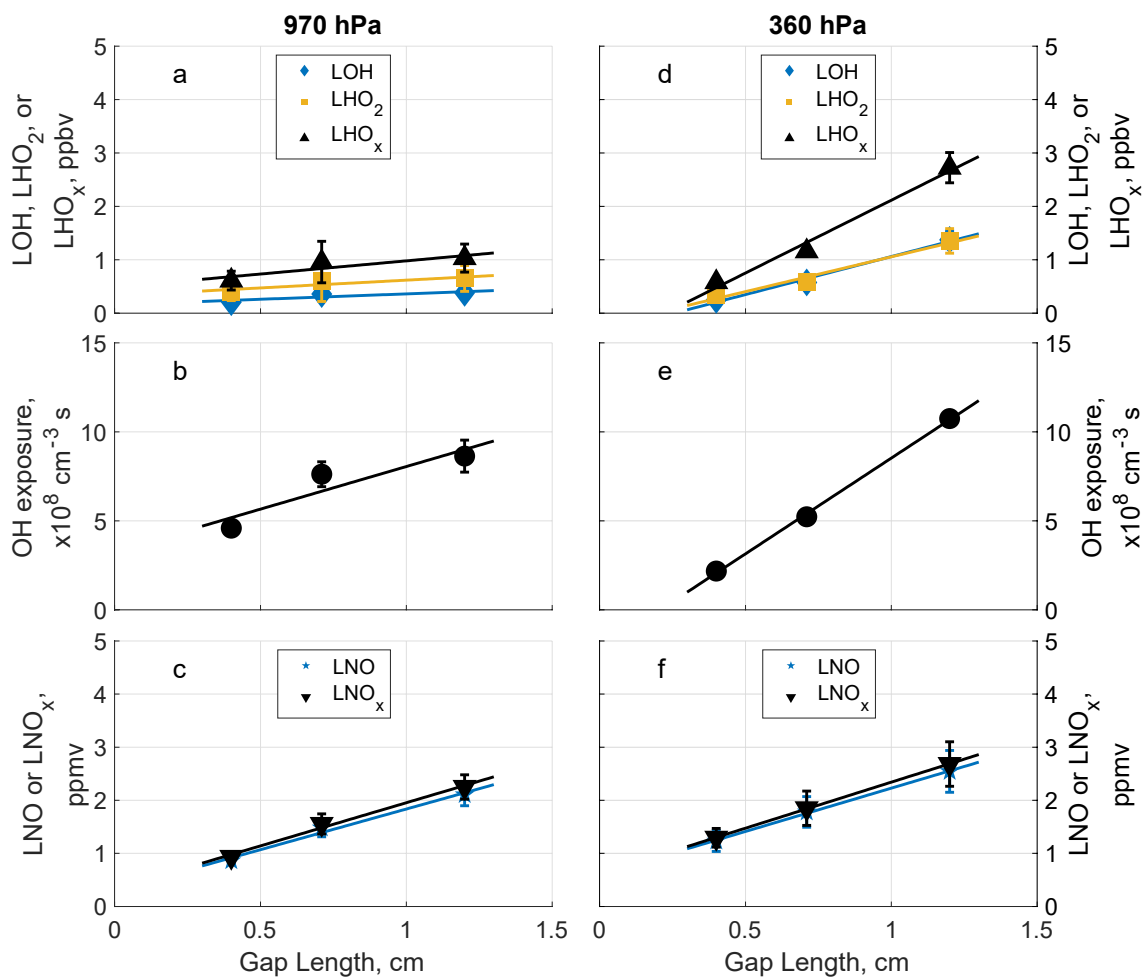


Figure S7. Electrical discharge generated quantities as a function of gap length: (a) & (d) LOH (diamonds), LHO₂ (squares), total LHO_x (upward triangles); (b) & (e) OH exposure (circles); (c) & (f) LNO (stars) and total LNO_x (downward triangles). Data in plots (a)-(c) were collected at 970 hPa, and the data in plots (d)-(f) were collected at 360 hPa. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

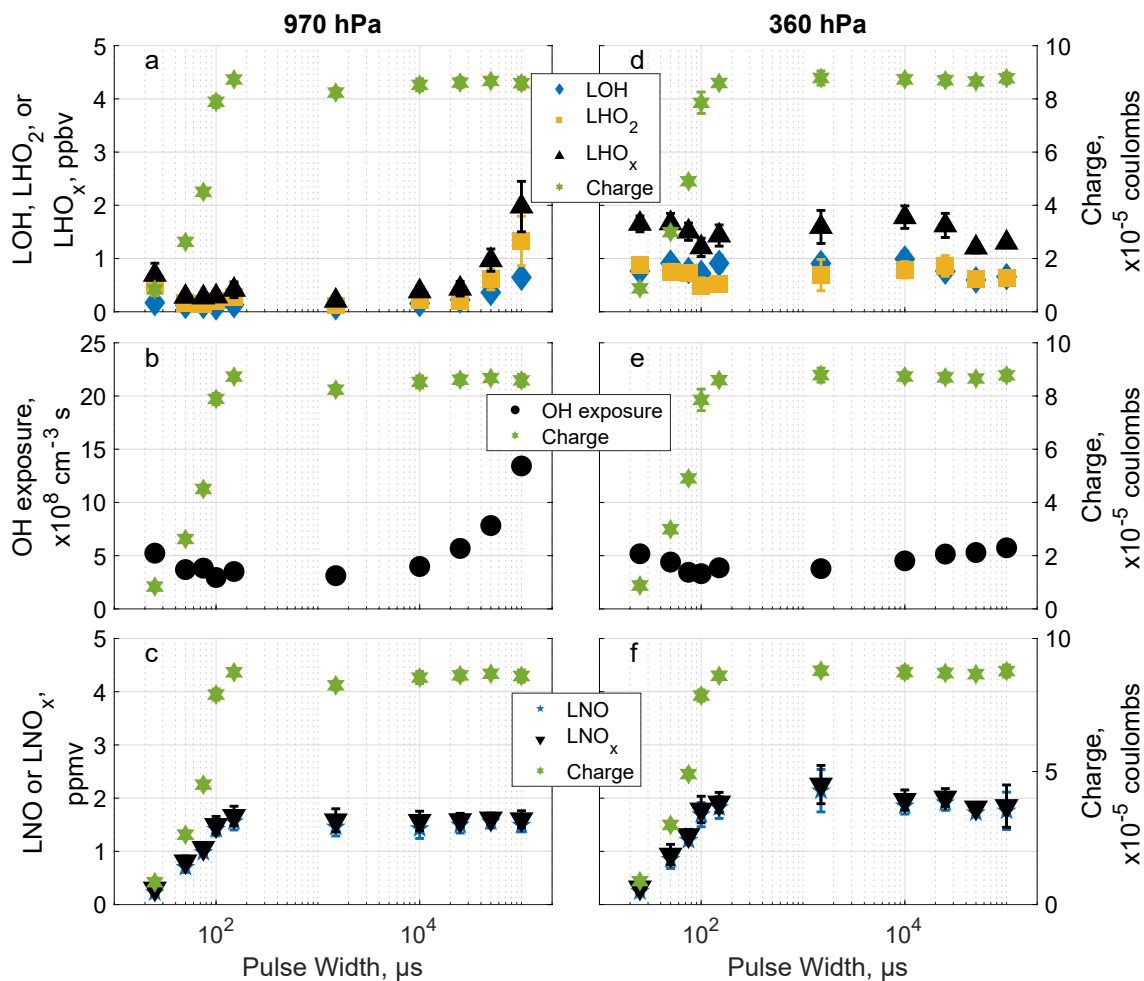


Figure S8. Electrical discharge generated quantities as a function of pulse width: (a) & (d) LOH (diamonds), LHO₂ (squares), total LHO_x (upward triangles); (b) & (e) OH exposure (circles); (c) & (f) LNO (stars) and total LNO_x (downward triangles). Spark charge (hexagrams) is also shown on each plot. Data in plots (a)-(c) were collected at 970 hPa, and the data in plots (d)-(f) were collected at 360 hPa. For each row of plots, the chemical mixing ratios use the far left axis while the spark charges uses the far right axis. Error bars represent the random error from multiple measurements at 68% confidence (1 sigma); error bars not visible are within the symbol.

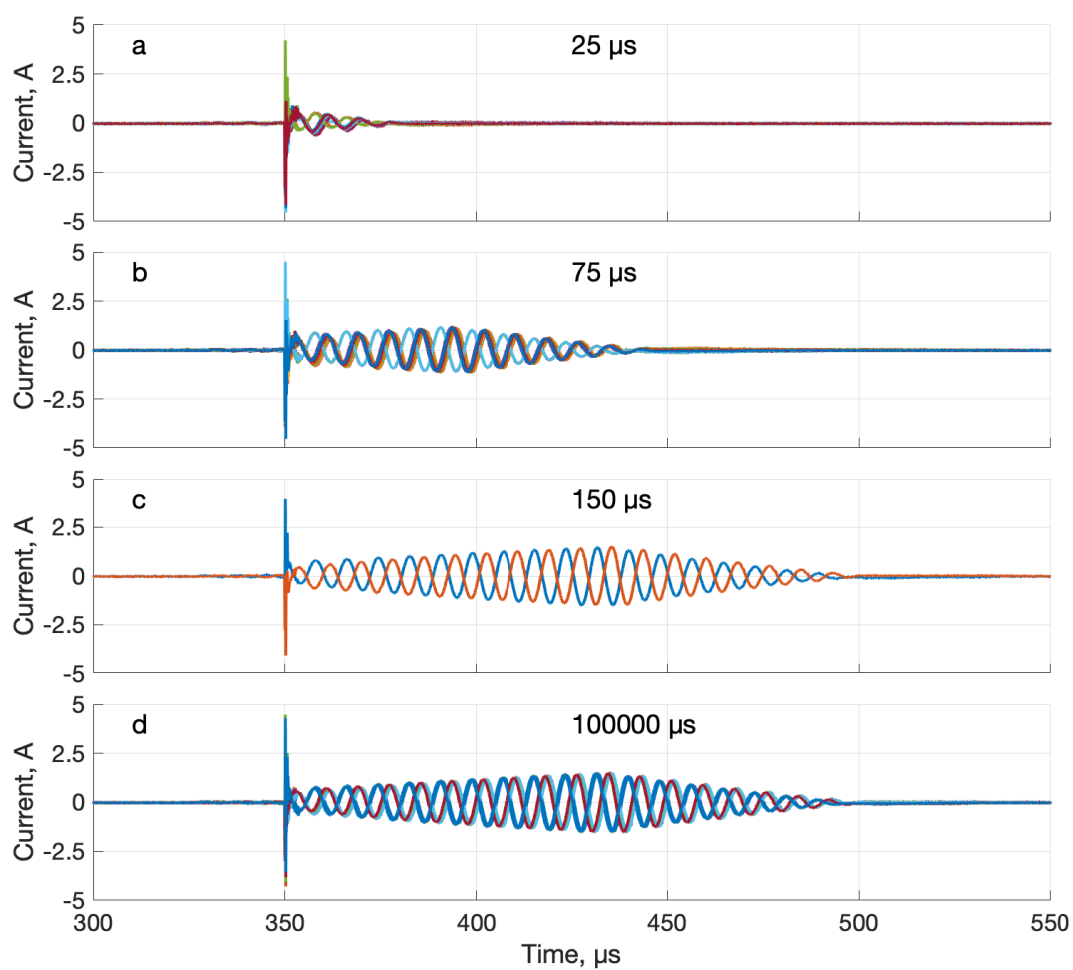


Figure S9. Waveforms for the data from Figure S6 at 970 hPa, at selected pulse widths (a) 25 μs : 14, (b) 75 μs : 15, (c) 150 μs : 2, (d) 100,000 μs : 14. The number after the colon represents the number of waveforms that are plotted at each pulse width.

Table S1. Slopes, Intercepts, and their standard errors for the linear fits in Figure 2.

Constant Velocity Linear Fits		
	Slope ^a	Intercept ^b
LOH	$(-4 \pm 3) \times 10^{-4}$	1.0 ± 0.3
LHO ₂	$(3 \pm 5) \times 10^{-4}$	0.6 ± 0.3
LHO _x	$(-1 \pm 8) \times 10^{-4}$	1.5 ± 0.6
OH exposure	$(7 \pm 3) \times 10^{-3}$	4 ± 2
LNO	$(-1.8 \pm 0.3) \times 10^{-3}$	2.9 ± 0.2
LNO _x	$(-1.8 \pm 0.4) \times 10^{-3}$	3.0 ± 0.3
Constant Mass Flow Linear Fits		
	Slope	Intercept
LOH	$(-8 \pm 3) \times 10^{-4}$	1.1 ± 0.2
LHO ₂	$(3 \pm 3) \times 10^{-4}$	0.5 ± 0.2
LHO _x	$(-5 \pm 5) \times 10^{-4}$	1.6 ± 0.4
OH exposure	$(0 \pm 3) \times 10^{-3}$	7 ± 1
LNO	$(-6 \pm 3) \times 10^{-4}$	2.1 ± 0.2
LNO _x	$(-7 \pm 3) \times 10^{-4}$	2.2 ± 0.2

^aUnits are ppbv hPa⁻¹ for LOH, LHO₂, and LHO_x; $\times 10^8$ cm⁻³ seconds hPa⁻¹ for OH exposure; and ppmv hPa⁻¹ for LNO and LNO_x.

^bUnits are ppbv for LOH, LHO₂, and LHO_x; $\times 10^8$ cm⁻³ seconds for OH exposure; and ppmv for LNO and LNO_x.