Near-Surface Plasma-Water Interactions

D. Elg[(a)], I. Yang[(a)], and D. B. Graves[(a)]
[(a)]University of California at Berkeley (graves@berkeley.edu)

Plasma-liquid interactions are often studied with dissolved "spin traps" that react with plasma-produced species to create stable radicals, which can be measured with electron paramagnetic resonance (EPR) spectroscopy. The disadvantage of such a method is that the reactant often lacks selectivity, which means that multiple species from the plasma can produce the same product. One process often used to test for the presence of reactive oxygen species is the oxidation of 2,2,6,6-tetramethylpiperidine (TEMP) to 2,2,6,6-tetramethylpiperidine-1oxyl (TEMPO). TEMPO is used in biological studies as an indicator of singlet oxygen ($^1O_2$), a reactive excited state of oxygen that has applications in cancer treatment [1]. However, plasmas produce a plethora of reactive species, and the production of TEMPO has not been shown to be selective. It has been thought that it is produced by a combination of O, $^1O_2$, and O_3 [1].

In a controlled-environment kHz He jet operated in air and incident on a 1mL cup of 100mM TEMP solution, experiments were performed to isolate the contributions of different species to TEMPO creation. O_3 concentration was measured with Fourier Transform Infrared Spectroscopy (FTIR) and was found not to correlate with TEMPO production (Fig. 1a). In fact, the condition with 0% O_2 in the jet (all oxygen from the air environment) produces no O_3 at all but causes an order-of-magnitude increase in the TEMPO yield. Additional experiments (not shown) with an independent O_3 generator confirmed that O_3 alone does not generate more than 10 µM TEMPO.

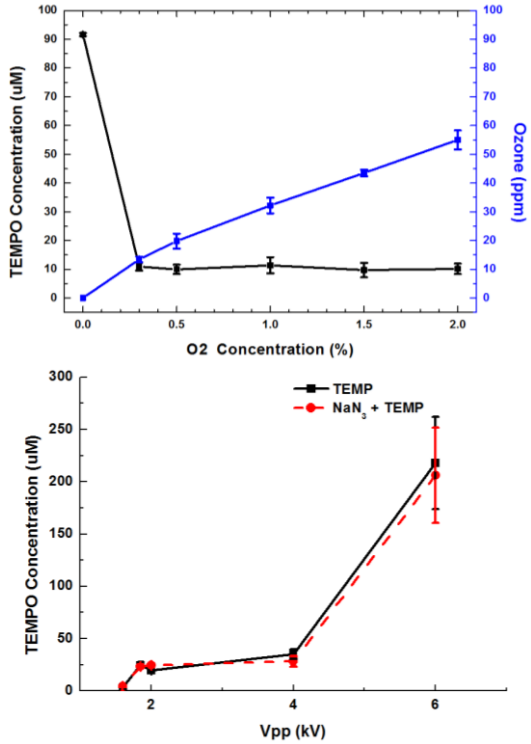


Fig. 1: (a) The top panel shows that TEMPO production is uncorrelated with O_3 concentration. (b) The bottom panel shows that NaN_3 does not reduce the TEMPO yield, implying an absence of $^1O_2$.

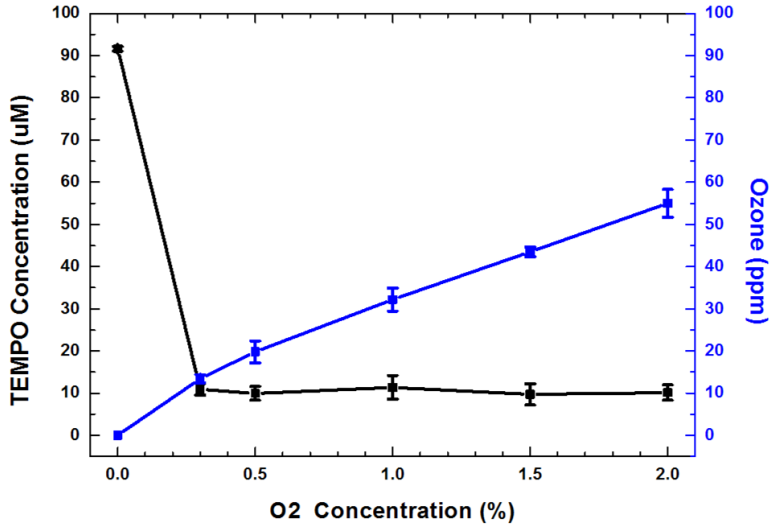
In other experiments with the same system, the $^1O_2$ scavenger NaN_3 was added to the TEMP solution with 0% O_2 in the jet. Fig. 1b shows that when the voltage is varied no difference in the TEMPO concentration is observed with and without NaN_3. The same is true when the distance between the jet and the liquid is varied. We conclude that $^1O_2$ is not being produced in significant quantities got these conditions. TEMPO is most likely produced by O atom-liquid interactions. This allows for selective measurements of interactions with important reactive species known to cause most of the oxidative effects in He/O_2 plasma-liquid interactions [2].

References

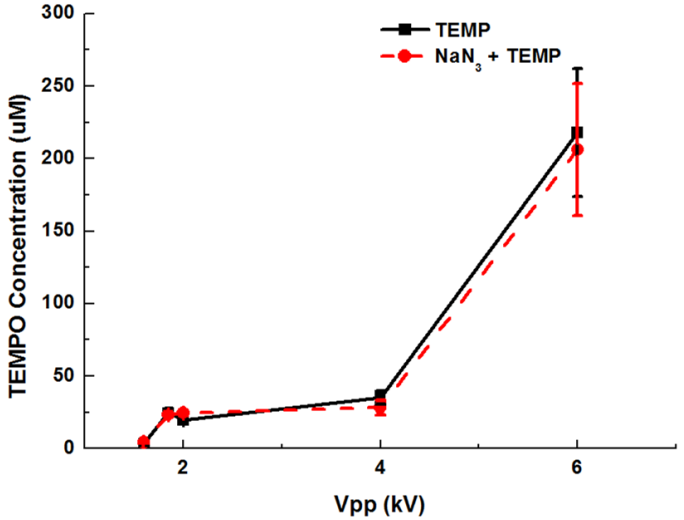
[1] Y. Gorbanev, D. O'Connell, and V. Chechik, *Chemistry* **22**, 3496-3505 (2016).
[2] M. Hefny, et al, *J. Phys. D.* **49**, 404002 (2016).

PLASMA-WATER INTERACTIONS: O ATOMS

- Methods used to measure plasma-liquid interactions are often not selective.
- Spin trap TEMP, an additive, is oxidized to TEMPO by O_3, $^1O_2$, and O.
- Plasma produced O_3 onto water has little effect on TEMPO production (highest TEMPO concentration is produced without plasma O_3 production).
- Use of $^1O_2$ scavenger NaN_3 shows a lack of $^1O_2$ in this system.
- TEMPO us produced by O atom-liquid interactions, which are the main contributors to oxidative effects in He/O_2 plasma treatments.



- TEMPO and O_3 production at 6 kV_{pp} in plasma jet.



- TEMPO production with 0% O_2 in plasma jet (all O_2 from air environment.

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HIGHLIGHT

Center for Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems

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Importance of Reactive Nitrogen Species in Plasma-Bio Interactions

Gaurav Nayak[(a)], Hamada Aboubark, Sagar Goyal[(b)] and Peter J. Bruggeman[(a)]

(a) University of Minnesota, College of Science and Engineering (pbruggem@umn.edu)
(b) University of Minnesota, College of Veterinary Medicine

Cold atmospheric pressure plasmas (CAPs) have been shown to be able to effectively disinfect heat sensitive surfaces due to a reactive cocktail of numerous reactive oxygen and nitrogen species (RONS) [1]. The interaction between this reactive cocktail and the biological substrates makes the understanding of the detailed underlying mechanisms of plasma-bio-interactions challenging.

In this study, we focus on assessing the effect of reactive nitrogen species (RNS) through studying the plasma-induced inactivation of a virus as a 'simple' model of a biological substrate. We use a flow-through reactor consisting of a 2D array of micro-dielectric barrier discharges [2] operated in atmospheric pressure dry air and Ar+20% O_2 producing the same ozone density (3.5×10^{21} m^{-3}). Using dry air and Ar eliminates a significant production of H_2O_2 and OH in the gas phase. The inactivation of Feline Calicivirus (FCV) is performed in the discharge afterglow and is thus only exposed to long-lived reactive species. Hence the key difference between the reactive species in the dry air and Ar+20% afterglow is the presence of reactive nitrogen species (RNS). We also compare the inactivation in the gas phase (virus is present on a metal surface) and in the liquid phase (virus is dispersed in distilled water).

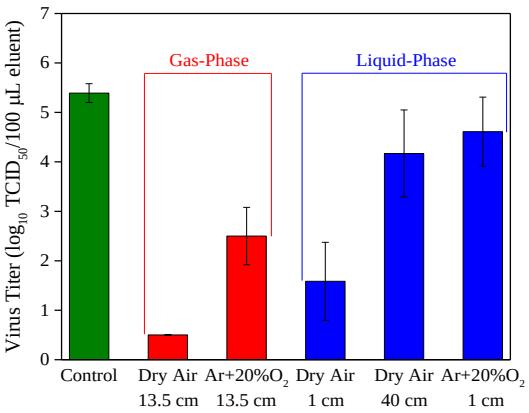


Figure 1 – Inactivation of FCV with air and Ar+20% O_2 plasma producing the same amount of ozone. The length scale is the distance between the array and the virus sample. The gas phase and liquid phase treatment is for 3 and 10 minutes respectively.

The gas-phase treatment in air shows complete FCV inactivation (see Fig. 1). Compared to previously published results of ozonizers [3], the measured O_3 density in this work is sufficient for complete FCV inactivation. However, the treatment by Ar + 20% O_2 plasma, leads to less inactivation, suggesting that RNS strongly contributes to the inactivation of FCV.

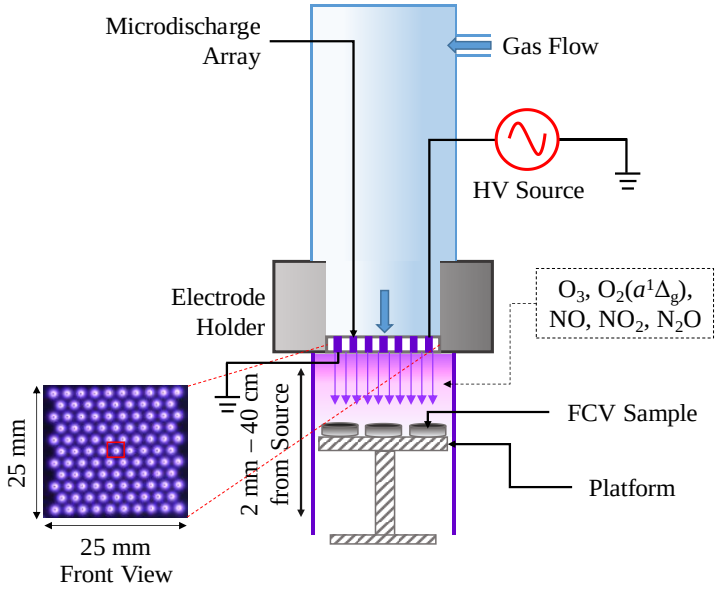
The inactivation of FCV in deionized water for the dry air and Ar + 20% O_2 plasmas is shown in Fig. 1. The dry air treatment of FCV leads to a significantly larger inactivation than for the Ar + 20% O_2 treatment. The concentration of NO_2^- in the deionized water correlates well with the different inactivation efficacy for 1 and 40 cm. The results suggest an inactivation pathway by acidified nitrites (NO_2^-) in the liquid and most likely NO_2 in the gas phase and not ozone.

References

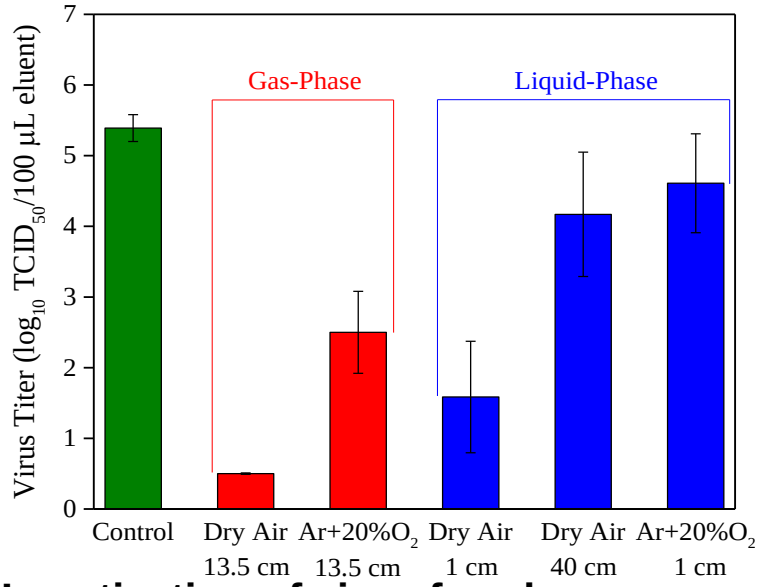
[1] D.B. Graves, J. Phys. D: Appl. Phys. **45** 263001 (2012).
[2] G. Nayak, Y. Du, R. Brandenburg, P.J. Bruggeman, Plasma Sources Sci. Technol. **26** 135001 (2017).
[3] J. B. Hudson, M. Sharma and S. Vimalanathan, Ozone: Science & Engineering **31** 3 216-223 (2009).

IMPORTANCE OF REACTIVE NITROGEN SPECIES IN PLASMA-BIO INTERACTIONS

- **Using a 2-D array of micro-dielectric barrier discharges (DBD), we investigated the effect of reactive nitrogen and oxygen species on virus (in liquid and on a substrate) as a 'simple' biological model.**
- **The air plasma having the same O_3 density as the Ar + 20% O_2 plasma leads to a significant larger inactivation of the virus. The results suggest an inactivation pathway by acidified nitrites (NO_2^-) in the liquid and most likely NO_2 in the gas phase and not ozone.**



- **2-D micro-DBD setup**



- **In activation of virus for plasma conditions with an ozone concentration of 3.5×10^{21} m^{-3}.**

HIGHLIGHT

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