

## Plasmas for Organic Synthesis and Chemical Probes for Plasma Diagnostics

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Although organic chemistry plays a critical role in many plasma applications, there is room for further cross-fertilization between the two disciplines. Here we explore two possible avenues: (1) plasma physics as a new tool for the organic chemist and (2) organic compounds as diagnostics for the plasma physicist.

*Organic synthesis:* The idea of using plasmas in organic synthesis is not new and early work in the 70's focused primarily on chemical modifications of organic compounds in low-pressure plasmas where all reactants were in gas phase<sup>1</sup>. The advancement of low-temperature atmospheric-pressure discharges and the possibility of operating plasmas in and in contact with liquids, however, open new possibilities that are yet to be explored. Plasmas produce non-equilibrium chemistries that when brought in contact with organic compounds may lead to new processes or novel compounds, potentially circumventing the need for dangerous or expensive precursors. We have initially focused our attention on two well-known and important chemical processes, namely, ozonolysis and tetrazole formation. Here we report our results on successful azide formation from nitrogen gas through generation of copper(I) azide (identified by XRD) by exposure of a copper(I) iodide acetonitrile solution to helium-nitrogen plasmas. Treatment of aryl nitriles under these conditions, with CuI as catalyst, affords the corresponding tetrazole products in unoptimised yields of 10-15% under batch conditions. We have also developed an in-flow system that uses a semipermeable Teflon tubing enclosed in a reaction vessel. An oxygen containing plasma is used to produce ozone and flowing alkenes are converted into aldehydes (ozonolysis reaction), minimizing the risk associated with the generation of large quantities of explosive intermediates.

*Chemical probes:* Detection of chemical compounds is of interest in many scientific and engineering fields and in particular it is often desirable to know the actual flux of reactive species reaching a plasma treated target. Chemical probes have the potential to provide this information without having to extrapolate data from the gas phase, enabling the quantification of the dose for the comparison of different treatments/devices. These chemical probes, however, need to be particularly selective as plasmas are very reactive environments. We have recently developed a fluorescent probe aimed at the quantification of ozone. The probe is derived from 2',7'-dichlorofluorescein (DCF) and it works by having a homoallylic group appended to a DCF analogue that is essentially non-fluorescent. On exposure to ozone, rapid ozonolysis of the double bond in the side-chain proceeds, followed by loss of propenal and liberation of DCF, a fluorescent product. The amount of ozone can then be quantified by measuring the fluorescence after the plasma exposure. The probe displays good selectivity and it provides a fluorescent product that is more stable than the one obtained is similar DCF derived ozone probes<sup>2</sup>.

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<sup>1</sup> Suhr H 1972 *Angewandte Chemie International Edition in English* **11** 781–92

<sup>2</sup> A. L. Garner et al, *Nature Chem*, 2009, **1**, 316-321