Non-thermal plasma-liquid interaction in imine macrocycle synthesis

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Abstract: While plasma-liquid interaction provides a high-yield and selective synthesis of imine macrocycle, the mechanisms remain unknown. Focusing on plasma-liquid interactions, this work uses optical emission spectroscopy to monitor reactive species at a plasma- solution interface. Building on a reported reaction, this study seeks to uncover the role of plasma for more efficient plasma-driven synthesis.

1. Introduction

Non-thermal plasma (NTP) interacting with liquids creates complex and dynamic reactive environments, driven by interactions with both solvents and reagents. These systems generate mixtures of short- and long-lived reactive species that are challenging to discern. [1] Despite these impediments, NTP offers unique properties, such as mild reaction conditions and highly energized environments, making it particularly valuable for radical-driven reactions but it also found application in oxidation, reduction and substitution, highlighting its potential in synthetic chemistry. [2]

An imine macrocycle synthesis is an example of a reaction that benefited from the NTP system. Previous work by the Slater group showed that NTP batch systems significantly accelerated this reaction with high yields, though the mechanisms behind this enhancement remain unclear. [3] Building on this foundation, our study replicates the Slater group's reaction setup by adding plasma diagnostics, one of which is optical emission spectroscopy (OES). OES is a widely used diagnostic tool for plasma analysis due to its simplicity and ability to provide critical information, including species identification and various temperatures. [4] By modifying densities of reactive species generated in plasma and various temperatures during this process, simultaneously observing their impact on the reaction outcome, the approach aims to uncover the mechanisms behind the exceptional performance of NTP for imine macrocycle synthesis and enhance the broader understanding of NTP-assisted synthetic methods.

2. Methods and Results

The experimental setup shown in Fig. 1, featured a plasma jet-like system connected to a round-bottom flask containing the reaction mixture or pure solvent. The solution was maintained under an argon atmosphere, with argon introduced through a quartz tube (ID 2mm, OD 4mm, length 15 cm) inserted into the flask. This quartz tube had a tungsten wire (diameter 0.4 mm) inside which functioned as the high-voltage electrode, completing the plasma jet system. We have used two systems; (1) with tube immersed into the liquid (Fig.1/1) and (2) above the liquid surface (Fig.1/2).

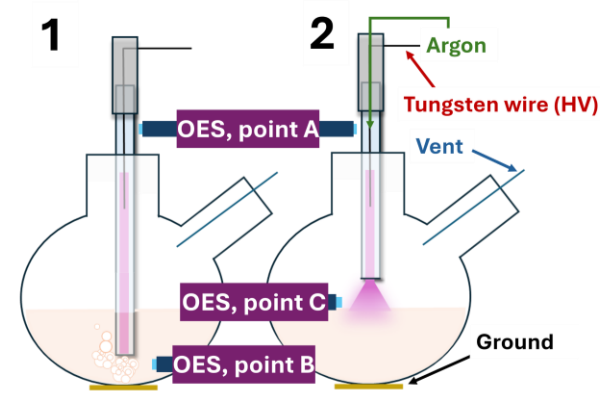

Fig. 1. The schematic representation of the setup used in the experiment.

The collecting lens of the OES system was positioned at the top of the quartz tube (A, Fig. 1) to capture the argon plasma spectra. Spectra from plasma interacting with the reaction mixture were collected at two locations: (1) the bottom of the tube (B, Fig. 1) when immersed in the solution, and (2) above the mixture (C, Fig. 1) when the plasma hovered over it. Preliminary results using chloroform reveal distinct spectral peaks and intensity variations. At point A, as expected only argon emission lines were detected, while additional peaks from chloroform appeared at points B and C. Broad peaks were also observed in a visible region.

3. Discussion and Conclusion

The observed differences in chloroform peaks provide valuable insights into plasma-liquid interactions. The stronger chloroform peaks at point C are likely due to higher chloroform vapor density in the plasma region, while broad peaks are attributed to Bremsstrahlung emissions. These findings guide the comparison of slightly different reaction setups. Plasma parameters, such as gas temperature and electron density/temperature, will be extracted using optical diagnostics, and imine macrocycle synthesis under varying plasma geometries and conditions will further clarify the role of plasma in the reaction.

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