Plasma-induced oxidation in micro-droplets: Quantifying H_2O_2 and OH fluxes and transport limitations

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Abstract: In this work, the OH flux in an RF-driven atmospheric pressure plasma-droplet reactor has been quantified using a combined approach of liquid phase measurement and 1D reaction-diffusion modeling. Utilizing compounds that readily react with OH, two transport limited trends were observed: 1) solute diffusion limited conversion and 2) gas phase species flux limited conversion.

1. Introduction

The unique reactive chemistry enabled by plasma-liquid interactions has been leveraged in a wide range of applications [1]. This redox chemistry is driven by the multi-phase transport of highly reactive species such as the OH radical. Thus, it is crucial to better understand the properties and underlying mechanisms at the plasma-liquid interface. Particularly, gas phase species flux quantification can be obtained through the conversion of chemicals in bulk liquid surface treatments [2]. In this study, we utilize a plasma-droplet reactor [3] for an indirect analysis of the plasma gas phase generated OH flux into the liquid phase, combining experimental results from a droplet reactor and a comprehensive 1D reaction-diffusion droplet model.

2. Methods

The plasma-droplet reactor has a highly controlled plasma environment (homogenous RF-driven atmospheric pressure discharge generated with He + 0.2% H_2O as working gas), well-controlled droplets (diameter of ~40 µm dispensed at 1600 Hz, with a residence time of ~10 ms in the discharge), and simplified transport (only diffusion, as convection was considered negligible inside the droplet for our operating condition). A detailed description of the reactor can be found in [3]. The chemical conversion of various compounds, that readily react with OH, at different initial concentrations allows for the quantification of transport limitations and the OH flux. A 1D reaction-diffusion model was also implemented as well as using previously measured gas phase OH and H_2O_2 densities for species flux boundary condition.

3. Results and Discussion

Figure 1 shows the conversion of two compounds (formate and ferrocyanide) that are readily oxidized by OH, as well as the 1D reaction-diffusion model results. Two transport limited regimes are observed: 1) solute diffusion limited conversion for lower initial compound concentration, and 2) gas phase species flux limited conversion for higher initial compound concentration. For formate, this second transport limited regime gives a conversion saturation that agrees with previous OH gas phase density measurements and thus allows for OH flux determination. For ferrocyanide, there is a discrepancy. The 1D reaction-diffusion model results, which have good agreement with the experimental results, reveals that this discrepancy is due to reaction-limited conversion – some of the ferricyanide oxidized by the OH radical are reduced back into ferrocyanide by long-lived species formed in the droplet.

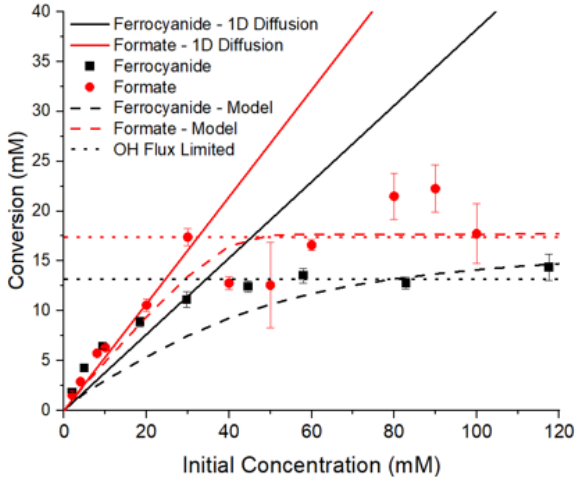

Fig. 1. Conversion vs initial concentration for formate and ferrocyanide, in He + 0.2% H_2O at 1slm, ~13 W.

4. Conclusion

By treating compounds at varying initial concentrations in the plasma-droplet reactor, we observed two transport limited conversion regimes: solute diffusion limited and gas phase species flux limited. We also found that reaction limited conversion can occur, as in the case of ferrocyanide, which can skew the OH flux quantification. If no competing reactions occur in the droplet, as in the case of formate in this study, this latter regime allows for the quantification of the gas phase OH injection into the droplet.

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