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Extreme oxidant amounts produced by lightning in storm clouds

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Lightning increases the atmosphere's ability to cleanse itself by producing nitric oxide (NO), leading to atmospheric chemistry that forms ozone (O₃) and the atmosphere's primary oxidant, the hydroxyl radical (OH). Our analysis of a 2012 airborne study of deep convection and chemistry demonstrates that lightning also directly generates the oxidants OH and the hydroperoxyl radical (HO₂). Extreme amounts of OH and HO₂ were discovered and linked to visible flashes occurring in front of the aircraft and to subvisible discharges in electrified anvil regions. This enhanced OH and HO₂ is orders of magnitude more than any previous atmospheric observation. Lightning-generated OH in all storms happening at the same time globally can be responsible for a highly uncertain but substantial 2-16% of global atmospheric OH oxidation.

Lightning contributes to the atmosphere's ability to cleanse itself through the production of reactive nitric oxide (NO) followed by its subsequent chemistry. The atmosphere's two primary oxidants, the hydroxyl radical (OH) and ozone (O₃), are produced when lightning NO reacts with the hydroperoxyl radical (HO₂) to produce OH and nitrogen dioxide (NO₂). NO₂ then decomposes in sunlight, leading to O₃ formation. The direct generation of O₃ from lightning (LO₃) has been inferred but not unambiguously observed in the atmosphere (1-3). Lightning production of nitrogen oxides (LNO_x) was first suggested in the early nineteenth century (4) and, in the past four decades, has been studied intensively in the atmosphere, laboratory, and model simulation (5-18). When global models of atmospheric chemistry include parameterized LNO_x emissions, tropospheric NO_x, O₃, and OH all increase substantially, primarily in the tropical to subtropical upper troposphere (19).

Electrified storms have charge distributions that are more horizontally stratified in anvils than in storm cores, but both anvils and cores contain granular electric field and charge distributions (20, 21), resulting in a range of electrical currents, from subvisible discharges to visible flashes (22-25). Some subvisible discharges have sufficient energy to overcome the dissociation bond strengths of H₂O, producing OH, H, and HO₂, and of O₂, producing O₃. Only visible flashes have sufficient energy to also dissociate N₂, which has a bond dissociation energy almost twice that of H₂O and O₂, and to

initiate the high-temperature chemistry that leads to NO formation (26). Previous modeling studies of lightning flash chemistry calculated that large amounts of OH and HO₂ (OH + HO₂ = HO_x) are produced by visible flashes, but the calculated OH lifetime is only milliseconds, too short for lightning HO_x (LHO_x) to contribute noticeably to atmospheric oxidation (27, 28).

However, these studies did not consider OH exposure, which is the integral of the OH concentration multiplied by time (Eq. 1).

$$OH_{\text{exposure}} = \int [OH] dt \quad (1)$$

OH exposure multiplied by the reaction rate coefficient between OH and another trace gas determines how much of that gas will be destroyed. If each of the lightning flashes and subvisible electrical discharges occurring simultaneously around the globe produces large amounts of OH and HO₂, it is possible that, even for short exposure times, LHO_x could make substantial contributions to the atmosphere's total OH exposure and therefore its oxidative capacity.

The NASA DC-8 aircraft flew through anvils of deep convective clouds during the Deep Convective Clouds and Chemistry (DC3) field study in summer 2012 (29). The aircraft carried instruments to measure in situ almost 100 atmospheric constituents, including OH and HO₂, which were measured by the Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS, see supplementary materials). Typically, the DC-8 flew in the near-surface inflow region of a growing

convective cell, spiraled up outside of it, and then sampled the convection outflow anvil. Simultaneously, a lightning mapping array (LMA) on the ground measured the position and intensity of the flashes within the convective storm and its anvil. Thus, DC3 presented an excellent opportunity to discover whether subvisible discharges and visible flashes produce substantial amounts of LHO_x.

Results from the 22-23 June flight

The DC-8 spent the most time in an anvil of active deep convection on 22-23 June over Colorado (Fig. 1). The DC-8 executed a low pass at 40.8° N latitude (Fig. 1A) before spiraling up beside the growing convective storm to 10 km altitude. HO_x was 5-20 pptv outside of the anvil, typical amounts for these altitudes (30). The first instance of enhanced HO_x of ~700 pptv was measured in the cloud on the edge of the storm convective core at 7 km altitude during the spiral, but all the other enhanced HO_x was observed as the DC-8 passed back and forth through the electrified anvil at three different altitudes between 10 and 11 km (Fig. 1, A and B). Finally, after the DC-8 did a loop through a fire plume (Fig. 1C, upper left), it passed through the edge of another convective cell to the south, where enhanced HO_x was again observed. These coincidences between enhanced HO_x and electrified regions in the convection anvils indicate that electrical discharges were the source of enhanced OH and HO₂.

A time series of measured HO_x, NO_x, and O₃ shows that HO_x and NO_x were enhanced only within the convection anvil, which is indicated by the ice water content (IWC) (Fig. 2). The HO_x and NO_x enhancements varied substantially in terms of peak values and duration, with enhanced HO_x varying from tens to thousands of pptv and persisting for distances between 0.1 to 8 km along the flight track. OH was often about half of enhanced HO_x (Fig. 2B).

Prior to this flight, the most HO_x ever observed in the atmosphere was about 150 pptv for HO₂ and a few pptv for OH (30, 31). Thus, these discharge-generated OH and HO₂ amounts are orders of magnitude above any amounts ever seen before in the atmosphere.

The NO_x enhancements above background were a few ppbv to occasionally more than 10 ppbv, as has been seen before (14, 16, 17). The enhanced HO_x and enhanced NO_x sometimes coincided, but not always, for two reasons. First, the NO_x lifetime is at least several hours, while the HO_x lifetime is at most a few minutes. Thus, enhanced NO_x could have come from Earth's boundary layer or from visible flashes in the convection core or anvil several minutes before the DC-8 arrived, whereas any lightning-generated enhanced HO_x would have reacted away. Second, enhanced HO_x with little to no enhanced NO_x is generated by weak subvisible electrical discharges because H₂O and O₂ have about half the bond dissociation energies of N₂ and NO production requires the high-

temperature chemistry made possible by visible flashes (26).

About one-third of the time, HO_x was enhanced in anvil regions where no electrical activity was detected by the LMA (Fig. 2B). For instance, the enhanced HO_x on the right of Fig. 2B reached 700 pptv while NO_x and O₃ were only a few times background, all in the anvil but outside of regions in which the LMA detected flashes. Thus, enhanced HO_x appears to be generated even by subvisible discharges too weak for the LMA to detect (32).

Some HO_x enhancements were accompanied by O₃ enhancements (Fig. 2). On the other hand, the DC-8 encountered stratospheric-like air that had wrapped itself around the outside of the anvil (33) and O₃ at the edge of the anvil often suddenly increased by as much as 100 ppbv, such as at 00:32 in Fig. 2. Thus, it is difficult to say with certainty that these coincident O₃ enhancements were definitely produced by electrical discharges, even though our laboratory studies show that they can be (26).

A careful review of the NASA DC-8 forward camera revealed several sub-second instances of visible lightning, including one at 00:16:01 and another at 00:16:11 UTC on 23 June. Less than a second after each visible lightning flash, large sub-second HO_x enhancements were measured. Enhancements were seen in NO_x and O₃, but they were considered spurious and thus were not included in the data set (see supplementary materials for explanation). Both flashes occurred in front of the aircraft and were recorded by the aircraft forward camera as short white lines that lasted just one frame (<33 ms). The second flash is seen as the short, curved white line in the photograph in Fig. 3 and is just a small segment of a much larger flash, according to the LMA (fig. S1). A few tenths of a second later, observed HO_x was enhanced by 2000 pptv (Fig. 3B). The time delay between the flash in the video and the enhanced HO_x indicates that this flash segment occurred tens of meters in front of the aircraft which traveled at 200 m s⁻¹. This result is consistent with the timing between the LMA flash and the enhanced HO_x spike in fig. S1 (34). Note that, for the smaller more diffuse HO_x spikes preceding and following these two flashes, no flashes were seen by either the forward or nadir camera. Because in-flight and laboratory evidence demonstrates that these HO_x spikes were generated by atmospheric electrical discharges (see supplementary materials and fig. S2), these observations provide conclusive evidence that lightning produces extreme amounts of HO_x.

Modeling the evolution of HO_x and NO_x

Several observations of enhanced HO_x peaks were modeled with a photochemical box model that was constrained with other DC-8 measurements (30). Of these, two cases are shown in Fig. 4. For the first case at 00:09:37, no visible flash was observed and the model was initialized with 0.5 ppbv of NO_x,

70 ppbv of O_3 , and 700 pptv of HO_x . For the second case at 00:16:11, the DC-8 sampled the air affected by the visible flash in Fig. 3 and the model was initialized with 230 ppbv of NO_x and 400 ppbv of O_3 , which were estimated from laboratory measurements, and 2000 pptv of HO_x . The names and numerical values for the other most important constraining chemical species are provided in the Photochemical Box Modeling section of the supplementary materials.

Modeled OH and HO_2 decay to background levels within a few minutes for the subvisible discharge case and within a second for the visible flash case. NO_x is effectively constant because its lifetime is typically several hours (18), although NO reacts with O_3 to produce NO_2 . For the low- NO_x case (a), the calculated OH and HO_2 decays are due primarily to the reactions $OH + HO_2 \rightarrow H_2O + O_2$ with a small contribution from $OH + NO + M \rightarrow HONO + M$, but for the high- NO_x case (b), the OH and HO_2 decays are due primarily to the reactions $OH + NO + M \rightarrow HONO + M$ and $OH + NO_2 + M \rightarrow HNO_3 + M$, with only a small contribution from $OH + HO_2 \rightarrow H_2O + O_2$.

As a result, the calculated OH exposure is 9.7×10^9 molecules cm^{-3} s for the case (a) and 1.2×10^9 molecules cm^{-3} s for case (b). Note that the OH exposure is the result of all OH production and loss processes. Once an electrical discharge produces enhanced OH and HO_2 , then OH will decay in a predictable way based on the rates of OH production, predominantly HO_2 reactions with NO and O_3 , and the rates of OH loss to HO_2 , NO, NO_2 , CO, CH_4 , and all other OH reactants. The OH exposure is just the integral of this decaying OH concentration over time (Eq. 1). Thus, for example, if a flash occurs once a second in the same volume of air, then the OH exposure (molecules cm^{-3} s) per flash times one flash per second will be the average OH concentration (molecules cm^{-3}) for that volume of air.

All flights into electrified anvils

Enhanced HO_x was observed on eight flights, always within electrified convective cores or anvils. On most flights, the DC-8 either flew inside the edge of the anvil or made only a few passes through it (figs. S3 and S4). For Table 1, the OH exposure was calculated for nine HO_x enhancements chosen to represent a range of initial HO_x and NO_x values, with four from the 22-23 June flight (Fig. 2). HO_x was enhanced by hundreds to thousands of pptv on all these flights, generally with little or no enhanced NO_x and O_3 and infrequent visible lightning. Peak OH was 125 to 600 pptv. As a result, the OH exposure calculated for these other flights was $3.3\text{--}11.8 \times 10^9$ OH molecules cm^{-3} s, consistent with that from the peaks on 22-23 June. Thus, the results from 22-23 June appear to be typical of the other DC3 flights in electrified storm anvils over Colorado or Oklahoma.

The electric field vertical structure was measured with

balloon-borne electrometers in convection also sampled by the DC-8 over Oklahoma on 19-20 May and 29 May (figs. S3 and S4). These storms had negative electric field extrema of -20 and -80 $kV\ m^{-1}$ and positive extrema of 10 to 40 $kV\ m^{-1}$, although the arrangement of negative and positive charge layers between these maxima was different between the two storms. These higher values are consistent with the breakdown electric fields that need to be exceeded before lightning can be initiated (35) and are fairly typical of the electric fields in electrified convection.

Discussion

Direct production of OH and HO_2 has now been observed in the anvils of deep convective clouds. The peak HO_x values were similar for subvisible discharges and the much less frequent visible flashes in regions where the LMA detected electrical discharges. In addition, about a third of enhanced HO_x was measured in the storm clouds outside of regions where the LMA detected flashes, indicating that low-energy subvisible electrical discharges not detected by the LMA also produced enhanced HO_x .

Global chemical transport models include parameterizations that use estimated LNO_x per visible flash (moles flash $^{-1}$ or molecules flash $^{-1}$) and thunderstorm visible flash distributions and then spread the LNO_x molecules throughout the grid cells affected by a visible flash to produce NO and NO_2 concentrations (36). Parameterizing LHO_x will be more complicated because subvisible discharges are such a substantial source. Our recent laboratory experiments have determined the LHO_x generated by individual sparks and subvisible discharges in terms of molecules m^{-1} discharge $^{-1}$ (26), but, in an electrified storm, LHO_x is likely generated by complex structures of subvisible discharges that vary in space and time but are currently unknown. At present, we can use only the OH mixing ratios measured during DC3 to estimate the LHO_x impact on atmospheric oxidation.

How important is LHO_x for atmospheric oxidation? For context, consider the global mean OH exposure per second, which is the same as the global mean number of OH molecules. Global model estimates of the mean [OH] are $1.03 - 1.15 \times 10^6$ molecules cm^{-3} (37-42), with an estimated uncertainty of ~25%, 68% confidence. Here we use the global number of OH molecules calculated from a global chemistry-climate model, which is 4×10^{30} molecules (42).

Two methods for estimating the OH generated each second by LHO_x are described in the supplementary materials. Both methods assume that the amount of enhanced HO_x observed along the DC-8 flight path through the anvil represents the amount of enhanced HO_x generated throughout the electrified anvil region. Both use the typical LMA volume (table S1), the fraction of the flight track for which the electrical discharge occurred within the past second, and the typical

OH exposure per electrical discharge. The first method uses flash rates in the anvil and the second method uses the ratio of enhanced HO_x inside and outside of the regions in which the LMA detected electrical discharges but still inside the anvil. From these calculations, the convective cell anvil on 22 - 23 June generated 2.7×10^{26} molecules for each second by the first method and 3.1×10^{25} molecules for each second by the second method.

The global number of active convective cells for each moment is thought to be 1800 (16). Thus, the electrically charged storm anvils would generate 4.9×10^{29} molecules each second by the first method and 5.6×10^{28} by the second method. The numbers are similar for the convective cell anvil sampled on 29 May (table S2). As a result, LHO_x in convective cell anvils could be responsible for 1.4 - 12% of global OH.

LHO_x further contributes to global OH in two other ways. First, much of the HONO produced from the reaction of enhanced OH and NO would eventually be photolyzed by sunlight, releasing OH and increasing the contribution of LHO_x to global OH. Second, from the DC3 LMA data, the convective core on 22-23 June contained 70% of the flashes (Fig. 1). During the spiral up on both 29 May and 23 June, the DC-8 flew through clouds associated with the convective core, encountering almost continuous enhanced HO_x in those clouds even though the DC-8 was kilometers from the nearest flashes. If total electrical activity is proportional to flash extent, then this core could have produced an OH exposure about a third that of the anvil, increasing the LHO_x contribution to global OH to 2 - 16%.

We emphasize that these estimates of the LHO_x contribution to global OH are highly uncertain by perhaps a factor of ten (fig. S5). These storms, their electrical activity, or their LHO_x generation may be atypical of global storms because Colorado and Oklahoma storms have different lightning characteristics from the more numerous tropical and subtropical storms (43). In addition, LHO_x generation by subvisible discharges as well as visible flashes makes estimating LHO_x more uncertain than estimating LNO_x. Thus, the ratio of LHO_x to LNO_x varies from less than 0.01 for visible flashes to more than 1000 for subvisible discharges. None-the-less, it may be possible to relate the amounts of LHO_x and LNO_x, but not from the DC3 data alone. These uncertainties must be narrowed before LHO_x can be included with any confidence in global chemical transport models and climate models.

Narrowing the LHO_x production uncertainty requires sampling a variety of electrified storms with an aircraft instrumented to measure environmental conditions, cloud particle properties, water vapor, electric fields and charge distributions, electrical discharge video and sound, OH, HO₂, NO, NO₂, O₃, and HONO at 5 Hz or faster. At a minimum, this aircraft should sample electrified anvils at different distances from the core, but optimally, it should penetrate the core

itself at different altitudes. These storms should be observed simultaneously by an LMA and satellites. Such aircraft studies would determine the globally observed factors needed to parameterize LHO_x in models.

LHO_x is contributing to the global OH calculated from observations of atmospheric constituents that react with OH, such as methane or methyl chloroform (37-42), implying that the OH actually produced by standard atmospheric chemistry is less than currently calculated. In addition, the impact of LHO_x on different atmospheric constituents depends on where it is generated. Our laboratory studies (26) indicate that LHO_x is generated in storm cores, cloud-to-ground lightning, and possibly even near high-voltage power lines, as well as in storm cloud anvils. Thus, LHO_x could be contributing to regional and global oxidation well beyond the storm cloud anvils. Furthermore, LHO_x may well be a larger contributor to global atmospheric oxidation than LNO_x. It is reasonable to assume that, in a warmer climate, an increase in storm intensity and lightning will increase the importance of lightning-generated OH to regional and global atmospheric oxidation.

REFERENCES AND NOTES

1. R. E. Orville, Ozone production during thunderstorms, measured by the absorption of ultraviolet radiation from lightning. *J. Geophys. Res.* **72**, 3557-3561 (1967). [doi:10.1029/J7072i014p03557](https://doi.org/10.1029/J7072i014p03557)
2. H. Bozem, H. Fischer, C. Gurk, C. L. Schiller, U. Parchatka, R. Koenigstedt, A. Stickler, M. Martinez, H. Harder, D. Kubistin, J. Williams, G. Eerdekens, J. Lelieveld, Influence of corona discharge on the ozone budget in the tropical free troposphere: A case study of deep convection during GABRIEL. *Atmos. Chem. Phys.* **14**, 8917-8931 (2014). [doi:10.5194/acp-14-8917-2014](https://doi.org/10.5194/acp-14-8917-2014)
3. H. Huntrieser, M. Lichtenstern, M. Scheibe, H. Aufmhoff, H. Schlager, T. Pucik, A. Minikin, B. Weinzierl, K. Heimerl, D. Fütterer, B. Rappenglück, L. Ackermann, K. E. Pickering, K. A. Cummings, M. I. Biggerstaff, D. P. Betten, S. Honomichl, M. C. Barth, On the origin of pronounced O₃ gradients in the thunderstorm outflow region during DC3. *J. Geophys. Res. Atmos.* **121**, 6600-6637 (2016). [doi:10.1002/2015JD024279](https://doi.org/10.1002/2015JD024279)
4. J. von Liebig, Note sur la Nitrification. *Ann. Chem. Phys.* **35**, 329-333 (1827).
5. A. F. Tuck, Production of nitrogen oxides by lightning discharges. *Q. J. R. Meteorol. Soc.* **102**, 749-755 (1976). [doi:10.1002/qj.49710243404](https://doi.org/10.1002/qj.49710243404)
6. W. L. Chameides, D. H. Stedman, R. R. Dickerson, D. W. Rusch, R. J. Cicerone, NO_x production in lightning. *J. Atmos. Sci.* **34**, 143-149 (1977). [doi:10.1175/1520-0469\(1977\)034<0143:NPIL>2.0.CO;2](https://doi.org/10.1175/1520-0469(1977)034<0143:NPIL>2.0.CO;2)
7. E. Franzblau, C. J. Popp, Nitrogen oxides produced from lightning. *J. Geophys. Res.* **94**, 11089-11104 (1989). [doi:10.1029/JD094iD08p11089](https://doi.org/10.1029/JD094iD08p11089)
8. C. Price, J. Penner, M. Prather, NO_x from lightning. 1. Global distribution based on lightning physics. *J. Geophys. Res.* **102**, 5929-5941 (1997). [doi:10.1029/96JD03504](https://doi.org/10.1029/96JD03504)
9. Y. Wang, A. W. DeSilva, G. C. Goldenbaum, R. R. Dickerson, Nitric oxide production by simulated lightning: Dependence on current, energy, and pressure. *J. Geophys. Res.* **103**, 19149-19159 (1998). [doi:10.1029/98JD01356](https://doi.org/10.1029/98JD01356)
10. A. J. DeCaria, K. E. Pickering, G. L. Stenchikov, J. R. Scala, J. L. Stith, J. E. Dye, B. A. Ridley, P. Laroche, A cloud scale model study of lightning-generated NO_x in an individual thunderstorm during STERAO-A. *J. Geophys. Res.* **105**, 11601-11616 (2000). [doi:10.1029/2000JD900033](https://doi.org/10.1029/2000JD900033)
11. B. Ridley, L. Ott, K. Pickering, L. Emmons, D. Montzka, A. Weinheimer, D. Knapp, F. Grahek, L. Li, G. Heymsfield, M. McGill, P. Kucera, M. J. Mahoney, D. Baumgardner, M. Schultz, G. Brasseur, Florida thunderstorms: A faucet of reactive nitrogen to the upper troposphere. *J. Geophys. Res.* **109**, D17305 (2004). [doi:10.1029/2004JD004769](https://doi.org/10.1029/2004JD004769)

12. A. J. DeCaria, K. E. Pickering, G. L. Stenchikov, L. E. Ott, Lightning-generated NO_x and its impact on tropospheric ozone production: A three-dimensional modeling study of a Stratosphere-Troposphere Experiment: Radiation, Aerosols and Ozone (STERAO-A) thunderstorm. *J. Geophys. Res.* **110**, D14303 (2005). [doi:10.1029/2004JD005556](https://doi.org/10.1029/2004JD005556)
13. B. A. Ridley, M. A. Avery, J. V. Plant, S. A. Vay, D. D. Montzka, A. J. Weinheimer, D. J. Knapp, J. E. Dye, E. C. Richard, Sampling of chemical constituents in electrified convective systems: Results and cautions. *J. Atmos. Chem.* **54**, 1–20 (2006). [doi:10.1007/s10874-005-9007-5](https://doi.org/10.1007/s10874-005-9007-5)
14. L. E. Ott, K. E. Pickering, G. L. Stenchikov, D. J. Allen, A. J. DeCaria, B. Ridley, R.-F. Lin, S. Lang, W.-K. Tao, Production of lightning NO_x and its vertical distribution calculated from three-dimensional cloud-scale chemical transport model simulations. *J. Geophys. Res.* **115**, D04301 (2010). [doi:10.1029/2009JD011880](https://doi.org/10.1029/2009JD011880)
15. H. Huntrieser, M. Lichtenstern, M. Scheibe, H. Aufmhoff, H. Schlager, T. Pucik, A. Minikin, B. Weinzierl, K. Heimerl, I. B. Pollack, J. Peischl, T. B. Ryerson, A. J. Weinheimer, S. Honomichl, B. A. Ridley, M. I. Biggerstaff, D. P. Betten, J. W. Hair, C. F. Butler, M. J. Schwartz, M. C. Barth, Injection of lightning-produced NO_x, water vapor, wildfire emissions, and stratospheric air to the UT/LS as observed from DC3 measurements. *J. Geophys. Res. Atmos.* **121**, 6638–6668 (2016). [doi:10.1002/2015JD024273](https://doi.org/10.1002/2015JD024273)
16. U. Schumann, H. Huntrieser, The global lightning-induced nitrogen oxides source. *Atmos. Chem. Phys.* **7**, 3823–3907 (2007). [doi:10.5194/acp-7-3823-2007](https://doi.org/10.5194/acp-7-3823-2007)
17. I. B. Pollack, C. R. Homeyer, T. B. Ryerson, K. C. Aikin, J. Peischl, E. C. Apel, T. Campos, F. Flocke, R. S. Hornbrook, D. J. Knapp, D. D. Montzka, A. J. Weinheimer, D. Riemer, G. Diskin, G. Sachse, T. Mikoviny, A. Wisthaler, E. Bruning, D. MacGorman, K. A. Cummings, K. E. Pickering, H. Huntrieser, M. Lichtenstern, H. Schlager, M. C. Barth, Airborne quantification of upper tropospheric NO_x production from lightning in deep convective storms over the United States Great Plains. *J. Geophys. Res. Atmos.* **121**, 2002–2028 (2016). [doi:10.1002/2015JD023941](https://doi.org/10.1002/2015JD023941)
18. B. A. Nault, J. L. Laughner, P. J. Wooldridge, J. D. Crounse, J. Dibb, G. Diskin, J. Peischl, J. R. Podolske, I. B. Pollack, T. B. Ryerson, E. Scheuer, P. O. Wennberg, R. C. Cohen, Lightning NO_x emissions: Reconciling measured and modeled estimates with updated NO_x chemistry. *Geophys. Res. Lett.* **44**, 9479–9488 (2017). [doi:10.1002/2017GL074436](https://doi.org/10.1002/2017GL074436)
19. L. J. Labrador, R. von Kuhlmann, M. G. Lawrence, The effects of lightning-produced NO_x and its vertical distribution on atmospheric chemistry: Sensitivity simulations with MATCH-MPIC. *Atmos. Chem. Phys.* **5**, 1815–1834 (2005). [doi:10.5194/acp-5-1815-2005](https://doi.org/10.5194/acp-5-1815-2005)
20. J. E. Dye, M. G. Bateman, H. J. Christian, E. Defer, C. A. Grainger, W. D. Hall, E. P. Krider, S. A. Lewis, D. M. Mach, F. J. Mercet, J. C. Willett, P. T. Willis, Electric fields, cloud microphysics, and reflectivity in anvils in Florida thunderstorms. *J. Geophys. Res.* **112**, D11215 (2007). [doi:10.1029/2006JD007550](https://doi.org/10.1029/2006JD007550)
21. S. A. Weiss, D. R. MacGorman, K. M. Calhoun, Lightning in the anvils of supercell thunderstorms. *Mon. Weather Rev.* **140**, 2064–2079 (2012). [doi:10.1175/MWR-D-11-00312.1](https://doi.org/10.1175/MWR-D-11-00312.1)
22. D. Petersen, M. Bailey, W. H. Beasley, J. Hallett, A brief review of the problem of lightning initiation and a hypothesis of initial lightning leader formation. *J. Geophys. Res. Atmos.* **113**, D17205 (2008). [doi:10.1029/2007JD009036](https://doi.org/10.1029/2007JD009036)
23. D. Petersen, M. Bailey, J. Hallett, W. Beasley, Laboratory investigation of corona initiation by ice crystals and its importance to lightning. *Q. J. R. Meteorol. Soc.* **141**, 1283–1293 (2014). [doi:10.1002/qj.2436](https://doi.org/10.1002/qj.2436)
24. W. Rison, P. R. Krehbiel, M. G. Stock, H. E. Edens, X.-M. Shao, R. J. Thomas, M. A. Stanley, Y. Zhang, Observations of narrow bipolar events reveal how lightning is initiated in thunderstorms. *Nat. Commun.* **7**, 10721 (2016). [doi:10.1038/ncomms10721](https://doi.org/10.1038/ncomms10721)
25. A. Y. Kostinskiy, T. C. Marshall, M. Stollenburg, The Mechanism of the origin and development of lightning from initiating event to initial breakdown pulses (v.2). *J. Geophys. Res. Atmos.* **125**, e2020JD033191 (2020). [doi:10.1029/2020JD033191](https://doi.org/10.1029/2020JD033191)
26. J. M. Jenkins, W. H. Brune, D. O. Miller, Electrical discharges produce prodigious amounts of hydroxyl and hydroperoxyl radicals. *J. Geophys. Res. Atmos.* **10.1029/2021JD034557** (2021).
27. R. D. Hill, R. G. Rinker, Production of nitrate ions and other trace species by lightning. *J. Geophys. Res. Oceans* **86**, 3203–3209 (1981). [doi:10.1029/JC086iC04p03203](https://doi.org/10.1029/JC086iC04p03203)
28. B. A. Bhetanabhotla, B. A. Crowell, A. Coucouvinos, R. D. Hill, R. G. Rinker, Simulation of trace species production by lightning and corona discharge in moist air. *Atmos. Environ.* **19**, 1391–1397 (1985). [doi:10.1016/0004-6981\(85\)90276-8](https://doi.org/10.1016/0004-6981(85)90276-8)
29. M. C. Barth, C. A. Cantrell, W. H. Brune, S. A. Rutledge, J. H. Crawford, H. Huntrieser, L. D. Carey, D. MacGorman, M. Weisman, K. E. Pickering, E. Bruning, B. Anderson, E. Apel, M. Biggerstaff, T. Campos, P. Campuzano-Jost, R. Cohen, J. Crounse, D. A. Day, G. Diskin, F. Flocke, A. Fried, C. Garland, B. Heikes, S. Honomichl, R. Hornbrook, L. G. Huey, J. L. Jimenez, T. Lang, M. Lichtenstern, T. Mikoviny, B. Nault, D. O'Sullivan, L. L. Pan, J. Peischl, I. Pollack, D. Richter, D. Riemer, T. Ryerson, H. Schlager, J. St. Clair, J. Walega, P. Weibring, A. Weinheimer, P. Wennberg, A. Wisthaler, P. J. Wooldridge, C. Ziegler, The Deep Convective Clouds and Chemistry (DC3) field campaign. *Bull. Am. Meteorol. Soc.* **96**, 1281–1309 (2015). [doi:10.1175/BAMS-D-13-00290.1](https://doi.org/10.1175/BAMS-D-13-00290.1)
30. W. H. Brune, X. Ren, L. Zhang, J. Mao, D. O. Miller, B. E. Anderson, D. R. Blake, R. C. Cohen, G. S. Diskin, S. R. Hall, T. F. Hanisco, L. G. Huey, B. A. Nault, J. Peischl, I. Pollack, T. B. Ryerson, T. Shingler, A. Sorooshian, K. Ullmann, A. Wisthaler, P. J. Wooldridge, Atmospheric oxidation in the presence of clouds during the Deep Convective Clouds and Chemistry (DC3) study. *Atmos. Chem. Phys.* **18**, 14493–14510 (2018). [doi:10.5194/acp-18-14493-2018](https://doi.org/10.5194/acp-18-14493-2018)
31. D. Stone, L. K. Whalley, D. E. Heard, Tropospheric OH and HO₂ radicals: Field measurements and model comparisons. *Chem. Soc. Rev.* **41**, 6348–6404 (2012). [doi:10.1039/c2cs35140d](https://doi.org/10.1039/c2cs35140d) [Medline](https://pubmed.ncbi.nlm.nih.gov/22514040/)
32. V. C. Chmielewski, E. C. Bruning, Lightning Mapping Array flash detection performance with variable receiver thresholds. *J. Geophys. Res. Atmos.* **121**, 8600–8614 (2016). [doi:10.1002/2016JD025159](https://doi.org/10.1002/2016JD025159) [Medline](https://pubmed.ncbi.nlm.nih.gov/27514040/)
33. L. L. Pan, C. R. Homeyer, S. Honomichl, B. A. Ridley, M. Weisman, M. C. Barth, J. W. Hair, M. A. Fenn, C. S. Diskin, J. H. Crawford, T. B. Ryerson, I. Pollack, J. Peischl, H. Huntrieser, Thunderstorms enhance tropospheric ozone by wrapping and shedding stratospheric air. *Geophys. Res. Lett.* **41**, 7785–7790 (2014). [doi:10.1002/2014GL061921](https://doi.org/10.1002/2014GL061921)
34. R. J. Thomas, P. R. Krehbiel, W. Rison, S. J. Hunyady, W. P. Winn, T. Hamlin, J. Harlin, Accuracy of the Lightning Mapping Array. *J. Geophys. Res.* **109**, D14207 (2004). [doi:10.1029/2004JD004549](https://doi.org/10.1029/2004JD004549)
35. T. C. Marshall, M. P. McCarthy, W. D. Rust, Electric field magnitudes and lightning initiation in thunderstorms. *J. Geophys. Res.* **100**, 7097–7103 (1995). [doi:10.1029/95JD00020](https://doi.org/10.1029/95JD00020)
36. L. T. Murray, D. J. Jacob, J. A. Logan, R. C. Hudman, W. J. Koshak, Optimized regional and interannual variability of lightning in a global chemical transport model constrained by LIS/OTD satellite data. *J. Geophys. Res.* **117**, D20307 (2012). [doi:10.1029/2012JD017934](https://doi.org/10.1029/2012JD017934)
37. R. G. Prinn, R. F. Weiss, B. R. Miller, J. Huang, F. N. Alyea, D. M. Cunnold, P. J. Fraser, D. E. Hartley, P. G. Simmonds, Atmospheric trends and lifetime of CH₃CCl₃ and global OH concentrations. *Science* **269**, 187–192 (1995). [doi:10.1126/science.269.5221.187](https://doi.org/10.1126/science.269.5221.187) [Medline](https://pubmed.ncbi.nlm.nih.gov/187187/)
38. S. A. Montzka, C. M. Spivakovsky, J. H. Butler, J. W. Elkins, L. T. Lock, D. J. Mondeel, New observational constraints for atmospheric hydroxyl on global and hemispheric scales. *Science* **288**, 500–503 (2000). [doi:10.1126/science.288.5465.500](https://doi.org/10.1126/science.288.5465.500) [Medline](https://pubmed.ncbi.nlm.nih.gov/10855000/)
39. M. G. Lawrence, P. Jöckel, R. von Kuhlmann, What does the global mean OH concentration tell us? *Atmos. Chem. Phys.* **1**, 37–49 (2001). [doi:10.5194/acp-1-37-2001](https://doi.org/10.5194/acp-1-37-2001)
40. J. Lelieveld, S. Gromov, A. Pozzer, D. Taraborrelli, Global tropospheric hydroxyl distribution, budget and reactivity. *Atmos. Chem. Phys.* **16**, 12477–12493 (2016). [doi:10.5194/acp-16-12477-2016](https://doi.org/10.5194/acp-16-12477-2016)
41. M. Li, E. Karu, C. Brenninkmeijer, H. Fischer, J. Lelieveld, J. Williams, Tropospheric OH and stratospheric OH and Cl concentrations determined from CH₄, CH₃Cl, and SF₆ measurements. *npj Clim. Atmos. Sci.* **1**, 29 (2018). [doi:10.1038/s41612-018-0041-9](https://doi.org/10.1038/s41612-018-0041-9)
42. A. T. Archibald, J. G. Levine, N. L. Abraham, M. C. Cooke, P. M. Edwards, D. E. Heard, M. E. Jenkin, A. Karunaharan, R. C. Pike, P. S. Monks, D. E. Shallcross, P. J. Telford, L. K. Whalley, J. A. Pyle, Impacts of HO_x regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres. *Geophys. Res. Lett.* **38**, L05804 (2011). [doi:10.1029/2010GL046520](https://doi.org/10.1029/2010GL046520)
43. E. Williams, V. Mushtak, D. Rosenfeld, S. Goodman, D. Boccippio, Thermodynamic

- conditions favorable to superlative thunderstorm updraft, mixed phase microphysics and lightning flash rate. *Atmos. Res.* **76**, 288–306 (2005). [doi:10.1016/j.atmosres.2004.11.009](https://doi.org/10.1016/j.atmosres.2004.11.009)
44. The flash extent is the number of flashes detected by the LMA in each grid cell (volume $\sim 1 \text{ km}^3$) in each minute, whether it was initiated in that cell or just propagated through it; thus, flash extent is a reliable variable for determining the total region of electrical activity.
 45. A. Aknan, G. Chen, NASA LaRC Airborne Science Data for Atmospheric Composition DC3 (2017); <https://doi.org/10.5067/Aircraft/DC3/DC8/Aerosol-TraceGas>.
 46. E. C. Bruning, “Streamed clustering of lightning mapping data in Python using sklearn,” paper presented at the 12th Python in Science Conference (SciPy), Austin, TX, 24 to 29 June 2013.
 47. B. R. Fuchs, E. C. Bruning, S. A. Rutledge, L. D. Carey, P. R. Krehbiel, W. Rison, Climatological analysis of LMA data with an open-source lightning flash-clustering algorithm. *J. Geophys. Res. Atmos.* **121**, 8625–8648 (2016). [doi:10.1002/2015JD024663](https://doi.org/10.1002/2015JD024663)
 48. B. M. Basarab, S. A. Rutledge, B. R. Fuchs, An improved lightning flash rate parameterization developed from Colorado DC3 thunderstorm data for use in cloud-resolving chemical transport models. *J. Geophys. Res. Atmos.* **120**, 9481–9499 (2015). [doi:10.1002/2015JD023470](https://doi.org/10.1002/2015JD023470)
 49. T. C. Davis, S. A. Rutledge, B. R. Fuchs, Lightning location, NO_x production, and transport by anomalous and normal polarity thunderstorms. *J. Geophys. Res. Atmos.* **124**, 8722–8742 (2019). [doi:10.1029/2018JD029979](https://doi.org/10.1029/2018JD029979)
 50. S. A. Weiss, D. R. MacGorman, E. C. Bruning, V. C. Chmielewski, Two methods for correcting range-dependent limitations of Lightning Mapping Arrays. *J. Atmos. Ocean. Technol.* **35**, 1273–1282 (2018). [doi:10.1175/JTECH-D-17-0213.1](https://doi.org/10.1175/JTECH-D-17-0213.1)
 51. R. J. Thomas, P. R. Krehbiel, W. Rison, T. Hamlin, J. Harlin, D. Shown, Observations of VHF source powers radiated by lightning. *Geophys. Res. Lett.* **28**, 143–146 (2001). [doi:10.1029/2000GL011464](https://doi.org/10.1029/2000GL011464)
 52. E. C. Bruning, D. R. MacGorman, 2013: Theory and observations of controls on lightning flash size spectra. *J. Atmos. Sci.* **70**, 4012–4029 (2013). [doi:10.1175/JAS-D-12-0289.1](https://doi.org/10.1175/JAS-D-12-0289.1)
 53. D. R. MacGorman, M. S. Elliott, E. DiGangi, Electrical discharges in the overshooting tops of thunderstorms. *J. Geophys. Res. Atmos.* **122**, 2929–2957 (2017). [doi:10.1002/2016JD025933](https://doi.org/10.1002/2016JD025933)
 54. I. C. Faloona, D. Tan, R. L. Leshner, N. L. Hazen, C. L. Frame, J. B. Simpas, H. Harder, M. Martinez, P. Di Carlo, X. Ren, W. H. Brune, A laser-induced fluorescence instrument for detecting tropospheric OH and HO_2 : Characteristics and calibration. *J. Atmos. Chem.* **47**, 139–167 (2004). [doi:10.1023/B:JOCH.0000021036.53185.0e](https://doi.org/10.1023/B:JOCH.0000021036.53185.0e)
 55. T. B. Ryerson, E. J. Williams, F. C. Fehsenfeld, An effective photolysis system for fast-response NO_2 measurements. *J. Geophys. Res.* **105**, 26447–26461 (2000). [doi:10.1029/2000JD900389](https://doi.org/10.1029/2000JD900389)
 56. P. A. Feiner, W. H. Brune, D. O. Miller, L. Zhang, R. C. Cohen, P. S. Romer, A. H. Goldstein, F. N. Keutsch, K. M. Skog, P. O. Wennberg, T. B. Nguyen, A. P. Teng, J. DeGouw, A. Koss, R. J. Wild, S. S. Brown, A. Guenther, E. Edgerton, K. Baumann, J. L. Fry, Testing atmospheric oxidation in an Alabama forest. *J. Atmos. Sci.* **73**, 4699–4710 (2016). [doi:10.1175/JAS-D-16-0044.1](https://doi.org/10.1175/JAS-D-16-0044.1)
 57. A. Zahn, C. A. M. Brenninkmeijer, P. J. Crutzen, D. D. Parrish, D. Sueper, G. Heinrich, H. Güsten, H. Fischer, M. Hermann, J. Heintzenberg, Electrical discharge source for tropospheric “ozone-rich transients”. *J. Geophys. Res.* **107**, 4638 (2002). [doi:10.1029/2002JD002345](https://doi.org/10.1029/2002JD002345)
 58. G. M. Wolfe, M. R. Marvin, S. J. Roberts, K. R. Travis, J. Liao, The framework for O-D atmospheric modeling (FOAM) v3.1. *Geosci. Model Dev.* **9**, 3309–3319 (2016). [doi:10.5194/gmd-9-3309-2016](https://doi.org/10.5194/gmd-9-3309-2016)
 59. G. M. Wolfe, FOAM Box Model (2017); <https://sites.google.com/site/wolfegm/models>.
 60. S. M. Saunders, M. E. Jenkin, R. G. Derwent, M. J. Pilling, Protocol for the development of the Master Chemical Mechanism, MCM, v3 (Part A): Tropospheric degradation of non-aromatic volatile organic compounds. *Atmos. Chem. Phys.* **3**, 161–180 (2003). [doi:10.5194/acp-3-161-2003](https://doi.org/10.5194/acp-3-161-2003)
 61. M. E. Jenkin, S. M. Saunders, V. Wagner, M. J. Pilling, Protocol for the development of the Master Chemical Mechanism, MCM, v3 (Part B): Tropospheric degradation of aromatic volatile organic compounds. *Atmos. Chem. Phys.* **3**, 181–193 (2003). [doi:10.5194/acp-3-181-2003](https://doi.org/10.5194/acp-3-181-2003)
 62. V. Chmielewski, D. R. MacGorman, C. L. Ziegler, E. DiGangi, D. Betten, M. Biggerstaff, Microphysical and transportive contributions to normal and anomalous polarity subregions in the 29–30 May 2012 Kingfisher storm. *J. Geophys. Res. Atmos.* **125**, (2020). [doi:10.1029/2020JD032384](https://doi.org/10.1029/2020JD032384)
 63. E. A. DiGangi, C. L. Ziegler, D. R. MacGorman, Lightning and secondary convection in the anvil of the 29 May 2012 Oklahoma supercell storm observed by DC3. *J. Geophys. Res. Atmos.* **126**, e2020JD033114 (2021). [doi:10.1029/2020JD033114](https://doi.org/10.1029/2020JD033114)

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SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S5

Tables S1 and S2

References (46–63)

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Fig. 1. Enhanced HO_x measured in an electrified anvil cloud. (A to C) HO_x abundances (colors, logarithmic scale) along the DC-8 flight track overlaid on LMA flash extent (44) and satellite anvil images during the flight on 22 June, 2012 for three one-hour periods: (A) 23:30-00:30; (B) 00:30-01:30; and (C) 01:30-02:30. All times are in UTC. The flash extent locations are shown for the entire hour as the storms moved from west to east. The storm cores are regions of the most intense flash extent.

Fig. 2. HO_x , O_3 , and NO_x during repeated flight passes through an electrified anvil cloud. Time series of HO_x (blue), NO_x (golden), O_3 (light blue), IWC (light gray), and LMA flash extent (orange) for the time period shown in Fig. 1. (A) Flash extents are given every minute, whereas 1-Hz NO_x and O_3 data and 5-Hz HO_x data are shown. (B) An expanded view of the region between 00:06:45 and 00:10:00 UTC. OH (green line) has been added to show that OH was often half of HO_x . Black bars below 0 indicate times when HO_x was not being measured. NO_x and O_3 were deemed to be unreliable between 00:16:00 and 00:16:13 and were not reported.

Fig. 3. A lightning flash and LHO_x . (A) Full frame photograph: lightning captured by the NASA DC-8 forward camera in a deep convection anvil at 00:16:11 UTC on 23 June 2012. (B) A time series plot of HO_x at 5 Hz (black line) and flash in video (gray vertical line). NO_x and O_3 data were not available during the flash.

Fig. 4. Modeled behavior of OH , HO_2 , NO , and NO_2 . (A and B) Photochemical box model calculations of the changes in OH (solid black line), HO_2 (solid gray line), NO (dashed black line), and NO_2 (dashed gray line) for two cases: (A) 00:09:37, no visible flash, with measured values; and (B) 00:16:12, visible flash, with assumed values for NO , NO_2 , and O_3 consistent with laboratory observations (26). The OH exposures were calculated using Eq. 1 and the modeled OH concentrations.

Table 1. Major HO_x peaks and resulting modeled OH exposure from six flights. These observed peaks may be lower than initially generated peaks because the sampling is probably not always coincident with the electrical discharge.

Day	Time (UTC)	Peak HO _x (pptv)	Peak OH (pptv)	OH exposure (10 ⁹ molecules s cm ⁻³)	Lightning visible?
18-May	23:18:34	1661.26	603.38	11.8	No
20-May	00:50:52	439.73	197.38	4.7	No
26-May	01:24:18	229.42	126.04	3.3	No
29-May	23:30:51	586.36	311.19	5.8	No
2-Jun	22:45:18	709.34	309.44	9.9	No
23-Jun	00:09:37	700.53	297.12	9.7	No
23-Jun	00:16:01	890.84	198.15	7.0	Yes
23-Jun	00:16:12	1992.62	334.34	1.2	Yes
23-Jun	00:56:27	1984.12	472.15	6.2	No